Notes

Diastereoselective Intramolecular Silylformylation of ω-Silylacetylenes

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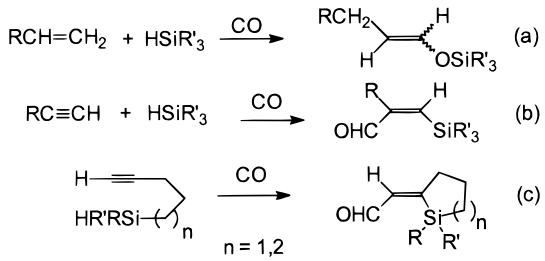
The silylformylation reaction of unsaturated compounds consists of the simultaneous introduction of a trialkylsilyl group and a formyl moiety into a carbon−carbon multiple bond in the presence of a rhodium catalyst. This reaction has been intensively studied in recent years[1] since it represents an extension of the well-known hydroformylation[2] process in which the H_2 molecule is replaced by a hydrosilane. Enol silyl ethers are formed as the major products when alkenes are used in the silylformylation reaction[3] (Scheme 1a). On the other hand, reactions involving an alkyne, carbon monoxide and a hydrosilane give carbon-centered silanes exclusively[4] (Scheme 1b).

In sharp contrast to the hydroformylation reaction, which often requires high CO/H_2 pressure and generates a mixture of saturated and unsaturated aldehydes, the silylformylation of acetylenes occurs under mild conditions and affords β-silylenaldehydes (Scheme 1b) in high yields. The regio- and stereochemical control of this process seems to be governed by the steric hindrance of the substituents: the formyl moiety is always introduced at the sp carbon bearing the bulkier group.[5] Thus, in the silylformylation of terminal acetylenes, (*Z*)-3-silyl-2-alkenals are obtained[6] (Scheme 1b).

Scheme 1



Scheme 2

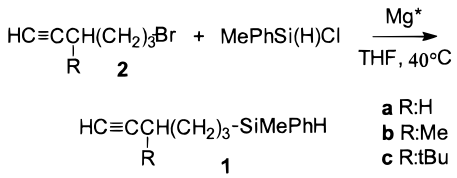


Table 1. Synthesis of ω-Silylacetylenes 1a−c[a]

entry	R	*t* (h)	Si:Br[b]	Mg:Br[c]	**1**	yield[d] (%)
1	H	3	1	10	**a**	40
2	H	24	1	2	**a**	38
3	CH_3	3	1	2	**b**	30
4	CH_3	72	3	2	**b**	8
5	tBu	3	1	2	**c**	37

[a] Reactions were carried out in THF on a 10 mmol scale of alkyne, at 40 °C; see the Experimental Section. [b] Chlorosilane: bromide (mmol/mmol) ratio. [c] Magnesium:bromide (mmol/mmol) ratio. [d] Yields of purified products.

Reverse regioselectivity is observed if terminal alkynylsilanes are reacted with CO[7] (Scheme 1c).

In contrast with the intermolecular reaction, in the intramolecular process it is not the internal sp carbon which is selectively formylated, but the terminal one, since the ring closure takes place according to the exo-dig Baldwin rule.[8] Here we report new results on the rhodium-catalyzed intramolecular silylformylation of substituted ω-silylacetylenes, which are building blocks of considerable potential in organic synthesis.

Results and Discussion

For this study, both linear and C_3-branched 6-(methylphenylsilyl)-1-hexynes **1** were synthesized starting from the corresponding bromides **2**, according to the procedure reported by Alper and co-workers (Scheme 2).[9] The yields are given in Table 1.

In a typical run, a mixture of the alkyne (10 mmol) and MePhSi(H)Cl in THF was slowly added to a suspension of magnesium turnings in THF, previously activated with 1,2-dibromoethane, and the reaction mixture was

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(9) ω-Bromoacetylenes **2** were obtained from the corresponding alkynyl alcohols[10] via the quantitative formation of *p*-toluenesulfonates.

