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Iridium-Catalyzed (*Z*)-Trialkylsilylation of Terminal Olefins

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Abstract

A complex of commercial $[\text{Ir(OMe)(cod)}]_2$ and 4,4-di-*tert*-butyl-2,2-bipyridine (dtbpy) catalyzes the *Z*-selective, dehydrative silylation of terminal alkenes, but not 1,2-disubstituted alkenes, with triethylsilane or benzyldimethylsilane in THF at 40 °C. Yields and *Z*-stereoselectivity were significantly improved by 2-norbornene, in contrast with other sacrificial alkenes. The reaction is compatible with many functional groups including epoxides, ketones, amides, alcohols, esters, halides, ketals and silanes. α,β -Unsaturated esters were unreactive. The reaction probably proceeds through a Heck-type mechanism.

Introduction

The unique reactivity profile¹ of trialkylsilylalkenes (vinylsilanes) combined with their low environmental impact² and distinctive physical properties,³ has led to ever-widening roles for them as synthetic intermediates⁴ and as building blocks in numerous material science/polymer applications.⁵ Accordingly, a variety of procedures are extant for the preparation of vinylsilanes, *inter alia*, additions of vinylolithiums or Grignard reagents to silyl electrophiles,⁶ Wittig/Peterson olefinations,⁷ alkyne hydrosilylation,⁸ and Suzuki cross-coupling.^{9,10} In more recent years, the direct silylation of alkenes mediated by transition metal catalysts,¹¹ e.g., iron,¹² cobalt,¹³ palladium,¹⁴ rhodium,¹⁵ ruthenium,¹⁶ iridium,¹⁷ and rhenium¹⁸ complexes, was introduced. Additionally, Kambe et al. reported the zirconocene catalyzed silylation of alkenes using chlorosilanes¹⁹ while Yorimitsu and Oshima developed an elegant silylation of terminal alkenes via Ni-catalyzed exchange with silacyclobutanes.²⁰ However, there are some important limitations associated with the stoichiometric and catalytic reactions. The former involve (i) strongly basic or harsh reaction conditions, (ii) multi-step processes, and/or (iii) give modest yields; the latter require (i) high alkene to silane ratios, (ii) conjugated or polyolefinic substrates, (iii) non-commercial reagents, and/or (iv) are *E*-selective. Herein, we offer a high yield *Z*-selective C-H silylation of terminal alkenes utilizing an iridium-dtbpy complex promoted by 2-norbornene (eq 1) and some insights into the parameters that influence stereoselectivity.

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Supporting Information Available: Analytical data, and ¹H/¹³C spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Results and Discussion

Motivated by our recent iridium-catalyzed C-H functionalization/silylation of heteroarenes and the mechanistic understanding gained therein,²¹ we sought to extend this methodology to the more challenging case of isolated alkenes.^{16,22} Initial attempts to silylate the model olefin 4-phenyl-1-butene **1** using [Ir(OMe)(cod)]₂/4,4-di-*tert*-butyl-2,2-bipyridine (dtbpy) (cod = cycloocta-1,5-diene)²³ and triethylsilane at either 80 °C or 40 °C in THF proved disappointing and gave rise to vinyl silane **2** in poor yield (Table 1, entries 1 and 2). The reversal of stereoselectivity towards the thermodynamically less favored *Z*-configuration at the lower temperature and the absence of aryl silylation, however, did not escape notice. Inclusion of mono- (entry 3), di- (entry 4), tri- (entry 5), and tetra-substituted (entry 6) olefins as sacrificial hydrogen repositories had little influence on the yield or stereoselectivity. In sharp contrast, 2-norbornene dramatically boosted yields (entries 7 and 8) and, in the latter case, the *Z/E*-ratio; at room temperature, the reaction was too sluggish to be useful (entry 9). Decreasing the amount of olefinic promoter and triethylsilane resulted in a proportionate lessening of both conversion and *Z*-isomer (entry 10). Silylations also proceeded well in DME (entry 11), dioxane (entry 12), and even ether (entry 13), albeit with reduced stereoselectivity; toluene and dichloromethane were unsatisfactory (<5%). Commercial bicyclic (entries 14–16) and tricyclic (entry 17) promoters related to norbornene were less efficacious, except for a slight increase in the *Z*-selectivity in some instances. It is noteworthy that the dtbpy ligand also plays an important role by inhibiting the isomerization of olefin. Other similar ligands weren't helpful (see Supporting Information).

