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Lanthanoid-metal-mediated Organic Reactions of Acyltrialkylsilanes

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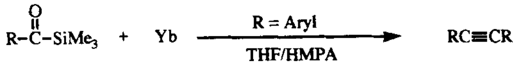
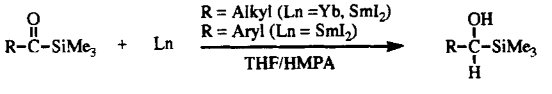
Aromatic acylsilanes such as benzoyltrimethylsilane react with ytterbium (Yb) metal to give the corresponding Yb-oxametallacycle of the aromatic acylsilane. The Yb-oxametallacycle thereby formed reacts with another aroylsilane to afford the symmetrical 1,2-diarylacetylene in good yield. These nucleophilic Yb-oxametallacycles have been found to react with a variety of electrophiles affording α-silyl alcohol derivatives. In contrast, aliphatic acylsilanes are reduced with lanthanoid reagents such as Yb metal and samarium(II) iodide (SmI_2) to give α-silyl alcohols, and the corresponding aliphatic acetylene was not obtained.

Keywords: lanthanoid metal; acylsilane; acetylene; α-silyl alcohol

INTRODUCTION

Organolanthanoids are useful reagents in organic syntheses. We previously reported the reactions of lanthanoid metals with carbonyl compounds. Lanthanoid-mediated reactions have played an important role in organic synthesis because of their unique reducing ability.[1,2] Recently, we reported that the reaction of lanthanoid metals [ytterbium (Yb), samarium (Sm)] with diaryl ketones produced the corresponding Yb- and Sm-oxametallacycles, which reacted easily with a variety of electrophiles such as ketones, esters, epoxides, nitriles, carbon dioxide and acetylenes to give the corresponding adducts.[3] We have succeeded in isolating and structurally characterizing the ytterbium(II)–benzophenone dianionic complex.[4] In continuing studies on exploring lanthanoid-mediated synthetic reactions, we have investigated the reactions of acylsilanes with Yb or SmI_2 under mild conditions and found that aromatic acylsilanes give the corresponding homocoupling products, 1,2-diarylacetylenes (**1a–1e**) and aliphatic acylsilanes give the reduction products, α-silyl alcohols (Eqns [1] and [2]).[5]


$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SiMe_3} + \mathrm{Yb} \xrightarrow[\text{THF/HMPA}]{\text{R = Aryl}} \mathrm{RC{\equiv}CR} \qquad (1)$$


$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SiMe_3} + \mathrm{Ln} \xrightarrow[\text{THF/HMPA}]{\substack{\text{R = Alkyl (Ln = Yb, Sm}I_2\text{)}\\ \text{R = Aryl (Ln = Sm}I_2\text{)}}} \mathrm{R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}SiMe_3} \qquad (2)$$

We report here the full details of the lanthanoid-mediated reactions of acylsilanes with respect to scope, limitations and mechanism.

RESULTS AND DISCUSSION

Synthesis of symmetric diarylacetylenes by homocoupling reaction of aroylsilanes

The coupling reaction of benzoyltrimethylsilane with ytterbium metal was examined. The reaction of benzoyltrimethylsilane with an equimolar amount of Yb was carried out at reflux temperature for 2 h in tetrahydrofuran–hexamethylphosphoric triamide (THF/HMPA) (4:1) solution. The reaction gave 1,2-diphenylacetylene (**1a**), stilbene (**2**), 1,2-diphenylethane (**3**), benzyl phenyl ketone (**4**) and bis(trimethylsilyl)phenylmethane (**5**) in 12, 11, 25, 20 and 32% yields, respectively (Eqn [3]). In marked contrast to the above reaction, the use of lithium metal in lieu of Yb metal did not give acetylene **1a**, the corresponding coupling adduct, but afforded ketone **4**, benzil and benzoin in 52, 25 and 22% yields, respectively. This result is similar to the reaction of acyl chloride with SmX_2 as depicted by Kagan and co-workers.[6] Equation [3] indicates that the reaction of acylsilanes with Yb metal may be a convenient synthetic method for symmetric acetylenes. Therefore, the optimization of the reaction conditions directed toward the acetylene synthe-

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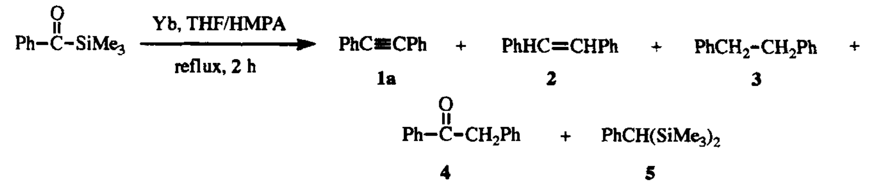