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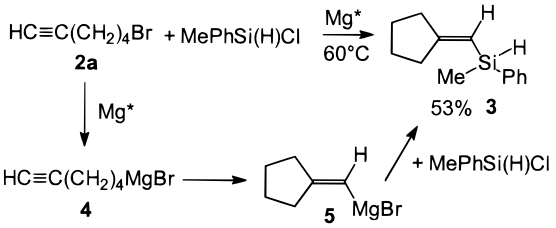
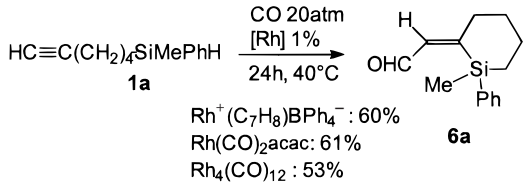
Scheme 3



Scheme 4[a]



[a] Reactions perfomed in a 40 mL stainless steel autoclave, with 1 mmol of reagent and 0.01 mmol of the catalyst (1%), at 40 °C for 24 h, under 20 atm of CO.

stirred at 40 °C for the times indicated in Table 1. The reaction was not affected either by a high chlorosilane: bromide ratio (Table 1, entry 4) or by long reaction times (Table 1, entries 2−4). The presence of a large excess of Mg turnings (Table 1, entry 1 vs entry 2) did not increase the yield of the *ω*-silylalkynes. Fair yields (30−40%) of **1** were obtained, and the reaction is probably dependent on the presence of two acidic protons in **2**, the acetylenic and the propargyl ones. It is well-known that Grignard reagents can easily undergo metal−proton exchange. Moreover, the reaction temperature must be strictly maintained at 40 °C to avoid carbometalation side reactions.[11] Indeed, when 6-bromo-1-hexyne (**2a**) and chloromethylphenylsilane were reacted with activated magnesium at higher temperature (60−70 °C), [(methylphenylsilyl)methylene]cyclopentane (**3**) was formed in 53% yield (Scheme 3). The latter may arise by intramolecular carbometalation[12] of **4** to generate **5** and subsequent coupling with the chlorosilane as shown in Scheme 3.

MePhSi(H)Cl was chosen as the silyl moiety precursor since it introduces an asymmetric silicon center in the *ω*-alkynes **1**. Furthermore, it has been shown that the silylformylation of alkynes with hydrosilanes bearing a phenyl group (i.e., Me_2PhSiH) proceeds approximately 10 times faster than that with trialkylsilanes[5] (i.e., Et_3SiH).

At the beginning of this study, different rhodium catalysts were tested, employing 6-(methylphenylsilyl)-1-hexyne (**1a**) as the model substrate, as shown in Scheme 4. All experiments were performed according to the following procedure: the *ω*-silylacetylene (1 mmol), freshly distilled dichloromethane (25 mL), and the rhodium complex (1 mmol %) were placed in a 40 mL stainless steel autoclave. The reactor was flushed three times with CO, pressurized to 20 atm of carbon monoxide, and stirred at 40 °C for 24 h. Both the zwitterionic and covalent complexes showed good catalytic activity, and

Scheme 5

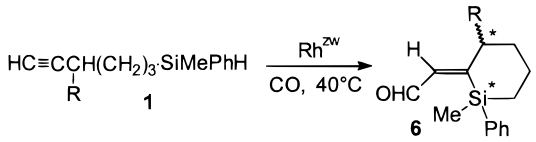


Table 2. Intramolecular Silylformylation of *ω*-Silylacetylenes Promoted by $Rh^+(C_7H_8)BPh_4^-$ [a]

entry	R	P_{CO} (atm)	*t* (h)	**6**	yield[b] (%)	ratio of diastereomers[c] (cis:trans)
1	CH_3	20	24	**b**	73	50:50
2	tBu	20	24	**c**	20	100:0
3	tBu	20	48	**c**	58	100:0
4	tBu	50	24	**c**	70	100:0

[a] Reactions were performed in a 40 mL stainless steel autoclave, with 1 mmol of reagent and 0.01 mmol of the catalyst (1%), at 40 °C. [b] Isolated yields. [c] Calculated from ^1H NMR peaks of the aldehydic protons.

the pure aldehyde **6a** was obtained in good yields (53−61%). The reaction is completely regioselective: exo-dig ring closure with (*Z*)-double bond formation, affording the six-membered formyl derivative.