The scope of this methodology was explored with a representative panel of alkenes (Table 2). Notably, only terminal alkenes proved reactive as illustrated by the nearly quantitative transformation of diene **3** to vinyl silane **4** (entry 1); all subsequent studies, therefore, were conducted with this in mind. Fortunately, the reaction conditions were compatible with a variety of functionality including, carbonate **5**, methyl ester **7**, and amide **9**, which furnished **6** (entry 2), **8** (entry 3), **10** (entry 4), respectively, in good to excellent yields and *Z*-selectivities. Even the readily reduced epoxide **13** and methyl ketone **15** were well behaved and gave rise to the corresponding vinylsilanes **12** (entry 5) and **14** (entry 6). The smooth transformation of TBS ether **15**, acetal **17** into **16** (entry 7) and **18** (entry 8) using commercial benzyldimethylsilane, instead of triethylsilane, demonstrates that other silyl moieties are accessible including those suitable for transition metal catalyzed cross-coupling reactions.²⁴

Aryl groups were likewise good substrates and afforded to silylated benzoate **20**, benzyl ether **22**, 4-fluorophenyl **24**, and 2-bromophenyl **26** beginning from **19** (entry 9), **21** (entry 10), **23** (entry 11), and **25** (entry 12), respectively. To our delight, even the free alcohol **27** generated silylated **28** (entry 13) in useful yield as did the related methyl ether **29** (entry 14). The corresponding allylic alcohol and methyl ether, on the other hand, produced complex product mixtures. NMR analysis of the crude mixtures suggested migration of the olefin might be a

contributing factor. Also, conjugated alkenes, e.g., *tert*-butyl acrylate **31** (entry 15), produced numerous unidentified products and little of the desired *Z*-vinylsilane.

The details of the reaction mechanism are uncertain at the present time, but a tentative sequence similar to earlier proposals²⁵ is likely (Figure 1). Initial oxidative insertion of the iridium into the silane followed by addition to the more reactive 2-norbornyl olefin generates intermediate *i*. Heck-type addition²⁵ to the terminal alkene forms intermediate *ii*. Due to the unfavorable steric interactions present in *ii**a*, intermediate *ii**b* is likely the predominate conformation. *Syn*- β -hydride elimination from *ii**b* would lead to *Z*-vinylsilane and iridium-hydride complex *iii*. Reductive elimination of norbornane *iv* regenerates the catalyst and completes the catalytic cycle. Furthermore, this proposal highlights an underappreciated role for some so-called “sacrificial olefins” like 2-norbornene, i.e., they can also influence the stereoselectivity of the reaction and, thus, should be taken into consideration when selecting reagent combinations.

Conclusion

In summary, we describe a mild, *Z*-stereoselective dehydrogenative trialkylsilylation of terminal alkenes utilizing a commercial iridium catalyst. Additionally, we demonstrate that 2-norbornene strongly promotes the reaction and also influences its stereoselectivity. Extensions of these concepts will follow in due course.

Experimental Section

General Information

All reactions were carried out under an argon atmosphere. Anhydrous solvents were freshly distilled from sodium benzophenone ketyl, except for CH₂Cl₂, which was distilled from CaH₂. Extracts were dried over anhydrous Na₂SO₄ and then filtered prior to removal of all volatiles under reduced pressure. Unless otherwise noted, commercially available materials were used without further purification. [Ir(OMe)(COD)]₂ was purchased from Strem or Aldrich Chem. Co. Flash chromatography (FC) was performed using silica gel 60 (240–400 mesh). Thin layer chromatography was performed using precoated plates purchased (silica gel 60 PF254, 0.25 mm).