$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}SiMe_3} \xrightarrow[\text{reflux, 2 h}]{\text{Yb, THF/HMPA}} \underset{\mathbf{1a}}{\mathrm{PhC{\equiv}CPh}} + \underset{\mathbf{2}}{\mathrm{PhHC{=}CHPh}} + \underset{\mathbf{3}}{\mathrm{PhCH_2{-}CH_2Ph}} + \underset{\mathbf{4}}{\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_2Ph}} + \underset{\mathbf{5}}{\mathrm{PhCH(SiMe_3)_2}} \quad (3)$$

sis was performed. These results are listed in Table 1. Of the reaction conditions tested, the reaction at −10 °C for 20 min in a THF/HMPA solution gave the best result to afford acetylene **1a** in 67% yield along with ketone **4** (19%) (entry 4 in Table 1). The yield of acetylene **1a** increases and the yields of **2** and **3** decrease with decreasing temperature. Control experiments revealed that **2** (31%) and **3** (47%) were formed by the reduction of acetylene **1a** by Yb metal.[7] On the other hand, when the reaction was carried out in THF solvent, ketone **4** was obtained predominantly (entries 6 and 7 in Table 1). Ketone **4** is derived from benzoin, as indicated by the reaction of lithium metal as described above and as depicted by Kagan.[6] Control experiments indicated that acetylene **1a** was not obtained from the reaction of ketone **4**. Interestingly, bis(trimethylsilyl)phenylmethane (**5**) was formed in a low yield at a higher reaction temperature, although the mechanistic course is not clear.

Representative results for the reaction of various aromatic acyltrimethylsilanes with Yb metal to give the symmetrical acetylenes are summarized in Table 2. As shown in this table, various aroyltrimethylsilanes were homo-coupled smoothly to give the corresponding symmetrical acetylenes. The reactions of aroyltrimethylsilanes with electron-donating substituents on the phenyl group (entries 1–4 in Table 2) give 1,2-diarylacetylenes (**1a–1d**) in high yields, while the reaction of *p*-chlorobenzoyltrimethylsilane gives acetylene **1e** in a low yield because of the complex side reactions (entry 5 in Table 2). The reaction of aliphatic acylsilanes gave no acetylenic compound but it gave α-silyl alcohols derived from the reduction of the carbonyl group of acylsilane by Yb metal as mentioned below.

Selective synthesis of α-silyl alcohols by reduction of acylsilanes

The reaction of aliphatic acylsilanes such as n-hexanoyltrimethylsilane with Yb metal under the reaction conditions described above did not take place because of their lower reactivity, but the reaction at reflux for 19 h gave 1-trimethylsilylhexan-1-ol (**6**) in 67% yield (Eqn [4]). Similarly, the reaction of n-hexanoyltrimethylsilane with an equimolar amount of SmI_2 in THF, which is a powerful single-electron reductant, at room temperature for 18 h afforded the silyl alcohol **6** in 56% yield.[4] Three equivalents of SmI_2 gave silyl alcohol **6** in a similar yield (54%). Obviously, this result is different from that of the acyl chloride reported by Kagan.[6] Reaction of sterically hindered cyclohexanecarbonyldimethylphenylsilane with Yb metal gave the reduction product,

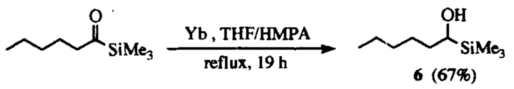

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Table 1 Reaction of benzoyltrimethylsilane promoted by Yb metal[a]

Entry	Solvent	Temp. (°C)	Time	Product and yield (%)[b] PhC≡CPh (**1a**)	PhCH=CHPh (**2**)	$(PhCH_2)_2$ (**3**)	$PhC(O)CH_2Ph$ (**4**)	$PhCH(SiMe_3)_2$ (**5**)
1	THF/HMPA	Reflux	2 h	12	11	25	20	32
2	THF/HMPA	rt[d]	3 h	16	14	10	43	17
3	THF/HMPA	0	5 min	47	8	—	29	—
4	THF/HMPA	−10	20 min	67	—	—	19	—
5	THF/HMPA	−40	1 h	26	20	—	—	—
6	THF[c]	rt	1 h	20	6	—	68	—
7	THF[c]	0	5 min	—	—	—	58	—

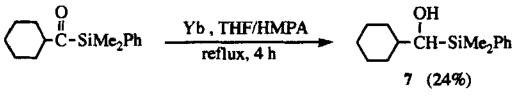
[a] Reaction conditions: Yb/benzoyltrimethylsilane = 1 : 1, THF (4 cm³), HMPA (1 cm³). [b] GLC yield. [c] 4 cm³. [d] rt, room temperature.

Table 2 Preparation of alkynes from aroylsilanes[a]

Entry	Ar	Product and yield (%)[b]
1	Ph	**1a**, 67
2	p-MeC_6H_4	**1b**, 91
3	m-MeC_6H_4	**1c**, 82
4	p-$MeOC_6H_4$	**1d**, 84
5	p-ClC_6H_4	**1e**, 31

[a] Conditions: Yb (1 mmol), aroylsilane(1 mmol), THF ($4\ cm^3$), HMPA ($1\ cm^3$), −10 °C, 20 min. [b] GLC yield.