The air-stable zwitterionic complex[13] $Rh^+(C_7H_8)BPh_4^-$ was used in subsequent reactions involving **1b** and **1c** (Scheme 5, Table 2). As is evident from the data in Table 2, the presence of a C_3-substituent on the *ω*-silylacetylenic precursor did not affect the regioselectivity of the process, with the exocyclic regioisomer being formed in all cases with net cis addition of the aldehyde and the silyl moiety. On the other hand, when a bulky substituent, such as a *tert*-butyl group, was present on the substrate, longer reaction times (48 h, Table 2, entry 3) and higher CO pressure (50 atm, Table 2, entry 4) were necessary to improve the yield of silacyclane **6c**.

The most interesting feature of these reactions is the total diastereoselectivity of the intramolecular process if a hindered substrate is reacted (Table 2, entries 2−4). Actually, the presence of two chiral centers in **6b** and **6c** (the silicon and the carbon atom in the positions α to the double bond) suggested the possibility of the formation of two different diastereoisomers (cis and trans). Surprisingly, when 3-*tert*-butyl-6-(methylphenylsilyl)-1-hexyne (**1c**) was submitted to intramolecular silylformylation, only one diastereoisomer was detected. On the contrary, when a methyl group was present on the alkynyl chain, no diastereoselectivity was observed, both isomers being formed in a 50:50 ratio (Table 2, entry 1).

NOE experiments performed on **6c** indicated that the aldehydic proton (C**H**O) was enhanced when the methyl to the silicon atom (CH_3−Si) was irradiated and the vinylic proton (=C**H**) was enhanced when the *tert*-butyl group ($(CH_3)_3C$) was irradiated (Figure 1). Thus, a 2-(formylmethylene)-1-silacyclohexane was formed with a phenyl (Si) and a *tert*-butyl (C_3) group in a trans geometry.

To investigate the influence of the catalyst on the stereoselectivity of the process, a different rhodium species was used as the catalytic precursor in the intramolecular silylformylation of **1c.** In fact, the dia-

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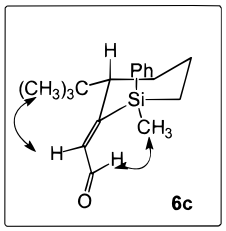
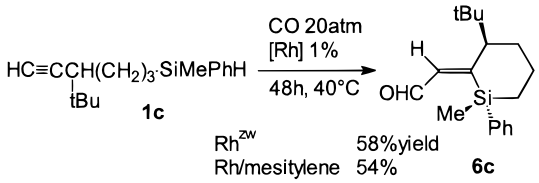


Figure 1.

Scheme 6



sterocontrol detected in this specific case could be related to the presence, in the zwitterionic complex, of bulky groups such as BPh_3 on the complexed arene ring. To test this hypothesis, the cocondensate Rh/mesitylene, prepared according to the metal vapor synthesis (MVS) technique,[14] was chosen as the catalyst since it exhibited high reactivity in the silylformylation reactions of variously branched acetylenes.[15] The reaction of rhodium vapors with mesitylene affords the so-called solvated metal atoms "solution", which is considered to be formed by highly reactive, small Rh metal clusters.[16] In this case no steric factors connected with the catalyst should affect the stereoselectivity of the reaction. As shown in Scheme 6, the activity and stereoselectivity of the MVS rhodium catalyst is comparable with that of the zwitterionic species, i.e., exclusive formation of *trans*-(*Z*)-2-(formylmethylidene)-3-*tert*-butyl-1-methyl-1-phenyl-1-silacyclohexane (**6c**) being observed in both cases.

