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An Efficient Solvent-Free Route to Silyl Esters and Silyl Ethers

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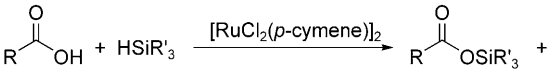
Abstract: Dinuclear metal complexes, especially (*p*-cymene)ruthenium dichloride dimer {[$RuCl_2$(*p*-cymene)]$_2$}, have been found to exhibit high catalytic performance for the dehydrosilylation of various kinds of carboxylic acids and alcohols. The dehydrosilylation with [$RuCl_2$(*p*-cymene)]$_2$ proceeded efficiently with only one equivalent of silane with respect to substrate (carboxylic acids or alcohols) under solvent-free conditions to give the corresponding silyl esters and ethers in excellent yields with a high turnover number (TON) and frequency (TOF). The ^{1}H NMR spectrum of a toluene-d_8 solution of [$RuCl_2$(*p*-cymene)]$_2$ and a silane showed a signal assignable to the ruthenium hydride species. In contrast, no new signals were detected in the ^{1}H NMR spectrum of a toluene-d_8 solution of [$RuCl_2$(*p*-cymene)]$_2$ and a carboxylic acid or an alcohol. Therefore, the ruthenium metal in [$RuCl_2$(*p*-cymene)]$_2$ activates a silane to afford the hydride intermediate, possibly a silylmetal hydride species. Then, the nucleophilic attack of a substrate (carboxylic acid or alcohol) to the hydride intermediate proceeds to give the corresponding silylated product. The present dehydrosilylation with an optically active silane proceeded exclusively under inversion of stereochemistry at the chiral silicon center, suggesting that the nucleophilic attack of a substrate to the hydride intermediate occurs from the backside of the ruthenium-silicon bond.

Keywords: alcohols; carboxylic acids; dehydrosilylation; ruthenium; silyl esters; silyl ethers

Introduction

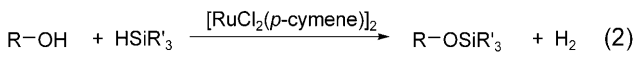
Silyl esters and silyl ethers are an important class of chemicals that have widely been used for the production of silicon-based polymeric materials in industry as well as for intermediates in organic syntheses.[1] The silylation of carboxylic acid derivatives or alcohols with expensive and reactive silylating reagents such as hexamethyldisilazane and aminosilanes usually requires continuous removal of NH_3 and amines formed.[2] Although silyl esters and silyl ethers have been synthesized by the cross-coupling of carboxylic acid derivatives or alcohols with chlorosilanes,[3] these procedures require high reaction temperatures to attain high yields of the corresponding silylated products with concomitant formation of by-products such as silanols and siloxanes.[3] In addition, HCl is formed in the cross-coupling and at least stoichiometric amounts of bases such as NH_3 and amines are necessary to neutralize it.

If the synthesis of silyl esters and silyl ethers directly from silanes and carboxylic acids or alcohols could be performed (catalytic dehydrosilylation), it would be more economical and environmentally-friendly because it produces only H_2 as a co-product. Although many transition metal catalysts have been reported for the dehydrosilylation of alcohols with silanes,[4] there are only a few reports for the dehydrosilylation of carboxylic acids.[5] In addition, the reported systems have shortcomings; low TON and TOF and/or narrow applicability to the limited silanes and carboxylic acids. In this paper, we report that simple dimeric metal complexes, especially [$RuCl_2$(*p*-cymene)]$_2$, act as efficient homogeneous catalysts for the dehydrosilylation of carboxylic acids with only one equivalent of silanes under solvent-free conditions [Eq. (1)]. The



(1)

applicability of the present system to the dehydrosilylation of alcohols is also reported [Eq. (2)]. The synthesis of silyl esters and ethers sometimes meets with difficulty because of their instability during isolation and purification processes. The dehydrosilylation reported herein would be ideal in that it produces H_2 gas as the only by-product and typically needs no solvents. The use of rather simple, easily available catalysts also benefits synthetic applications of this system.



