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Highly Regioselective Rhenium-Catalyzed Hydrosilylation of Styrenes

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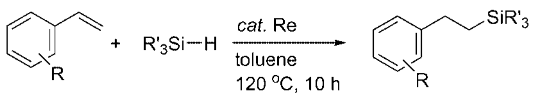
The addition reaction of silanes to styrenes is efficiently catalyzed by $ReBr(CO)_5$ in toluene heated at 120 °C and selectively affords *anti*-Markovnikov adducts in good to high yields.

Introduction

Transition-metal-catalyzed hydrosilylation reactions of unsaturated compounds that result in the formation of C–Si bonds have been investigated extensively in the past two decades because of the potential use of the silylated compounds and the transformation of the C–Si bond in organic synthesis.[1] A number of examples of the catalytic addition of hydrosilanes to alkynes catalyzed by a variety of transition metal complexes such as platinum,[2] rhodium,[2b,2d,3] ruthenium,[4] and other metal complexes[5] have been well-documented in the literature. Conversely, the investigation of the addition reactions of alkenes with hydrosilanes have focused on the use of electron-deficient hydrosilanes such as $HSiR_nX_{3-n}$ (X = Cl, n = 0, 1) and H_mSiR_{4-m} (m = 2, 3) in the presence of the late-transition-metal complexes.[6] Examples of hydrosilylation reactions of alkenes with $HSiR_3$ (R = alkyl, aryl) are relatively few.[2a,2c,6,7] Moreover, late-transition-metal-catalyzed hydrosilylation reactions of alkenes often proceed with the occurrence of some side reactions such as isomerization, polymerization, and dehydrogenative silylation.[8]

During the course of our investigation on the application of low-valent rhenium complexes in organic synthesis as catalysts, we found that $ReBr(CO)_5$ showed high catalytic activity and high regioselectivity in the addition reactions of carboxylic acids with terminal alkynes,[9] and the reactions of secondary amines and carbon dioxide with alkynes.[10] These results indicated that $ReBr(CO)_5$ could be employed as an effective catalyst for the activation of heteroatom–hydrogen bonds such as the O–H bond (carboxylic acids) and the N–H bond (amines). Recently, some high-valent rhenium complexes have been proven to be efficient catalysts for the hydrosilylation of aldehydes and ketones.[11]

In this paper, with the aim to extend the application of low-valent rhenium complexes in the catalytic activation of heteroatom–hydrogen bonds, we report the addition of hydrosilanes to styrenes catalyzed by $ReBr(CO)_5$ to selectively afford *anti*-Markovnikov adducts in good to high yields (Scheme 1). To the best of our knowledge, there have been very few reports in the literature on the early-transition-metal-catalyzed hydrosilylation of alkenes.[12]



Scheme 1.

Results and Discussion

First, we examined the reaction of styrene (**1a**) with methyldiphenylsilane with various rhenium complexes and solvents; the obtained results are summarized in Table 1. In the presence of a catalytic amount of $ReBr(CO)_5$, the reaction of **1a** with methyldiphenylsilane (1.2 equiv.) in toluene heated at 120 °C for 10 h resulted in the formation of methyldiphenyl(2-phenylethyl)silane (**2a**) in 89% GC yield with 96% selectivity (Table 1, Entry 1). A low reaction temperature (100 °C) led to an increase in the selectivity of the reaction, but a considerable decrease in the yield was observed (Table 1, Entry 2). Other rhenium complexes, such as $ReCl(CO)_5$ and $Re_2(CO)_{10}$, also showed catalytic activity for the hydrosilylation of **1a**, albeit less actively than $ReBr(CO)_5$, to give **2a** in moderate yields, as well as a slightly decreased selectivity (Table 1, Entries 3 and 4). However, $CpRe(CO)_3$ and NH_4ReO_4 did not show any catalytic activity at all (Table 1, Entries 5 and 6). In addition, the present $ReBr(CO)_5$-catalyzed addition reaction

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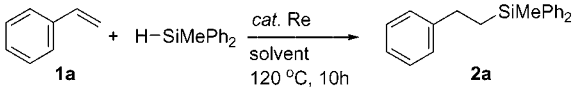
of **2a** with silane was found to be a solvent-dependent reaction. For example, repetition of the $ReBr(CO)_5$-catalyzed addition reaction in *n*-octane as the solvent resulted in a decrease in the yield; in this case, **2a** was formed in 73% GC yield with 96% selectivity (Table 1, Entry 7). Furthermore, the use of other solvents such as $CHCl_2CHCl_2$, THF, and DMF led to a very low yield or no formation of **2a** (Table 1, Entries 8–10).