In conclusion, both linear and branched ω-silylacetylenes can undergo intramolecular silylformylation reactions in the presence of carbon monoxide and a rhodium catalyst. The zwitterionic complex $Rh^+(C_7H_8)BPh_4^-$ and the Rh/mesitylene cocondensate are comparable in effectiveness (i.e., reactivity and stereoselectivity) and catalyze a totally regio- and diastereoselective cyclization if a sterically hindered alkynylsilane (**1c**) is used as the reactant. The compounds **6a**−**c** can be easily transformed into dienes,[17] dienones,[18] and α,β-unsaturated ketones[19] and can be important precursors for the synthesis of more complicated molecules via Peterson olefination,[20] Nazarov type cyclopentenone anulation,[21] or Trost type cyclopentane anulation.[22]

Experimental Section

General Methods. IR spectra were measured on KBr plates as neat films. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded in $CDCl_3$ solution with Me_4Si or $CHCl_3$ as internal standards. Mass spectra were obtained with a Perkin-Elmer Q-Mass 910 connected to a Perkin-Elmer 8500 gas chromatograph. GLC analyses were performed with a DB1 capillary column (30 m × 0.52 mm, 5 μm) using He as the carrier gas and a flame ionization detector (FID). Column chromatography was performed on silica gel 60 (230−400 mesh) purchased from Fluka. All solvents were reagent-grade materials, purchased by C. Erba, Fluka, and Merck, and purified by standard methods. Tetrahydrofuran and mesitylene were distilled from sodium immediately before use. Dichloromethane was distilled from P_2O_5 and stored over molecular sieves. Methylphenylchlorosilane (Fluka) was distilled under reduced pressure and stored over molecular sieves. 1,2-Dibromoethane (Fluka) was used without any further purification. $Rh_4(CO)_{12}$[23] and $[Rh^+C_7H_8BPh_4^-]$[13] were prepared according to published procedures. $Rh(CO)_2$acac was purchased from Aldrich.

General Procedure for the Synthesis of 6-(Methylphenylsilyl)-1-hexynes 1a−c. All reactions were carried out (at least in duplicate) under a dry nitrogen atmosphere. To a THF suspension of excess magnesium turnings (20 mmol), activated with 1,2-dibromoethane, was added dropwise a mixture of the 3-alkyl-6-bromo-1-hexyne **2** (10 mmol) and chlorodimethylphenylsilane (10 mmol). The reaction mixture was stirred for 3 h at 40 °C, then hydrolyzed with excess water, and extracted with pentane. The combined organic fractions were dried (Na_2SO_4), filtered, and concentrated in vacuo (15−20 mmHg). The residual oil, after purification by column chromatography using pentane as eluant, gave pure **1a**−**c** (Table 1).

6-(Methylphenylsilyl)-1-hexyne (1a):[7] IR 3294, 2110 cm^{-1}; ^{1}H NMR δ 0.34 (d, 3H, J = 3.8 Hz), 0.84−0.91 (m, 2H), 1.40−1.70 (m, 4H), 1.92 (t, 1H, J = 2.6 Hz), 2.19 (dt, 2H, J = 7 and 2.6 Hz), 4.35 (sext, 1H, J = 3.8 Hz), 7.35−7.42 (m, 3H), 7.52−7.59 (m, 2H); ^{13}C NMR δ −5.70, 12.89, 18.03, 23.50, 31.73, 68.17, 84.51, 127.87, 129.24, 134.29, 136.43; MS *m*/*z* (relative intensity) 187 (M^+ − 15, 13), 121 (100).