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Results and Discussion

First, the dehydrosilylation of acetic acid (**1a**) with one equivalent of dimethylphenylsilane (**2a**) was examined in the presence of various transition metal catalysts under solvent-free conditions. The results are summarized in Table 1. The sterically less-hindered silane **2a** was chosen as a model substrate because its transformation to the desired silyl ester **3a** is very sensitive to the reaction conditions and catalysts used, and the decomposition to the silanol and the condensation to the disiloxane easily proceed. Under the present conditions, no reactions proceeded in the absence of catalysts. The dehydrosilylation with dimeric metal complexes such as $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(CO)_3]_2$, $[RhCl_2Cp^*]_2$, $[RhCl(cod)]_2$, $[IrCl_2Cp^*]_2$, and $[PdCl(\pi\text{-allyl})]_2$ efficiently proceeded and $[RuCl_2(p\text{-cymene})]_2$ showed the highest catalytic activity and chemoselectivity among the transition metal catalysts tested. For example, in the presence of 0.5 mol% of $[RuCl_2(p\text{-cymene})]_2$, the dehydrosilylation was almost completed within 2 h at 50 °C and the corresponding silyl ester **3a** was obtained in 94% yield with 98% chemoselectivity. In this case, the stoichiometric amount of gaseous H_2 with respect to **3a** was formed. Although other transition metal catalysts such as $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, $Ru_3(CO)_{12}$, $RuCl_3$, $RhCl(PPh_3)_3$, and $Pd(OAc)_2$ showed high catalytic activity for the transformation, the chemoselectivities to **3a** (70–82%) were lower than the 98% obtained with $[RuCl_2(p\text{-cymene})]_2$.

Table 1. Dehydrosilylation of **1a** with **2a** by various catalysts.[a]

Run	Catalyst	Conv. [%]	Select. [%]
1	$[RuCl_2(p\text{-cymene})]_2$	96	98
2	$[RuCl_2(CO)_3]_2$	91	92
3	$RuCl_2(PPh_3)_3$	>99	80
4	$Ru_3(CO)_{12}$	96	82
5	$RuCl_3 \cdot n H_2O$	>99	74
6	$RuH_2(PPh_3)_4$	50	70
7	$K_2RuCl_5 \cdot H_2O$	6	67
8	$Ru(acac)_3$	3	67
9	$[Ru(NH_3)_6]Cl_3$	<1	–
10	$(NH_4)_2RuCl_6$	<1	–
11	$RuCp_2$	<1	–
12	$[RhCl_2Cp^*]_2$	>99	92
13	$[RhCl(cod)]_2$	94	93
14	$RhCl(PPh_3)_3$	>99	76
15	$[IrCl_2Cp^*]_2$	76	95
16	$[PdCl(\pi\text{-allyl})]_2$	>99	86
17	$Pd(OAc)_2$	>99	75
18	$[CuH(PPh_3)]_6$	4	75
19	$[Mn(CO)_5]_2$	<1	–
20	blank	<1	–

[a] *Reaction conditions:* **1a** (5 mmol), **2a** (5 mmol), catalyst (metal: 1 mol%), 50 °C, 2 h.

Next, the scope of the present $[RuCl_2(p\text{-cymene})]_2$-catalyzed system toward various kinds of structurally diverse carboxylic acids and silanes was examined (Table 2).[6] The reactions were carried out with equimolar amounts of silanes with respect to carboxylic acids under solvent-free conditions.[7] The reactions were typically carried out under an air atmosphere. The reaction rate for the dehydrosilylation under Ar or O_2 atmosphere was almost the same as that under an air atmosphere. A number of carboxylic acids including aliphatic (**1a**–**1g**), aromatic (**1h**–**1k**), and unsaturated (**1l**) ones efficiently reacted with silanes (**2a**–**2c**) and all combinations gave the corresponding silyl esters (**3a**–**3u**) in good yields. In the case of chlorobenzoic acid (**1i**), the reaction efficiently proceeded to afford the desired silyl ester without formation of the dechlorinated product. Also, no reduction of the nitro group was observed for nitrobenzoic acid (**1j**). Under the present conditions, the desired unsaturated silyl ester was obtained by the reaction of a silane with an unsaturated carboxylic acid (**1l**) with the formation of a small amount of an over-reduced product. In the case of 4-acetylbenzoic acid (**1m**), no hydrogenation and hydrosilylation of the carbonyl group proceeded to give the desired silyl ester in high yield.