α-(dimethylphenylsilyl)cyclohexylmethanol (**7**) in only 24% yield (Eqn [5]). Interestingly, the similar reaction of benzoyltrimethylsilane with three equivalents of SmI_2 in THF resulted in the formation of α-trimethylsilylbenzyl alcohol (**8**) in 62% yield without the formation of acetylene **1a** (Eqn [6]). We can see that, in the reaction with SmI_2 as a reducing agent, single-electron transfer to acylsilane occurs to afford an anion radical even with the use of excess amounts of SmI_2.



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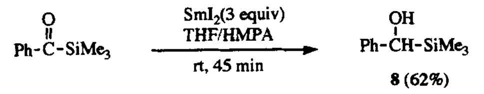


$$Ph\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}SiMe_3 \xrightarrow[\text{rt, 45 min}]{\text{SmI}_2\text{(3 equiv)},\ \text{THF/HMPA}} Ph\text{-}\overset{OH}{\overset{|}{C}H}\text{-}SiMe_3 \quad \mathbf{8}\ (62\%) \tag{6}$$

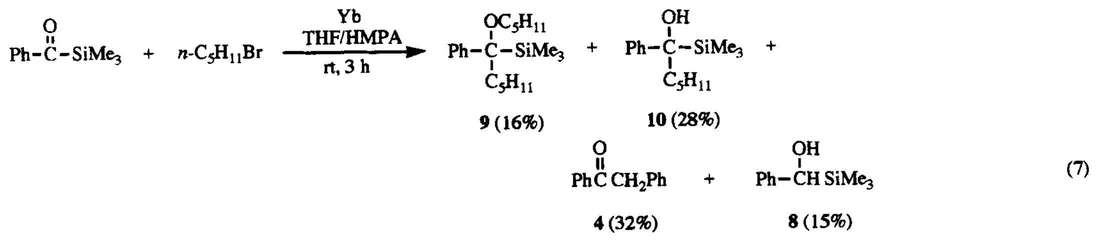
Ytterbium-mediated reaction of benzoyltrimethylsilane with various electrophiles

In order to clarify the reaction mechanism, the following trapping experiments were carried out using several electrophiles such as n-pentyl bromide and trimethylsilyl chloride. From the reaction with excess of n-pentyl bromide at room temperature for 3 h in THF/HMPA, there were obtained the C, O-bisalkylated adduct, pentyl 1-trimethylsilyl-1-phenylhexyl ether (**9**) (16%) and the C-alkylated adduct, 1-trimethylsilyl-1-phenyl-1-hexanol (**10**) (28%) along with **4** (32%) and **8** (15%) (Eqn [7]). With four equivalents of trimethylsilyl chloride under the same reaction conditions, the C,O-bis-silylated adduct, α,α-bis(trimethylsilyl)benzyl trimethylsilyl ether (**11**) was obtained in 80% yield along with α-silyl alcohol **8** (20%) (Eq. 8). These results clearly indicate that the Yb–acylsilane complex is readily formed as in the case of diaryl ketones.[4] Therefore, Yb metal can act as a double-electron reductant forming the oxametallacycle intermediacy.

Interestingly, the use of trimethylsilyl bromide (TMSBr) in lieu of trimethylsilyl chloride gave neither **11** nor **8**, but afforded the corresponding acetylene **1a** and 1,2-bis(trimethylsilyl)-1,2-bis(p-trimethylsilylphenyl)ethene (**12**) as a single stereoisomer in 12 and 26% yields, respectively (Eqn [9]). It seems that the reductive double silylation of **1a** with Yb metal and TMSBr, and subsequent addition of the trimethylsilyl (TMS) radical, which is generated by the action of Yb and TMSBr,[8] to aromatic rings affords the corresponding adduct **12**.

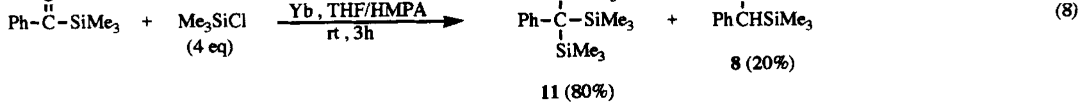
Reaction mechanism

A possible reaction mechanism of acyltrimethylsilanes with Yb is shown in Scheme 1. The acylsilane reacts with lanthanoid metal (or divalent lanthanoid reagents) to afford a lanthanoid(I) anion radical **A** by single-electron transfer to the carbonyl group of the acylsilane. Since the reaction with electrophiles, such as pentyl bromide and trimethylsilyl chloride, gave the C- and O-substituted adducts (Eqns [7] and [8]), the