Table 1. Rhenium-catalyzed hydrosilylation of styrene with $HSiMePh_2$.[a]

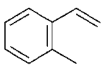
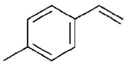
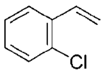
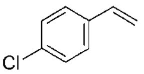
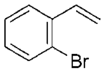
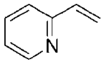
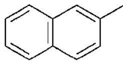


Entry	Catalyst	Solvent	Yield of **2a** [%][b]	Selectivity [%][c]
1	$ReBr(CO)_5$	toluene	89 (83)	96
2[d]	$ReBr(CO)_5$	toluene	76	> 99
3	$ReCl(CO)_5$	toluene	70	91
4	$Re_2(CO)_{10}$	toluene	50	90
5	$CpRe(CO)_3$	toluene	0	—
6	NH_4ReO_4	toluene	0	—
7	$ReBr(CO)_5$	*n*-octane	73	96
8	$ReBr(CO)_5$	$CHCl_2CHCl_2$	14	> 99
9	$ReBr(CO)_5$	THF	2	—
10	$ReBr(CO)_5$	DMF	0	—

[a] The reactions were carried out with **1a** (1.0 mmol), $HSiMePh_2$ (1.2 mmol), and the rhenium complex (0.03 mmol) in the appropriate solvent (1.0 mL) heated at 120 °C for 10 h while under a nitrogen atmosphere. [b] GC yield (isolated yield) based on the amount of **1a** used. [c] Determined by GC analysis of the reaction mixture. [d] The reaction was heated at 100 °C.

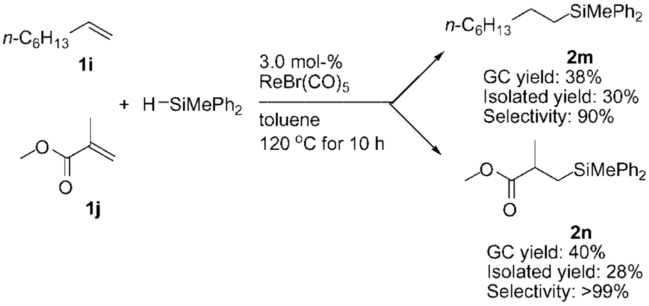
Results obtained from the addition reaction of various styrene derivatives with methyldiphenylsilane or dimethylphenylsilane in the presence of $ReBr(CO)_5$ are summarized in Table 2. Styrene (**1a**) reacted with dimethylphenylsilane to give corresponding adduct **2b** in high yield with 97% selectivity (Table 2, Entry 1). The present catalyst system could be applied to a variety of substituted styrenes including the electron-rich and electron-deficient styrenes, and all the addition reactions proceeded with high selectivity. The addition reaction of styrenes bearing an electron-donating substituent (methyl group) at the *ortho*- (**1b**) or *para* (**1c**) position of the aromatic ring occurred to give corresponding adducts **2c**, **2d**, and **2e** in high yields (Table 2, Entries 2–4). The formation of **2c** in a slightly low yield was considered to arise from the steric hindrance of the *ortho* methyl substituent in the aromatic ring with the $SiMePh_2$ group. Although electron-withdrawing group (Cl, Br) substituted styrenes **1d–f** also showed high reactivity in the addition reactions (Table 2, Entries 5–9), much more electron-deficient aromatic compound **1g** displayed the low reactivity for the same addition reaction (Table 2, Entry 10). As expected, $ReBr(CO)_5$-catalyzed hydrosilylation of 2-vinylnaphthalene (**1h**) afforded adduct **2l** in good yield (Table 2, Entry 11).

Table 2. $ReBr(CO)_5$-catalyzed hydrosilylation of styrenes.[a]

Entry	Styrene		Yield of **2** [%][b]		Selectivity [%][c]
1[d]	**1a**		**2b**	90	97
2		**1b**	**2c**	67 (82)	95
3[d]	**1b**		**2d**	85	96
4		**1c**	**2e**	94	96
5		**1d**	**2f**	95	>99
6[d]	**1d**		**2g**	85	>99
7		**1e**	**2h**	95	97
8[d]	**1e**		**2i**	91	>99
9		**1f**	**2j**	92	>99
10		**1g**	**2k**	48	95
11		**1h**	**2l**	69	>99

[a] The reactions were carried out with styrene **1** (1.0 mmol), $HSiMePh_2$ (1.2 mmol), and $ReBr(CO)_5$ (0.03 mmol) in toluene (1.0 mL) heated at 120 °C for 10 h while under a nitrogen atmosphere. [b] Isolated yield (GC yield) based on the amount of styrene used. [c] Determined by GC analysis of the reaction mixture. [d] $HSiMe_2Ph$ was used.