In order to establish the applicability of the present system to larger scale productions, a 50-mmol scale reaction of **1a** with **2a** (one equivalent with respect to **1a**) was carried out with 0.007 mol% of $[RuCl_2(p\text{-cymene})]_2$. This solvent-free larger-scale reaction showed a TOF of 380 h^{-1} and the TON reached up to 12,000 [Eq. (3)]. These TOF and TON values were

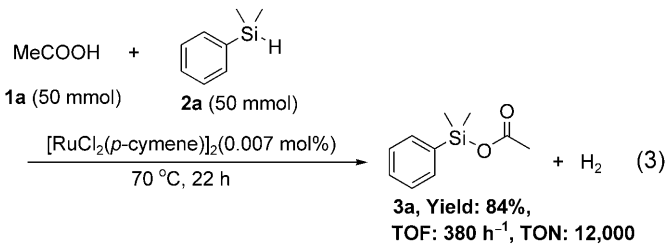

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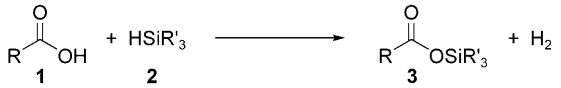
Table 2. Dehydrosilylation of various carboxylic acids with silanes catalyzed by $[RuCl_2(p\text{-cymene})]_2$.[a]



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Run	Carboxylic acid	Silane	Silyl ester	*t* [h]	Yield [%]
1	MeCOOH (**1a**)	$PhMe_2SiH$ (**2a**)	**3a**	2	94
2	**1a**	Ph_2MeSiH (**2b**)	**3b**	6	82
3	**1a**	Et_3SiH (**2c**)	**3c**	6	89
4	EtCOOH (**1b**)	**2a**	**3d**	2	76
5	**1b**	**2b**	**3e**	6	83
6	*n*-PrCOOH (**1c**)	**2a**	**3f**	3	75
7	**1c**	**2b**	**3g**	6	84
8	*i*-PrCOOH (**1d**)	**2a**	**3h**	3	74
9	*n*-BuCOOH (**1e**)	**2a**	**3i**	3	75
10	**1e**	**2b**	**3j**	6	85
11	$n\text{-}C_5H_{11}COOH$ (**1f**)	**2a**	**3k**	3	76
12	**1f**	**2b**	**3l**	7	84
13	**1f**	**2c**	**3m**	6	73
14[b]	AdCOOH[c] (**1g**)	**2a**	**3n**	4	84
15[b]	PhCOOH (**1h**)	**2a**	**3o**	2	88
16[b]	**1h**	**2c**	**3p**	3	96
17[d]	$4\text{-}ClC_6H_4COOH$ (**1i**)	**2c**	**3q**	6	85
18[d]	$4\text{-}NO_2C_6H_4COOH$ (**1j**)	**2c**	**3r**	7	75
19[b]	$Ph(CH_2)_2COOH$ (**1k**)	**2a**	**3s**	2	84
20[b]	**1k**	**2c**	**3t**	3	97
21[b]	PhCH=CHCOOH (**1l**)	**2c**	**3u**	7	76[e]
22[f]	4-acetyl-C_6H_4COOH (**1m**)	**2c**	**3v**	7	90

[a] *Reaction conditions:* carboxylic acid (5 mmol), silane (5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.5 mol%), 50 °C. Yields were determined by ^1H NMR or GC.
[b] *Reaction conditions:* carboxylic acid (1 mmol), silane (1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (1 mol%), toluene (3 mL), 50 °C.
[c] Ad = 1-adamantyl.
[d] *Reaction conditions:* carboxylic acid (1 mmol), silane (1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (1 mol%), 1,4-dioxane (3 mL), 50 °C.
[e] Compound **3t** was formed as a by-product (7%).
[f] *Reaction conditions:* carboxylic acid (1 mmol), silane (1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (1 mol%), 1,4-dioxane (5 mL), 50 °C.