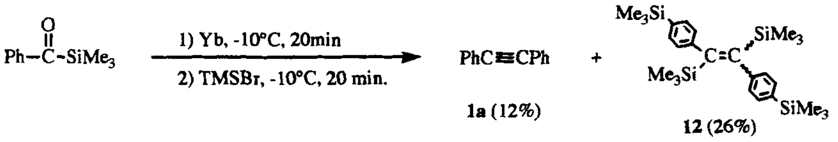
$$Ph\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}SiMe_3 + n\text{-}C_5H_{11}Br \xrightarrow[\text{rt, 3 h}]{\text{Yb},\ \text{THF/HMPA}} Ph\text{-}\underset{C_5H_{11}}{\overset{OC_5H_{11}}{C}}\text{-}SiMe_3 + Ph\text{-}\underset{C_5H_{11}}{\overset{OH}{C}}\text{-}SiMe_3 + PhC\overset{O}{\overset{\Vert}{}}CH_2Ph + Ph\text{-}\overset{OH}{CH}SiMe_3 \tag{7}$$

9 (16%) **10** (28%) **4** (32%) **8** (15%)



$$Ph\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}SiMe_3 + \underset{(4\ eq)}{Me_3SiCl} \xrightarrow[\text{rt, 3h}]{\text{Yb},\ \text{THF/HMPA}} Ph\text{-}\underset{SiMe_3}{\overset{OSiMe_3}{C}}\text{-}SiMe_3 + Ph\overset{OH}{C}HSiMe_3 \tag{8}$$

11 (80%) **8** (20%)



(9)

carbonyl group of the acylsilane was umpoled by the lanthanoid metal. Therefore, **A** formed in this way would be further reduced by the lanthanoid metal (not a divalent lanthanoid) giving a Ln-oxametallacycle **B**. As for the route to 1,2-diarylacetylenes, the Ln-oxametallacycle **B** would react with another molecule of aroyltrimethylsilane to give an intermediate **C** which undergoes the Peterson olefination[9] to give an intermediate **D**. The intermediate **D** would give rise to the 1,2-diarylacetylene.

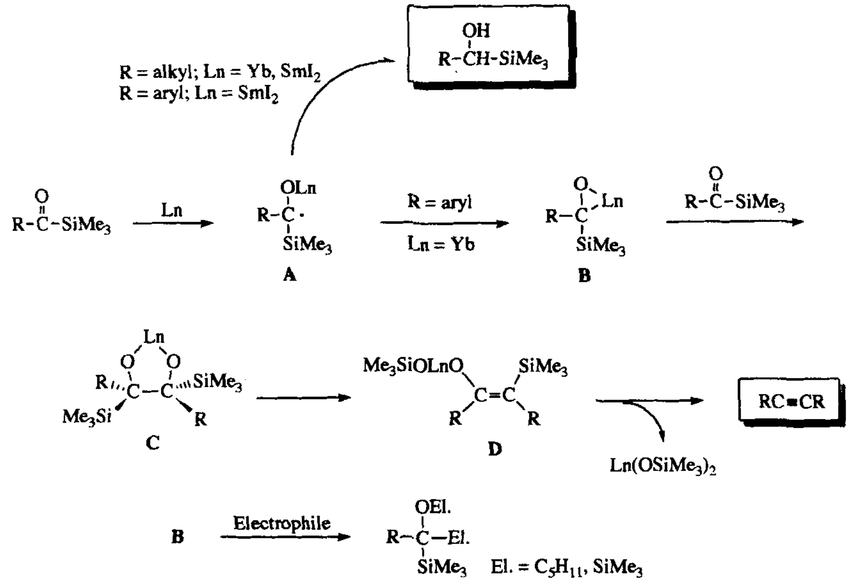
The formation of α-silyl alcohols would be explained best by a hydrogen abstraction of **A** or **B** from the solvent (THF).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-EX270 (^{1}H at 270 MHz and ^{13}C at 67.8 MHz) spectrometer. Chemical shifts (δ) were expressed in parts per million downfield from tetramethylsilane. Analytical GLC evaluations of product mixtures were performed on a Shimadzu GC-14A flame ionization chromatograph by using a 1 m × 3.2 mm analytical column packed with 2% silicone OV-17 on 60–80-mesh Uniport HP under the conditions: injection temperature 280 °C; detector temperature 280 °C. Mass spectra were obtained on a Shimadzu GC–MS QP1000 by using a 1.1 m × 3.2 mm glass column packed with 2% silicone OV-17 on 60–80-mesh Uniport HP. Elemental analyses were performed on a Yanagimoto MT-2 CHN corder. IR spectra were obtained on a Hitachi 260-30 or a Perkin–Elmer 1600 Series FTIR. Melting points were measured on a Yanaco micro melting-point apparatus.

Tetrahydrofuran (THF) was distilled from sodium benzophenone-ketyl under argon prior to use. Hexamethylphosphoric triamide (HMPA) was dried over calcium hydride, distilled under reduced pressure, and stored over activated 4 Å molecular sieves under argon. Ytterbium and samarium in mineral oil were commercially available and were used after washing with hexane.