(*R*)(*S*)-3-Methyl-6-(methylphenylsilyl)-1-hexyne (1b): IR 3306, 2117 cm^{-1}; ^{1}H NMR δ 0.35 (d, 3H, J = 3.8 Hz), 0.89 (t, 2H, J = 6.8 Hz), 1.16 and 1.18 (2d, 3H, J = 6.9 and 5.8 Hz), 1.24−1.60 (m, 4H), 2.16 and 2.18 (2d, 1H, J = 2.4 and 3.3 Hz), 2.34−2.52 (m, 1H), 4.34 (sext, 1H, J = 3.8 Hz), 7.30−7.40 (m, 3H), 7.45−7.60 (m, 2H); ^{13}C NMR δ −6.15, (13.07, 14.00), (20.91, 22.02), (25.32, 27.30), 29.23, (36.90, 40.01), 68.14, 88.85, 127.84, 129.20, 134.29; MS *m*/*z* (relative intensity) 201 (M^+ − 15, 8), 121 (100).

(*R*)(*S*)-3-*tert*-Butyl-6-(methylphenylsilyl)-1-hexyne (1c): IR 3308, 2113 cm^{-1}; ^{1}H NMR δ 0.35 (d, 3H, J = 3.9 Hz), 0.95 (s, 9H), 1.20−1.85 (m, 6H), 2.00−2.10 (m, 2H), 4.36 (m, 1H), 7.30−7.40 (m, 3H), 7.48−7.57 (m, 2H); ^{13}C NMR δ −5.61, (13.22, 13.31), (23.26, 23.19), 27.46, (32.70, 32.78), 33.11, 43.26, 70.48, 86.47, 127.81, 129.16, 134.30, 136.60; MS *m*/*z* (relative intensity) 243 (M^+ − 15, 1), 121 (100).

Synthesis of [(Methylphenylsilyl)methylene]cyclopentane (3). Following the general procedure for the preparation of 6-(methylphenylsilyl)-1-hexynes **1a**−**c**, 20 mmol of Mg turnings, 10 mmol of **2a**, and 10 mmol of chlorodimethylphenylsilane were reacted at 60 °C for 5 h. After the usual workup, 1.07 g (53%yield) of pure **3** was obtained: ^{1}H NMR δ 0.43 (d, 3H, J = 3.9 Hz), 1.63−1.77 (m, 4H), 2.30−2.48 (m, 4H), 4.67−4.75 (m, 1H), 5.54−5.59 (m, 1H), 7.35−7.43 (m, 3H), 7.54−7.65 (m, 2H); MS *m*/*z* (relative intensity) 202 (M^+, 5), 121(100). Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.28; H, 8.83.

Rhodium-Catalyzed Intramolecular Silylformylation of 6-(Methylphenylsilyl)-1-hexynes. Carbonylation reactions were run in a 40 mL stainless steel autoclave containing a glass liner. In a typical run, 1 mmol of 6-(methylphenylsilyl)-1-hexyne,

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15 mL of freshly distilled dichloromethane, and 0.01 mmol of the rhodium catalyst were placed in the autoclave. The reactor was flushed three times with CO and pressurized with carbon monoxide. The reactor mixture was stirred for a specified period of time at 40 °C, and then cooled to room temperature. After removal of excess CO (fume hood) the reaction mixture was diluted with pentane and filtered (Celite), and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel using pentane/EtOAc (93:7) as eluant, affording pure **6a**−**c** (Table 2, Schemes 4−6).

(*Z*)-2-(Formylmethylidene)-1-methyl-1-phenyl-1-silacyclohexane (6a): IR 1675, 1428, cm^{-1}; ^1H NMR δ 0.57 (s, 3H), 0.75−1.30 (m, 2H), 1.60−1.90 (m, 4H), 2.46−2.70 (m, 2H), 6.43 (dt, 1H, J = 8.5 and 1.4 Hz), 7.33−7.43 (m, 3H), 7.50−7.57 (m, 2H), 9.54 (d, 1H, J = 8.5 Hz); ^{13}C NMR δ −1.57, 14.43, 23.93, 29.96, 41.78, 128.48, 129.34, 133.90, 136.00, 141.34, 171.29, 193.69; MS *m*/*z* (relative intensity) 230 (M^+, 9), 187 (100). Anal. Calcd for $C_{14}H_{18}SiO$: C, 72.99; H, 7.88. Found: C, 73.17; H, 7.92.