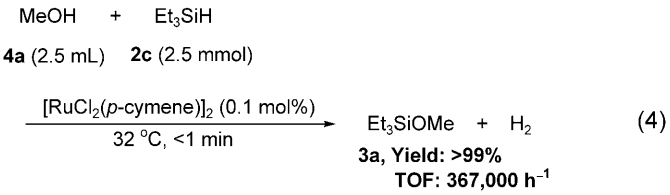
the highest among those for the previously reported dehydrosilylation reactions (TOF: 0.25–168 h^{-1}, TON: 6–192).[5]

In addition, the present system could be applied to the dehydrosilylation of alcohols with silanes.[6,8] The dehydrosilylation with dimeric metal complexes such as $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(CO)_3]_2$, $[RhCl_2Cp^*]_2$, $[RhCl(cod)]_2$, $[IrCl_2Cp^*]_2$, and $[PdCl(\pi\text{-allyl})]_2$ efficiently proceeded (Table 3). When **2a** (2.5 mmol) was added to methanol solution of $[RuCl_2(p\text{-cymene})]_2$ (1.0 mM, 2.5 mL) at 32 °C, the reaction was completed within 1 min [Eq. (4)]. In this case, the TOF (determined by the initial rate) reached up to 367,000 h^{-1} and the value was the highest among those previously reported dehydrosilylation of alcohols (TOF: 1–130,000 h^{-1}).[4] Furthermore, the catalyst amount could be much reduced: In a 150-mmol scale reaction of **4b** with **2a** (one equivalent with respect to **4b**) using 0.0013 mol% of $[RuCl_2(p\text{-cymene})]_2$, the TON reached up to 60,000 [Eq. (5)]. This value was of the highest level among those with previously reported systems (TON: 50–7,000)[4] except for the [Au]-SMAP-Rh system, which was recently reported by Sawamura and co-workers (12,000–90,000).[4p]

Table 3. Dehydrosilylation of **4a** with **2a** by various catalysts.[a]

Run	Catalyst	Conv. [%]	Select. [%]
1	$[RuCl_2(p\text{-cymene})]_2$	>99	92
2	$[RuCl_2(CO)_3]_2$	90	92
3	$RuCl_2(PPh_3)_3$	4	89
4	$RuCp_2$	2	62
5	$[Ru(NH_3)_6]Cl_3$	2	88
6	$RuCl_3 \cdot n\,H_2O$	<1	–
7	$Ru(acac)_3$	<1	–
8	$Ru_3(CO)_{12}$	<1	–
9	$K_2RuCl_5 \cdot H_2O$	<1	–
10	$(n\text{-}Pr)_4NRuO_4$	<1	–
11	$RuH_2(PPh_3)_4$	<1	–
12	$[RhCl_2Cp^*]_2$	>99	95
13	$[RhCl(cod)]_2$	73	99
14	$RhCl(PPh_3)_3$	<1	–
15	$[IrCl_2Cp^*]_2$	95	97
16	$[PdCl(\pi\text{-allyl})]_2$	95	97
17	$Pd(OAc)_2$	88	77
18	blank	<1	–

[a] *Conditions:* **4a** (5 mmol), **2a** (5 mmol), catalyst (metal: 1 mol%), 0 °C (ice bath), 5 min.