Benzoyl-,[10,11] *p*-toluoyl-,[10] *m*-toluoyl-,[10] *p*-methoxybenzoyl-,[11] *p*-chlorobenzoyl-11 and hexanoyl-[12] trimethylsilanes were prepared by literature procedures. Cyclohexanecarbonyl



Scheme 1 Reaction mechanism for the lanthanoid-mediated reaction of acylsilane.

chloride was prepared by a literature method.[13] Samarium di-iodide was prepared as a THF solution by a literature method.[14]

Preparation of cyclohexanecarbonyldimethylphenylsilane

In a 100-cm^3 round-bottomed flask equipped with two dropping funnels, CuI (3.72 g, 20 mmol) was placed and dried under reduced pressure overnight. After the flask was flushed with argon, THF (5 cm^3) was added to the flask. $PhMe_2SiLi$ (0.651 mol dm^{-3}, 20 mmol) in THF was added to the flask from the dropping funnel at −20 °C. After stirring for 1 h, the flask was cooled to −78 °C. Cyclohexanecarbonyl chloride (2.7 cm^3, 20 mmol) was added from the other dropping funnel. After stirring for 4 h at −78 °C, the mixture was warmed to 0 °C. The reaction was quenched with saturated aqueous NH_4Cl (20 cm^3) and 2 mol dm^{-3} HCl (20 cm^3). The reaction mixture was extracted with ether (30 cm^3 × 3). The combined extracts were washed with a saturated aqueous $Na_2S_2O_3$ solution (20 cm^3 × 2) and dried over $MgSO_4$. Filtration and removal of the solvent gave a crude product. Purification with Medium Pressure Liquid Chromatography (MPLC) (SiO_2) using hexane–ethyl acetate as eluent followed by distillation afforded cyclohexanecarbonyldimethylphenylsilane (402 mg, 8% yield) as a colorless oil: b.p. 80 °C/1 mm Hg. IR (neat): ν(C=O) 1634 cm^{-1}. MS (70 eV): $m/z = 246$ (M^+), 231 ($M^+ - Me$), 135 ($PhMe_2Si^+$). ^1H NMR (C_6D_6): δ 0.57 (s, 6H), 1.13–1.87 (m, 10H), 2.71–2.82 (m, 1H), 7.35–7.42 (m, 3H), 7.66–7.69 (m, 2H).

Reaction of benzoyltrimethylsilane with ytterbium metal

Optimization of reaction condition

In a 20-cm^3 round-bottomed flask, equipped with a three-way stopcock, were placed Yb metal (173 mg, 1 mmol) and a magnetic stirring bar. The flask was flame-dried under reduced pressure for 30 min, then flushed with argon after cooling. THF (4 cm^3), HMPA (1 cm^3) and methyl iodide (3 μl) were successively added. Benzoyltrimethylsilane (1 mmol) was added by a syringe at −35 °C to room temperature. The flask was stirred under the conditions cited in Table 1. The reaction was quenched with 2 mol dm^{-3} HCl (20 cm^3). The reaction mixture was extracted with ether (20 cm^3 × 3). The combined ethereal extracts were washed with brine (30 cm^3 × 2) and dried over $MgSO_4$. Filtration and removal of the solvent gave a mixture of 1,2-diphenylacetylene (**1a**), stilbene (**2**), 1,2-diphenylethane (**3**), benzyl phenyl ketone (**4**) and bis(trimethylsilyl)phenylmethane (**5**). The yields of each adduct were calculated by GLC analysis using authentic samples. These results are listed in Table 1. Bis(trimethylsilyl)phenylmethane (**5**) was isolated by MPLC (SiO_2) using hexane–ethyl acetate as eluent.

Bis(trimethylsilyl)phenylmethane (5)

Colorless oil. IR (neat): ν(Si—C) 1250 cm^{-1}. MS (70 eV): $m/z = 236$ (M^+), 221 ($M^+ - Me$), 73 (TMS^+). ^1H NMR ($CDCl_3$): δ 0.01 (s, 18H), 1.46 (s, 1H), 6.86–7.25 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 0.18, 29.7, 123.3, 128.0, 128.8, 143.2.

General procedure for the preparation of diaryacetylenes

As described above, the reaction of aroyltrimethylsilane (1 mmol) with Yb metal (173 mg, 1 mmol) in THF (4 cm^3) HMPA (1 cm^3) was carried out at −10 °C for 20 min in a 20-cm^3 round-bottomed flask. The usual work-up gave a crude product. Purification with MPLC (SiO_2) using hexane–ethyl acetate as eluent followed by recrystallization gave a symmetric diarylacetylene. The results for homocoupling reactions of a variety of aroylsilanes are listed in Table 2.

Diphenylacetylene (1a)

Colorless crystals. MS (70 eV): $m/z = 178$ (M^+), 89 ($M^+/2$). ^1H NMR ($CDCl_3$): δ 7.11–7.30 (m, 6H), 7.42–7.46 (m, 4H).