(*Z*)-2-(Formylmethylidene)-1,3-dimethyl-1-phenyl-1-silacyclohexane (6b): diastereomeric ratio 50:50; IR 1682, 1428 cm^{-1}; ^1H NMR δ 0.55 and 0.58 (2s, 3H), 0.80−2.08 (m, 6H), 1.09 and 1.14 (2d, 3H, J = 6.8 and 6.7 Hz), 2.53−2.79 (m, 1H), 6.43 and 6.51 (2dd, 1H, J = 8.3 and 1.6 Hz), 7.30−7.40 (m, 3H), 7.45−7.60 (m, 2H), 9.44 and 9.75 (2d, 1H, J = 8.3 Hz); ^{13}C NMR δ −2.13, (14.14, 14.23), 20.44, (21.06, 21.15), 37.17, (42.15, 42.43), (128.35, 128.49), (129.67, 129.88), (133.77, 133.80), (136.48, 137.04), (138.96, 139.43), (174.55, 174.79), (193.90, 194.11); MS *m*/*z* (relative intensity) 244 (M^+, 49), 137 (100). Anal. Calcd for $C_{15}H_{20}SiO$: C, 73.71; H, 8.25. Found: C, 74.02; H, 8.43.

(*Z*)-2-(Formylmethylidene)-1-methyl-1-phenyl-3-(*tert*-butyl)-1-silacyclohexane (6c): diastereomeric ratio 100:0; IR 1668, 1429 cm^{-1}; ^1H NMR δ 0.54 (s, 3H), 0.91 (s, 9H), 1.00−1.25 (m, 1H), 1.54−1.76 (m, 3H), 1.86−2.14 (m, 2H), 2.36−2.46 (m, 1H), 6.62 (dd, 1H, J = 8.3 and 1.2 Hz), 7.32−7.40 (m, 3H), 7.45−7.58 (m, 2H), 9.62 (d, 1H, J = 8.3 Hz); ^{13}C NMR δ 0.64, 12.70, 21.00, 29.09, 30.83, 35.09, 57.24, 128.42, 129.77, 133.99, 136.84, 143.76, 176.00, 193.69; MS *m*/*z* (relative intensity) 286 (M^+, 100). Anal. Calcd for $C_{18}H_{26}SiO$: C, 75.46; H, 9.15. Found: C, 75.25; H, 8.99.

Silylformylation of 3-*tert*-butyl-6-(methylphenylsilyl)-1-hexyne Catalyzed by Rh/Mesitylene Cocondensate. The reaction was performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. A 0.258 g (1 mmol) sample of **1c**, 1.5 mL of Rh/mesitylene cocondensate (0.01 mmol Rh), and 8.5 mL of freshly distilled dichloromethane were added, via syringe and under CO atmosphere, into a Pyrex "Schlenk" tube. This solution was introduced into the autoclave, previously placed under vacuum (0.1 mmHg), by a steel siphon. The reactor was pressurized to 20 atm of CO, and the mixture was stirred at 40 °C for 48 h. After removal of excess CO (fume hood), the reaction mixture was diluted with pentane, filtered (Celite), and concentrated by bulb to bulb distillation (1 mmHg) of the solvents. The residue was purified by column chromatography on silica gel using pentane/EtOAc (93:7) as eluant, affording 0.155 g (54%) of pure (*Z*)-2-(formylmethylidene)-3-*tert*-butyl-1-methyl-1-phenyl-1-silacyclohexane (**6c**).

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