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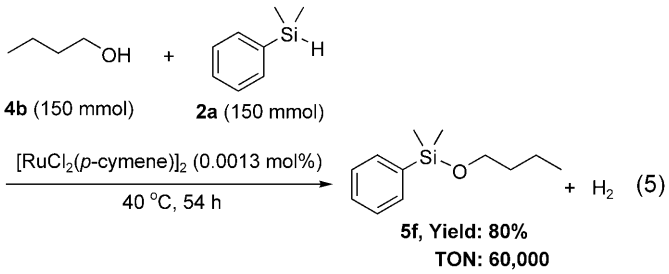
As shown in Table 4, various kinds of structurally diverse primary and secondary alcohols including aliphatic (**4a**–**4e** and **4j**), aromatic (**4f**), alkenic (**4g**), alk-

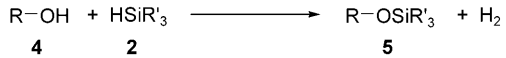


(5)

ynic (**4h**), and epoxy (**4i**) ones efficiently reacted with silanes (**2a**–**2e**) and all combinations gave the corresponding silyl esters (**5a**–**5r**) in good yields. Under the present conditions, the desired unsaturated silyl ethers (**5e** and **5n**–**5p**) were obtained with the formation of small amounts of over-reduced products. Interestingly, the desired silyl ether was obtained by the reaction of a silane with an epoxy alcohol (**4i**) without the formation of ring-opening and hydrosilylation products. Although it took a longer reaction time (900 min), the dehydrosilylation of a tertiary alcohol **4j** with **2a** gave the corresponding silyl ether **5r** in good yield.

The ^{1}H NMR spectrum of a toluene-d_8 solution of $[RuCl_2(p\text{-cymene})]_2$ (5 mM) and **2a** (50 mM) at 25 °C showed a signal at −10.6 ppm assignable to the ruthenium hydride species.[9] In contrast, no new signals were detected in the ^{1}H NMR spectrum of the toluene-d_8 solution of $[RuCl_2(p\text{-cymene})]_2$ (5 mM) and **4b** (or **1a**) (50 mM). These results suggest that the $[RuCl_2(p\text{-cymene})]_2$ catalyst cannot activate carboxylic acids and alcohols, and that the reaction is initiated by the activation of silanes by the $[RuCl_2(p\text{-cymene})]_2$ catalyst. To a toluene-d_8 solution of $[RuCl_2(p\text{-cymene})]_2$ (5 mM) and **2a** (50 mM) at 25 °C, ten equivalents of **4b** (or **1a**) with respect to **2a** were added, resulting in the disappearance of the hydride signal and the production of the corresponding silylated compound and the evolution of H_2. On the basis of these results, we here propose a possible reaction mechanism for the present dehydrosilylation. First, the ruthenium metal in $[RuCl_2(p\text{-cymene})]_2$ activates a silane to afford the hydride intermediate, possibly the silylmetal hydride species.[11] Then, the nucleophilic attack of a substrate (carboxylic acid or alcohol) to the hydride intermediate proceeds to give the corresponding silylated product.[10] The present $[RuCl_2(p\text{-cymene})]_2$-catalyzed dehydrosilylation with an optically active silane proceeded exclusively with inversion of stereochemistry at the chiral silicon center: the silylation of **4b** (1.5 equivalents with respect to **2f**) with *R*-(+)-methyl(1-naphthyl)phenylsilane (92% *ee*) (**2f**) afforded *R*-(−)-butoxymethyl(1-naphthyl)phenylsilane (**5s**) in 84% *ee*, for example [Eq. (6)].[12–14] This inversion of the stereochemistry suggests that the nucleophilic attack of a substrate to the hydride intermediate occurs from the backside of the ruthenium-silicon bond.