Di(*p*-tolyl)acetylene (1b)

Colorless crystals: m.p. 135–137 °C. IR (Nujol): δ(C—H) 814 cm^{-1}. MS (70 eV): $m/z = 206$ (M^+), 191 ($M^+ - CH_3$). ^1H NMR ($CDCl_3$): δ 2.35 (s, 6H), 7.13 (d, $J = 8.0$ Hz, 4H), 7.41 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 21.5, 88.9, 120.5, 129.1, 131.5, 138.1.

Di(*m*-tolyl)acetylene (1c)

Colorless crystals: m.p. 76–78 °C (hexane), IR (Nujol): δ(C—H) 786 cm^{-1}. MS (70 eV): $m/z =$ 206 (M^+), 191 ($M^+ - CH_3$). ^1H NMR ($CDCl_3$): δ 2.36 (s, 6H), 7.16–7.37 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 21.2, 89.2, 123.1, 128.2, 128.6, 129.1, 132.2, 138.0.

Analysis: calcd for $C_{16}H_{14}$: C, 93.15; H, 6.84. Found: C, 93.15; H, 6.76%.

Di(*p*-anisyl)acetylene (1d)

Pale yellow crystals: m.p. 146–147 °C. IR (Nujol): ν_{as}(C—O—C) 1246, ν_s(C—O—C) 1026, δ(C—H) 835 cm^{-1}; MS (70 eV): *m*/*z* = 238 (M^+), 223 ($M^+ - CH_3$). ^1H NMR($CDCl_3$): δ 3.83 (s, 6H), 6.87 (d, *J* = 8.7 Hz, 4H), 7.46 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 55.3, 87.9, 114.0, 115.8, 132.9, 159.5.

Analysis: calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.56; H, 5.75%.

Di(*p*-chlorophenyl)acetylene (1e)

Colorless crystals: m.p. 179–180 °C. IR (Nujol): δ(C—H) 831 cm^{-1}. MS (70 eV): *m*/*z* = 247 (M^+), 176 ($M^+ - 2Cl$), 123 ($M^+/2$). ^1H NMR ($CDCl_3$): δ 7.31 (d, *J* = 9.0 Hz, 4H), 7.47 (d, *J* = 9.0 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 89.2, 121.5, 128.7, 132.8, 134.6.

Analysis: calcd for $C_{14}H_8Cl_2$: C, 68.04; H, 3.26. Found: C, 68.03; H, 3.23%.

General procedure for the reduction of acyltrialkylsilanes with ytterbium metal

In a 20-cm^3 round-bottomed flask, Yb metal (173 mg, 1 mmol) and a magnetic stirring bar were placed. The flask was flame-dried under reduced pressure for 30 min and then flushed with argon after cooling. THF (4 cm^3), HMPA (1 cm^3) and methyl iodide (3 μL) were successively added. Acyltrialkylsilane (1 mmol) was added by a syringe at room temperature. The mixture was refluxed for 3–19 h. The reaction was quenched with 2 mol dm^{-3}HCl (20 cm^3). After the usual work-up, the product was purified with MPLC (SiO_2) using hexane–ethyl acetate as eluent to give an α-silyl alcohol.

1-Trimethylsilyl-1-hexanol (6)

The reaction of hexanoyltrimethylsilane with Yb metal afforded **6** in 67% yield. Colorless oil. IR (neat): ν(OH) 3352 cm^{-1}. MS (70 eV): *m*/*z* = 159 ($M^+ - CH_3$), 117 ($M^+ - C_4H_9$), 101 ($M^+ - SiMe_3$), 73 (TMS^+). ^1H NMR ($CDCl_3$): δ −0.11 (s, 9H), 0.75 (t, *J* = 6.6 hz, 3H), 1.14–1.42 (m, 9H), 3.14 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (C_6D_6): δ −4.0, 14.0, 22.6, 26.5, 31.8, 33.4, 65.9.

α-(Dimethylphenylsilyl)cyclohexylmethanol (7)

The reaction of cyclohexanecarbonyldimethylphenylsilane with Yb metal afforded **7** in 24% yield. Colorless oil. IR (neat): ν(OH) 3441 cm^{-1}. MS (70 eV): *m*/*z* = 233 ($M^+ - CH_3$), 165 ($M^+ - C_6H_{11}$), 135 ($PhMe_2Si^+$). ^1H NMR (C_6D_6): δ 0.42 (s, 3H), 0.44 (s, 3H), 1.07–1.25 (m, 7H), 1.53–1.73 (m, 4H), 1.89–1.93 (m, 1H), 3.28 (d, *J* = 5.3 Hz, 1H), 7.28–7.33 (m, 3H), 7.65–7.68 (m, 2H). ^{13}C NMR (C_6D_6): δ −3.9, −3.8, 26.6, 26.7, 26.9, 29.7, 31.0, 42.5, 70.7, 128.1, 129.3, 134.4, 138.5.