In contrast with the results of the hydrosilylation of styrenes, the present $ReBr(CO)_5$-catalyzed addition reaction of aliphatic alkenes with silanes gave the corresponding adducts in a rather poor yield (<50%). For example, the addition reaction of 1-octene (**1i**) or methyl methacrylate (**1j**), an electron-deficient alkene, with methyldiphenylsilane produced corresponding adducts **2m** and **2n** in 38% and 40% GC yields, respectively (Scheme 2). In both cases, the alkenes were completely consumed, which indicates that the polymerization of aliphatic alkenes easily occurred in the presence of $ReBr(CO)_5$.



Scheme 2.

Although the mechanism for the present hydrosilylation is not yet clear, a possible mechanism is considered to be similar to that of the Lewis acid catalyzed hydrosilylation of alkynes[13] and alkenes.[14] It involves the decarbonylation of $ReBr(CO)_5$ to form 16-electron intermediate $ReBr(CO)_4$,[15] which displays the catalytic activity of a transition metal Lewis acid catalyst.[16] Also, it cannot be ruled out that the present hydrosilylation reaction proceeds through the similar mechanism[17] as the late transition metal complex catalyzed hydrosilylation reaction that includes an oxidative addition step of the Si–H bond to the rhenium complex to generate a Re(H)Si species. The oxidative addition of Si–H to the 16-electron low-valent rhenium intermediate $ReBr(CO)_4$ is also likely to occur. In addition, stable rhenium–silicon complexes have been well-documented.[18]

Conclusions

In summary, the $ReBr(CO)_5$-catalyzed hydrosilylation of styrenes has been developed. The addition reaction proceeds with high regioselectivity to afford *anti*-Markovnikov adducts in good to high yields. This work has shown the first examples that prove that the early transition metal complex $ReBr(CO)_5$ is an efficient catalyst for the activation of silicon–hydrogen bonds and its addition to the carbon–carbon double bond of styrenes.

Experimental Section

General Methods: ^{1}H- and ^{13}C NMR spectra were recorded with a JOEL JNM-ECA 300 spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are referenced to TMS or the internal solvent resonance. GC–MS were obtained with a HEWLETT 5890 PACKARD SERIES II GC–MS spectrometer. High-resolution mass spectra were obtained with a ZAB-HS mass spectrometer in the Department of Chemistry of Peking University. GC analyses were performed with an Agilent Technologies 1790 GC instrument. Solvents and all reagents were used as received.

Typical Procedure for the Hydrosilylation of Styrene (1a) with $HSiMePh_2$ To Afford Methyldiphenyl(2-phenylethyl)silane (2a): A mixture of **1a** (116 µL, 1.0 mmol), methyldiphenylsilane (240 µL, 1.2 mmol), and $ReBr(CO)_5$ (12.2 mg, 0.03 mmol) in toluene (1.0 mL) under a nitrogen atmosphere was heated with stirring in a thick-walled Pyrex sealed tube at 120 °C for 10 h. After cooling, the reaction was diluted with toluene to 4.0 mL and n-$C_{18}H_{38}$ (101.6 mg, 0.4 mmol as internal standard) was added. The resulting mixture was then analyzed by GC and GC–MS. Volatiles were removed in vacuo and the residue was purified by column chromatography (silica gel, eluted with hexane, then hexane/diethyl ether, 10:1). Product **2a** was obtained as a colorless oil. Yield: 250.5 mg, 83%. The GC analysis of the reaction mixture revealed that the formation of adducts in 89% GC yield, and the selectivity of **2a** was 96% (Table 1, Entry 1).