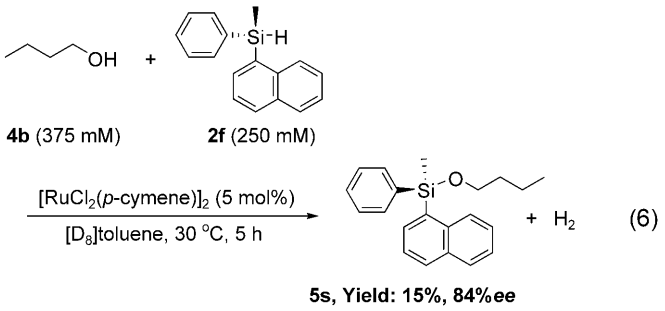
Table 4. Dehydrosilylation of various alcohols with silanes catalyzed by $[RuCl_2(p\text{-cymene})]_2$.[a]



Run	Alcohol	Silane	Silyl ether	*t* [min]	Yield [%]
1	MeOH (**4a**)	**2a**	**5a**	5	91
2	**4a**	**2b**	**5b**	5	93
3	**4a**	**2c**	**5c**	5	99
4[b]	**4a**	Ph_2SiH_2 (**2d**)	**5d**	30	82
5	**4a**	$PhMe(CH_2{=}CH)SiH$ (**2e**)	**5e**	5	83[c]
6	*n*-BuOH (**4b**)	**2a**	**5f**	5	98
7	**4b**	**2b**	**5g**	30	96
8	n-$C_6H_{13}OH$ (**4c**)	**2a**	**5h**	5	92
9	**4c**	**2b**	**5i**	60	92
10	cyclopentanol (**4d**)	**2a**	**5j**	5	91
11	cyclohexanol (**4e**)	**2a**	**5k**	30	86
12	BnOH (**4f**)	**2a**	**5l**	5	88
13	**4f**	**2b**	**5m**	30	92
14	allyl alcohol (**4g**)	**2a**	**5n**	5	88
15	**4g**	**2b**	**5o**	30	95
16	4-pentyn-2-ol (**4h**)	**2a**	**5p**	5	90
17	*trans*-2,3-epoxy-1-hexanol (**4i**)	**2a**	**5q**	15	85
18	*t*-BuOH (**4j**)	**2a**	**5r**	900	68

[a] *Reaction conditions:* alcohol (5 mmol), silane (5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.5 mol%), 0 °C (ice bath). Yields were determined by ^{1}H NMR or GC.
[b] *Reaction conditions:* alcohol (10 mmol), silane (5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.5 mol%), 0 °C (ice bath).
[c] Ethylmethoxymethylphenylsilane was formed as a by-product (10%).

Conclusions



We have demonstrated that $[RuCl_2(p\text{-cymene})]_2$ could act as an efficient homogeneous catalyst for the dehydrosilylation of carboxylic acids or alcohols with silanes. The dehydrosilylation of various kinds of structurally diverse carboxylic acids or alcohols with silanes efficiently proceeded to afford various kinds of the corresponding silylated products in good yields and selectivities, and showed high TON and TOF values. A wide variety of functional groups such as phenyl, chloro, nitro, alkenic, alkynic, carbonyl, and epoxy groups remained intrinsically intact under the present conditions. The reaction mechanism involving the formation of a silylmetal hydride species followed by the nucleophilic attack of a substrate (carboxylic acid or alcohol) has been proposed for the present dehydrosilylation.

Experimental Section

General Remarks

GC analyses were performed on a Shimadzu GC-2014 with an FID detector equipped with a TC-1 or TC-5 capillary column. The mass spectra were recorded on a Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. LC analyses were performed on a Shimadzu Prominence with a CD (Jasco CD-2095 Plus) detector equipped with a DAICEL CHILALCEL OD-H column. The liquid-state NMR spectra were recorded on a JEOL JNM-EX-270. The ^1H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, with TMS as an internal standard. Dynamic light scattering (DLS) measurements of the reaction solutions were performed on a Malvern Zetasizer Nano. The complex $[RuCl_2(p\text{-cymene})]_2$ was obtained from Aldrich (reagent grade) and used as received. Other metal salts and complexes were obtained from Wako Pure Chemical Industries, Kanto Chemical, TCI, or Aldrich (reagent grade) and used as received. Alcohols, carboxylic acids, silanes, and solvents were obtained from TCI or Aldrich (reagent grade) and purified prior to the use.[15] Compounds **1m**,[16] **2f**,[17] and **4i**[18] were synthesized according to the literature procedures.