Analysis: calcd for $C_{15}H_{24}OSi$: C, 72.51; H, 9.73. Found: C, 72.51; H, 9.73%.

General procedure for the reduction of acyltrialkylsilanes with samarium di-iodide

A 20-cm^3 round-bottomed flask containing a magnetic stirring bar was flame-dried under reduced pressure for 30 min and was flushed with argon after cooling. THF (2 cm^3) and acyltrialkylsilane (0.5 mmol) were added to the flask by a syringe at room temperature. Samarium di-iodide (0.1 mol dm^{-3}, 5.0 cm^3, 0.5 mmol) in THF was added from a dropping funnel to the flask. The mixture was stirred at room temperature for 0.5–18 h. The reaction was quenched with 2 mol dm^{-3} HCl (20 cm^3). After the usual work-up, the product was purified with MPLC (SiO_2) using hexane–ethyl acetate as eluent to give an α-silyl alcohol.

α-Trimethylsilylhexan-1-ol (6)

The reaction of hexanoyltrimethylsilane with an equimolar amount of SmI_2 afforded **6** in 56% yield. Similarly, the treatment with three equivalents of SmI_2 afforded **6** in 54% yield.

α-Trimethylsilylbenzyl alcohol (8)

The reaction of benzoyltrimethylsilane with three equivalents of SmI_2 afforded **8** in 62% yield. Colorless oil. IR (neat): ν(OH) 3400 cm^{-1}. MS (70 eV): *m*/*z* = 180 (M^+), 73 (TMS^+). ^1H NMR ($CDCl_3$): δ 0.01 (s, 9H), 1.42 (brs, 1H), 4.51 (s, 1H), 7.12–7.29 (m, 5H).

Ytterbium-mediated reaction of benzoyltrimethylsilane with electrophiles

In a 20-cm^3 round-bottomed flask were placed Yb metal (173 mg, 1 mmol) and a magnetic stirring bar. The flask was flame-dried under reduced pressure for 30 min, then flushed with argon after cooling. THF (4 cm^3), HMPA (1 cm^3) and methyl iodide (3 μl) were successively added. An electrophile (4 mmol) and benzoyltrimethylsilane (1 mmol) were successively added to the flask by a syringe at room temperature. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with 2 mol dm^{-3} HCl (20 cm^3). The reaction mixture was extracted with ether (20 $cm^3 \times 3$). After the usual work-up the product mixture was purified with MPLC (SiO_2) using hexane–ethyl acetate as eluent, to give adducts.

Reaction with pentyl chloride

Pentyl 1-trimethylsilyl-1-phenylhexyl ether (**9**), 1-trimethylsilyl-1-phenyl-1-hexanol (**10**), **4** and **8** were obtained in 16, 28, 32 and 15% yields (GLC yields) respectively.

Pentyl 1-trimethylsilyl-1-phenylhexyl ether (**9**)

Colorless oil. IR (neat): ν(C—O—C) 1246 cm^{-1}. MS (70 eV): $m/z = 320$ (M^+), 247 ($M^+ - TMS$). ^1H NMR ($CDCl_3$): δ −0.06 (s, 9H), 0.73–1.70 (m, 20H), 2.57 (t, $J = 7.6$ Hz, 2H), 7.10 (s, 5H).

1-Trimethylsilyl-1-phenyl-1-hexanol (**10**)

Colorless oil. IR (neat): ν(OH) 3120 cm^{-1}. MS (70 eV): $m/z = 250$ (M^+), 177 ($M^+ - TMS$). ^1H NMR ($CDCl_3$): δ −0.05 (s, 9H), 0.15–1.26 (m, 11H), 1.64 (brs, 1H), 7.11–7.30 (m, 5H). ^{13}C NMR (C_6D_6): δ −4.2, 14.0, 21.4, 22.6, 32.4, 36.6, 72.7, 124.7, 124.9, 127.9, 145.7.

Reaction with trimethylsilyl chloride

α,α-Bis(trimethylsilyl)benzyl trimethylsilyl ether (**11**) and **8** were obtained in 80 and 20% yields (GLC yields), respectively.

α,α-Bis(trimethylsilyl)benzyl trimethylsilyl ether (**11**)

Colorless oil. IR (neat): ν(Si—C) 1250, ν(Si—O—C) 1074 and 1100 cm^{-1}. MS (70 eV): $m/z =$ 324 (M^+), 251 ($M^+ - TMS$). ^1H NMR ($CDCl_3$): δ 0.05 (s, 18H), 0.22 (s, 9H), 7.10–7.22 (m, 5H). ^{13}C NMR ($CDCl_3$): δ −0.85, 3.9, 76.5, 123.6, 126.5, 127.4, 146.5.