¹H and ¹³C NMR spectra were recorded in CDCl₃ unless stated otherwise. Chemical shifts (δ) are given in ppm relative to residual solvent (usually chloroform δ 7.26 for ¹H NMR or δ 77.23 for proton decoupled ¹³C NMR) and coupling constants (J) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quadruplet, and m for multiplet. The prefix app is applied in cases where the true multiplicity is unresolved and br when the signal in question is broadened.

General Procedure for Iridium-Catalyzed (*Z*)-Trialkylsilylation

A flame-dried Schlenk tube was charged with terminal alkene (0.2 mmol), [Ir(OMe)(cod)]₂ (6.6 mg, 0.01 mmol) and dtbpy (5.4 mg, 0.02 mmol), then evacuated and flushed with argon three times. Under a positive flow of argon, 2-norbornene (56 mg, 0.6 mmol) and dry THF (1 mL) were added. After stirring for 5 min, trialkylsilane (0.6 mmol) was added dropwise and the reaction mixture was stirred at 40 °C for 2h. The solvent was concentrated under reduced pressure and the residue was purified by flash chromatography using silica gel to give the vinylsilane generally as a *Z/E*-mixture. More extensive purification via PTLC was required to obtain the individual *Z*- and *E*-isomers.

Compound 2, combined yield 92%, *Z/E* = 9:1.

(Z)-Triethyl(4-phenylbut-1-enyl)silane—¹H NMR (300 MHz) δ 7.32-7.18 (m, 5H), 6.42 (dt, *J* = 14.1, 6.6 Hz, 1H), 5.44 (d, *J* = 14.1 Hz, 1H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.46-2.38 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 9H), 0.59 (q, *J* = 7.5 Hz, 6H); ¹³C NMR (75 MHz) δ 149.1, 142.1, 128.6, 128.6, 126.2, 126.1, 36.4, 36.3, 7.7, 4.9. HRMS (EI) calcd. for C₁₆H₂₆Si [M]⁺ *m/z* 246.1804, found 246.1805.

(E)-Triethyl(4-phenylbut-1-enyl)silane—¹H NMR (300 MHz) δ 7.30-7.17 (m, 5H), 6.07 (dt, *J* = 18.9 Hz, 6.3 Hz, 1H), 5.57 (d, *J* = 18.9 Hz, 1H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.47-2.40 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 9H), 0.53 (q, *J* = 7.5 Hz, 6H); ¹³C NMR (75 MHz) δ 147.7, 142.1, 128.7, 128.4, 126.7, 125.9, 39.0, 35.6, 7.6, 3.7.

Compound 4, combined yield 99%, *Z/E* = 8:1.

1-Triethylsilyl-pentadeca-1(Z),12(Z)-diene—¹H NMR (300 MHz) δ 6.37 (dt, *J* = 13.8, 7.5 Hz, 1H), 5.39 (d, *J* = 13.8 Hz, 1H), 5.36-5.31 (m, 2H), 2.10-1.99 (m, 6H), 1.36-1.28 (m, 14H), 0.98-0.92 (m, 12H), 0.64-0.56 (m, 6H); ¹³C NMR (75 MHz) δ 150.6, 131.7, 129.6, 125.1, 34.3, 30.0 (2×C), 29.78 (2×C), 29.75, 29.6, 29.5, 27.3, 20.7, 14.6, 7.8, 4.9. HRMS (EI) calcd. for C₂₁H₄₂Si [M]⁺ *m/z* 322.3056, found 322.3063.