Methyl[2-(2-methylphenyl)ethyl]diphenylsilane (2c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.02 (m, 14 H), 2.66–2.60 (m, AA′BB′, 2 H), 2.21 (s, 3 H), 1.40–1.34 (m, AA′BB′, 2 H), 0.61 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 136.9, 135.4, 134.4, 134.0, 130.1, 129.2, 127.9, 126.0, 125.7, 27.2, 19.0, 15.1, –4.60 ppm. GC–MS: m/z (%) = 316 (0.1) $[M]^+$, 301 (3), 238 (50), 223 (8), 197 (100), 183 (12), 121(6), 105 (14), 91(4). HRMS: calcd. for $C_{22}H_{24}Si$ 316.1647; found 316.1650.

Dimethyl[2-(2-methylphenyl)ethyl]phenylsilane (2d): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.03 (m, 9 H), 2.61–2.55 (m, AA′BB′, 2 H), 2.22 (s, 3 H), 1.08–1.02 (m AA′BB′, 2 H), 0.33 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.18, 138.99, 135.32, 133.56, 130.07, 128.93, 127.91, 127.79, 125.99, 125.64, 27.29, 19.05, 16.57, –3.16 ppm. GC–MS: m/z (%) = 254 (0.1) $[M]^+$, 239(14), 211(9), 176(61), 161(25), 135(100), 121(31), 105(12), 91(7), 77(4), 43(5). HRMS: calcd. for $C_{17}H_{22}Si$ 254.1491; found 254.1488.

Methyl[2-(4-methylphenyl)ethyl]diphenylsilane (2e): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.30 (m, 10 H), 7.06 (s, 4 H), 2.67–2.61 (m AA′BB′, 2 H), 2.30 (s, 3 H), 1.45–1.38 (m AA′BB′, 2 H), 0.56 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 137.0, 134.5, 134.0, 129.2, 129.0, 127.8, 127.6, 29.4, 20.9, 16.4, –4.50 ppm. GC–MS: m/z (%) = 316 (0.4) $[M]^+$, 301 (3), 272 (2), 238 (67), 223 (14), 197 (100), 183 (19), 105 (17), 91 (5). HRMS: calcd. for $C_{22}H_{24}Si$ 316.1647; found 316.1643.

[2-(2-Chlorophenyl)ethyl]methyldiphenylsilane (2f): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.05 (m, 14 H), 2.79–2.73 (m, AABB′, 2 H), 1.45–1.38 (m, AA′BB′, 2 H), 0.61 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 136.8, 133.5, 134.5, 129.6, 129.4, 129.3, 127.9, 127.1, 126.8, 28.1, 14.9, –4.59 ppm. GC–MS: m/z (%) = 336 (0.1) $[M]^+$, 321 (24), 258 (14), 197 (100), 183 (10), 165 (6), 105 (10), 91 (2). HRMS: calcd. for $C_{21}H_{21}SiCl$ 336.1101; found 336.1091.

[2-(2-Chlorophenyl)ethyl]dimethylphenylsilane (2g): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.05 (m, 9 H), 2.74–2.68 (m, AA′BB′, 2 H), 1.13–1.07 (m, AA′BB′, 2 H), 0.32 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 138.9, 133.6, 129.5, 129.4, 128.9, 127.8, 127.0, 126.9, 28.0, 16.2, –3.18 ppm. GC–MS: m/z (%) = 274 (0.1) $[M]^+$, 259 (50), 231 (5), 196 (14), 135 (100), 121 (28), 105 (10), 91 (6), 77 (6). HRMS: calcd. for $C_{17}H_{22}SiCl$ 259.0710; found 259.0712.

[2-(4-Chlorophenyl)ethyl]methyldiphenylsilane (2h): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.36 (m, 10 H), 7.20 (d, 2 H, J = 7.9 Hz), 7.08 (d, 2 H, J = 7.9 Hz), 2.67–2.62 (m, AABB′, 2 H), 1.43–1.37 (m AA′BB′, 2 H), 0.56 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.1, 133.6, 134.4, 131.2, 129.3, 129.1, 128.3, 127.9, 29.3, 16.3, –4.51 ppm. GC–MS: m/z (%) = 336 (0.1) $[M]^+$, 321 (0.3), 258 (18), 197 (100), 105 (20), 93 (5), 77 (9). HRMS: calcd. for $C_{21}H_{21}SiCl$ 336.1101; found 336.1096.