Reaction with trimethylsilyl bromide

The reaction of benzoyl trimethylsilane (0.089 g, 0.5 mmol) with ytterbium metal (87 mg, 0.5 mmol) in THF (2 cm^3) and HMPA (0.5 cm^3) was carried out at −10 °C for 20 min. The subsequent treatment with trimethylsilyl bromide (0.066 cm^3, 0.5 mmol) was carried out at the same temperature for 20 min. The usual work-up followed by silica-gel column chromatography afforded **1a** and 1,2-bis(trimethylsilyl)-1,2-bis(*p*-trimethylsilylphenyl)ethene (**12**) in 12% and 26% yields, respectively.

1,2-Bis(trimethylsilyl)-1,2-bis(p-trimethylsilylphenyl)ethene (**12**)

Colorless needles: m.p. 188–189 °C. IR (Nujol): ν(Si—C) 1274 cm^{-1}. MS (70 eV): $m/z = 468$ (M^+), 453 ($M^+ - Me$), 73 (TMS^+). ^1H NMR ($CDCl_3$): δ −0.38 (s, 18H), −0.37 (s, 18H), 7.01 (d, $J = 7.3$ Hz, 4H), 7.42 (d, $J = 7.3$ Hz, 4H). ^{13}C NMR ($CDCl_3$): δ −0.95, 0.25, 127.5, 132.5, 137.1, 146.3, 148.6. ^{29}Si NMR ($CDCl_3$): δ −4.7, −7.4.

Analysis: calcd for $C_{26}H_{44}Si_4$: C, 66.58; H, 9.45. Found: C, 66.53; H, 9.39%.

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REFERENCES

1. (a) J. L. Namy, P. Girard and H. B. Kagan, *Nouv. J. Chim.* **1**, 5 (1977); (b) H. B. Kagan, J. L. Namy, *Tetrahedron* **42**, 6573 (1986); (c) H. B. Kagan, *New J. Chem.* **14**, 453 (1990); (d) Y. Fujiwara, *Organomet. News* 1 (1982).
2. (a) Y. Fujiwara, K. Takaki and Y. Taniguchi, *J. Alloys Compds.* **192**, 200 (1993); (b) K. Takaki and Y. Fujiwara, *Appl. Organomet. Chem.* **4**, 297 (1990).
3. Z. Hou, K. Takamine, O. Aoki, H. Shiraishi, Y. Fujiwara and H. Taniguchi, *J. Org. Chem.* **53**, 6077 (1988).
4. (a) Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara and H. Taniguchi, *J. Chem. Soc., Chem. Commun.* 222 (1992); (b) Z. Hou, H. Yamazaki, Y. Fujiwara and H. Taniguchi, *Organometallics* **11**, 2711 (1992); (c) K. Takaki, Y. Tsubaki, F. Beppu and Y. Fujiwara, *Chem. Express* **6**, 57 (1991).
5. Y. Taniguchi, N. Fujii, Y. Makioka, K. Takaki and Y. Fujiwara, *Chem. Lett.* 1165 (1993).
6. (a) P. Girard, R. Couffignal and H. B. Kagan, *Tetrahedron Lett.* **22**, 3959 (1981); (b) J. Souppe, J. L. Namy and H. B. Kagan, *Tetrahedron Lett.* **25**, 2869 (1984); (c) J. Collin, F. Dallemer, J. L. Namy and H. B. Kagan, *Tetrahedron Lett.* **30**, 3118 (1989); (d) J. Collin, J. L. Namy, F. Dallemer and H. B. Kagan, *J. Org. Chem.* **56**, 3118 (1991).
7. (a) Z. Hou, H. Taniguchi and Y. Fujiwara, *Chem. Lett.*

305 (1987); (b) Z. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo and H. Taniguchi, *J. Org. Chem.* **52**, 3524 (1987).

8. (a) Y. Taniguchi, M. Nakahashi, T. Kuno, M. Tsuno, Y. Makioka, K. Takaki and Y. Fujiwara. *Tetrahedron Lett.* **35**, 4111 (1994); (b) Y. Taniguchi, T. Kuno, M. Nakahashi, K. Takaki and Y. Fujiwara, *J. Alloys Compds.* **216**, L9 (1994); (c) Y. Taniguchi, T. Kuno, M. Nakahashi, K. Takaki and Y. Fujiwara, *Appl. Organomet. Chem.* **9**, 491 (1995).
9. (a) D. J. Ager, *Synthesis* 384 (1984); (b) A. G. M. Barrett, J. M. Hill, E. M. Wallace and J. A. Flygare, *Synlett* 764 (1991), and references cited therein.
10. J.-P. Picard, R. Calas, J. Dunogues, N. Duffant, J. Gerval, P. Lapouyade, *J. Org. Chem.* **44**, 420 (1979).
11. K. Yamamoto, S. Suzuki and J. Tsuji, *Tetrahedron Lett.* **21**, 1653 (1980).
12. J. A. Miller and G. Zweifel, *Synthesis* 288 (1981).
13. A. C. Cope and E. Ciganek, *Org. Synth., Coll. Vol. 4* 339 (1963).
14. P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.* **102**, 2693 (1980).