Synthesis of *R*-(+)-Methyl(1-naphthyl)phenylsilane (2f)

Compound **2f** (92% *ee*) was synthesized according to the literature procedures.[17] The Grignard reagent was prepared from 1-bromonaphthalene (14.8 g, 71.5 mmol) with magnesium turnings (2.09 g, 86.0 mmol) in a mixed solvent of ether (5 mL), toluene (10 mL), and THF (5 mL). To the mixture was added a solution of dimethoxymethylphenylsilane (13.0 g, 71.3 mmol) in THF (10 mL) and the reaction mixture was stirred under reflux. After 13 h, the reaction mixture was cooled to *ca.* 20 °C and treated with saturated aqueous NH_4Cl (20 mL). The aqueous phase was extracted with ether (20 mL × 2). The ether solution was washed with water (20 mL × 2), dried over Na_2SO_4, and ether was removed under reduced pressure. The crude product was distilled, followed by crystallization to give purified *methoxymethyl(1-naphthyl)phenylsilane* as colorless crystals; yield: 16.1 g (89% yield based on 1-bromonaphthalene).

To a solution of methoxymethyl(1-naphthyl)phenylsilane (10.0 g, 35.9 mmol) in toluene (10 mL) were added (−)-menthol (5.66 g, 36.2 mmol) and solid NaOH (0.131 g, 2.34 mmol). The reaction mixture was maintained at 140 °C for 11 h, while the methanol-toluene azeotrope was distilled over a Vigreux column. After cooling to *ca.* 20 °C, NaOH was removed by passing the reaction mixture through a short column of silica gel with ether as an eluent. The extract was concentrated to afford a pale yellow oil. The pale yellow oil containing a mixture of the diastereomers was diluted with twice its volume of pentane and chilled to −50 °C. After several days, colorless needle-like crystals were formed, followed by recrystallization from pentane to afford *(−)-menthoxymethyl(1-naphthyl)phenylsilane*; yield: 1.25 g (17% yield based on methoxymethyl(1-naphthyl)phenylsilane).

To a slurry of $LiAlH_4$ (0.277 g, 7.30 mmol) in dry ether (2 mL) was added a solution of (−)-menthoxymethyl(1-naphthyl)phenylsilane (0.772 g, 1.92 mmol) in *n*-butyl ether (2 mL) and the resulting mixture was stirred vigorously at 80–90 °C. After 24 h, the mixture was cooled to *ca.* 20 °C and unreacted $LiAlH_4$ was slowly decomposed by the addition of water. To the mixture was added concentrated HCl and the mixture was extracted with ether (10 mL × 3). The combined extract was dried with Na_2SO_4 and evaporated. The crude product was purified by a column chromatography on silica gel with *n*-hexane as an eluent to give *R-(+)-methyl(1-naphthyl)phenylsilane* (**2f**) as colorless crystals; yield: 0.44 g [92% yield based on (−)-menthoxymethyl(1-naphthyl)phenylsilane]. MS (EI): *m/z* (%) = 249 (22), 248 (86) [M^+], 233 (33), 171 (18), 170 (100), 169 (21), 167 (14), 156 (10), 155 (62), 129 (15), 121 (15), 120 (88), 105 (54); ^1H NMR (270 MHz, chloroform-d_1, 25 °C, TMS): $\delta = 0.742$ (d, $^3J_{H,H} = 3.79$ Hz, 3H, $SiCH_3$), 5.36 (q, $^3J_{H,H} = 3.96$ Hz, 1H, SiH), 7.28–8.07 (m, 12H, aryl H); ^{13}C {^1H} NMR (67.8 MHz, chloroform-d_1, 25 °C, TMS): $\delta = -4.50$($SiCH_3$), 125.2, 125.6, 126.0, 128.0, 128.9, 129.5, 130.5, 133.2, 133.3, 134.9, 135.2, 135.4, 137.0; HPLC: $t_R{}^R = 25.6$ min (*cf.* $t_R{}^S = 29.8$ min, DAICEL CHIRALCEL OD-H, 0.46 cm $\phi \times 0.25$ cm, eluent: *n*-hexane).