[2-(4-Chlorophenyl)ethyl]dimethylphenylsilane (2i): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.60 (m, 5 H), 7.30 (d, 2 H, J = 7.9 Hz), 7.15 (d, 2 H, J = 7.9 Hz), 2.69–2.63 (m, AA′BB′, 2 H), 1.18–1.12 (m, AA′BB′, 2 H), 0.36 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4, 138.8, 133.5, 131.1, 129.1, 129.0, 128.3, 127.8, 29.4, 17.7, –3.12 ppm. GC–MS: m/z (%) = 274 (0.2) $[M]^+$, 259 (5), 196 (40), 135 (100), 121 (31), 105 (9), 91 (3), 77 (4). HRMS: calcd. for $C_{16}H_{19}SiCl$ 274.0945; found 274.0944.

[2-(2-Bromophenyl)ethyl]methyldiphenylsilane (2j): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00–7.60 (m, 14 H), 2.79–2.73 (m, AA′BB′, 2 H), 1.44–1.38 (m, AA′BB′, 2 H), 0.62 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 136.7, 134.5, 132.7, 129.6, 129.3, 127.9, 127.5, 127.3, 123.9, 30.7, 15.2, –4.58 ppm. GC–MS: m/z (%) = 365 (19) $[M - Me]^+$, 302 (10), 223 (4), 197 (100), 183 (11), 165 (6), 105 (11), 93 (2). HRMS: calcd. for $C_{22}H_{24}SiBr$ 365.0361; found 365.0347.

Methyldiphenyl[2-(2-pyridinyl)ethyl]silane (2k): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, 1 H, J = 4.1 Hz), 7.58–7.05 (m, 13

H), 2.87–2.82 (m, AA′BB′, 2 H), 1.56–1.51 (m, AA′BB′, 2 H), 0.59 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 149.1, 136.7, 136.3, 134.5, 129.2, 127.9, 122.1, 120.9, 32.5, 14.5, –4.50 ppm. GC–MS: *m*/*z* (%) = 303 (2) $[M]^+$, 188 (17), 226 (100), 197 (30), 181 (7), 106 (16), 93 (3), 78 (3). HRMS: calcd. for $C_{20}H_{21}NSi$ 303.1443; found 303.1462.

Methyl[2-(2-naphthyl)ethyl]diphenylsilane (2l): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85–7.25 (m, 17 H), 2.87–2.82 (m, AA′BB′, 2 H), 1.56–1.50 (m, AA′BB′, 2 H), 0.60 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3, 136.9, 134.5, 133.6, 131.9, 129.2, 127.9, 127.8, 127.6, 127.4, 127.0, 125.8, 125.4, 125.0, 30.1, 16.1, –4.46 ppm. GC–MS: *m*/*z* (%) = 352, (11) $[M]^+$, 337 (3), 274 (35), 259 (10), 197 (100), 183 (11), 121 (6), 105 (12), 93 (3), 77 (1). HRMS: calcd. for $C_{25}H_{24}Si$ 352.1647; found 352.1635.

Methyl(*n*-octyl)diphenylsilane (2m): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.21 (m, 10 H), 1.50–1.15 (m, 12 H), 1.10–1.02 (m, AA′BB′, 2 H), 0.86 (t, 3 H, J = 6.8 Hz), 0.53 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 134.4, 129.0, 127.7, 33.6, 31.9, 29.2, 29.1, 23.8, 22.6, 14.1, 14.10, –4.44 ppm. GC–MS: *m*/*z* (%) = 310 (0.1) $[M]^+$, 295(0.2), 232(16), 197(100), 183(15), 121(6), 105(9). HRMS: calcd. for $C_{22}H_{33}Si$ 295.1882; found 295.1886.

Methyl 2-Methyl-3-(methyldiphenylsilyl)propanoate (2n): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.20, (m, 10 H), 3.42 (s, 3 H), 2.60 (m, 1 H), 1.61 (m, 1 H), 1.22 (m, 1 H), 1.14 (d, 3 H, J = 7.2 Hz), 0.59 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.6, 136.8, 136.4, 134.4, 129.2, 127.8, 51.4, 35.4, 20.8, 19.2, –4.05 ppm. GC–MS: *m*/*z* (%) 298 (0.1) $[M]^+$, 283 (15), 221 (100), 197 (81), 181 (18), 151 (46), 105 (24), 91 (14), 77 (12). HRMS: calcd. for $C_{18}H_{22}SiO_2$ 298.1389; found 298.1394.

Supporting Information (see footnote on the first page of this article): Spectroscopic data for known compounds **2a** and **2b**, copies of the ^{1}H- and ^{13}C NMR spectra of all products.

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