Catalytic Dehydrosilylation

The catalytic dehydrosilylation of carboxylic acids was carried out as follows: To a mixture of **1a** (5 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.035 mmol, 0.7 mol%) was added **2c** (5 mmol) at 50 °C under an air atmosphere. The reaction mixture was stirred at 50 °C for 4 h and the progress was monitored by GC and ^{1}H NMR. The desired silyl ester **3c** was obtained in 79% isolated yield after Kugelrohr distillation under reduced pressure.

The catalytic dehydrosilylation of alcohols was carried out as follows: To a mixture of **4b** (5 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol, 0.5 mol%) was added **2a** (5 mmol) at 0 °C (ice bath) under an air atmosphere. The reaction mixture was stirred at 0 °C for 5 min and the progress was monitored by GC and ^{1}H NMR. The desired silyl ester **5f** was obtained in 95% isolated yield after Kugelrohr distillation under reduced pressure.

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[6] It was confirmed by the DLS measurements of the reaction solutions that no ruthenium clusters (detection limit: 0.6 nm) were detected during the dehydrosilylation.

[7] For solid carboxylic acids, toluene or 1,4-dioxane was used as a solvent.

[8] Lee and co-workers have reported the efficient synthesis of siloxacycles from terminal alkenyl alcohols and alkynylsilanes.[4k] The synthesis consists of two consecutive reactions of silylation of the terminal alkenyl alcohols with alkynylsilanes followed by the intramolecular methathesis, and $[RuCl_2(p\text{-cymene})]_2$ is used for the former silylation.[4k] Although the silylation of alkenyl and alkynyl alcohols is reported in the literature, the applicability to aliphatic and benzylic alcohols as well as carboxylic acids is not mentioned.[4k].

[9] In this case, the stoichiometric amounts of H_2 with respect to the corresponding silyl ethers were also formed.

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[12] The *ee* value of **5r** was determined by HPLC ($t_R{}^R$ = 23.0 min, $t_R{}^S$ = 19.9 min, DAICEL CHIRALCEL OD-H, 0.46 cm $\phi \times 0.25$ cm, eluent: *n*-hexane) with a CD-detector: S. Shinke, T. Tsuchimoto, Y. Kawakami, *Silicon Chem.* **2005**, *3*, 243.

[13] Under the conditions described in Eq. (6) (1.5 equivalents of **4b** with respect to **2f**), the reaction rate was very slow and the corresponding silyl ether was obtained in 30% yield after 48 h. In this case, the *ee* values of the product were almost unchanged during the reaction (84–88% *ee*).

[14] When the reaction of **2f** with ten equivalents of **4b** with respect to **2f** was carried out for 8 h [Other conditions were the same as those described in Eq. (6)], the corresponding silyl ether was obtained in 80% yield with 18% *ee* of the *R*-isomer. In addition, the reaction of a butyl ether **5f** with **4a** (five equivalents) gave the corresponding methyl ether **5a** in 50% yield under the conditions described in Eq. (7). All these results show that the transetherification of silyl ethers proceeds in the presence of $[RuCl_2(p\text{-cymene})]_2$ and excess amounts of alcohols. Therefore, the optical purity of the *R*-isomer **5s** was decreased by the transetherification (racemization)in the presence of large excess amounts of **4b** [Eq. (7)].

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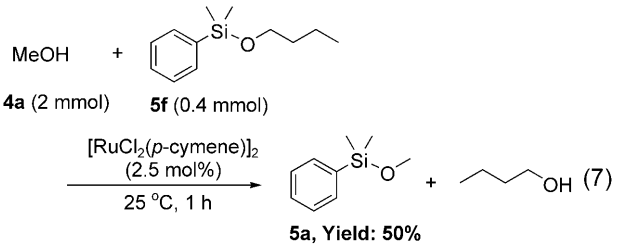

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