1-Triethylsilyl-pentadeca-1(E),12(Z)-diene—¹H NMR (300 MHz) δ 6.02 (dt, *J* = 18.6 Hz, 6.3 Hz, 1H), 5.52 (d, *J* = 18.6 Hz, 1H), 5.44-5.38 (m, 2H), 2.12-1.93 (m, 6H), 1.40-1.26 (m, 14H), 0.96-0.88 (m, 12H), 0.58-0.50 (m, 6H); ¹³C NMR (75 MHz) δ 149.1, 132.1, 129.6, 125.7, 37.3, 32.8, 29.9, 29.8, 29.7, 29.4, 29.3, 29.0, 25.8, 14.2, 7.6, 3.7.

Compound 6, combined yield 96%, *Z/E* = 8:1.

Ethyl 6-(triethylsilyl)hex-5(Z)-enyl carbonate—¹H NMR (300 MHz) δ 6.35 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.42 (d, *J* = 14.4 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 2H), 4.14 (t, *J* = 6.6 Hz, 2H), 2.17-2.09 (m, 2H), 1.72-1.66 (m, 2H), 1.52-1.44 (m, 2H), 1.31 (t, *J* = 6.6 Hz, 3H), 0.96-0.91 (m, 9H), 0.64-0.56 (m, 6H); ¹³C NMR (75 MHz) δ 155.5, 149.5, 126.1, 68.0, 64.1, 33.7, 28.5, 26.1, 14.5, 7.7, 4.9. HRMS (EI) calcd. for C₁₅H₃₁O₃Si [M+H]⁺ *m/z* 287.2042, found 287.2039.

(E)-Ethyl 6-(triethylsilyl)hex-5-enyl carbonate—¹H NMR (300 MHz) δ 6.00 (dt, *J* = 18.6, 6.3 Hz, 1H), 5.42 (d, *J* = 18.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 2.18-2.12 (m, 2H), 1.71-1.62 (m, 2H), 1.52-1.46 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.96-0.89 (m, 9H), 0.58-0.49 (m, 6H); ¹³C NMR (75 MHz) δ 155.5, 147.9, 126.7, 68.0, 64.1, 36.6, 28.3, 25.1, 14.5, 7.6, 3.7.

Compound 8, combined yield 84%, *Z/E* = 7:1.

Methyl 7-(triethylsilyl)hept-6(Z)-enoate—¹H NMR (300 MHz) δ 6.35 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.41 (d, *J* = 14.1 Hz, 1H), 3.67 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 1H), 2.15-2.07 (m, 2H), 1.70-1.60 (m, 2H), 1.45-1.38 (m, 2H), 0.96-0.90 (m, 9H), 0.64-0.55 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 174.4, 149.7, 125.9, 51.7, 34.2, 33.9, 29.5, 24.9, 7.8, 4.9. HRMS (EI) calcd. for C₁₄H₂₈O₂Si [M]⁺ *m/z* 256.1859, found 256.1855.

Methyl 7-(triethylsilyl)hept-6(E)-enoate—¹H NMR (300 MHz) δ 6.00 (dt, *J* = 18.6, 6.0 Hz, 1H), 5.55 (d, *J* = 18.6 Hz, 1H), 3.67 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 1H), 2.17-2.10 (m, 2H), 1.69-1.58 (m, 2H), 1.48-1.40 (m, 2H), 0.96-0.89 (m, 9H), 0.57-0.47 (m, 6H); ¹³C NMR (75 MHz) δ 174.4, 148.1, 126.4, 51.7, 36.8, 34.2, 28.4, 24.6, 7.6, 3.7.

Compound 10, combined yield 87%, *Z/E* = 10:1.

***N,N*-Dibenzyl-7-(triethylsilyl)hept-6(*Z*)-enamide**—¹H NMR (300 MHz) δ 7.39-7.14 (m, 10H), 6.35 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 4.61 (s, 2H), 4.44 (s, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.15-2.07 (m, 2H), 1.78-1.70 (m, 2H), 1.45-1.38 (m, 2H), 0.95-0.89 (m, 9H), 0.62-0.54 (m, 6H); ¹³C NMR (75 MHz) δ 173.7, 149.8, 137.7, 136.8, 129.2, 128.8, 128.5, 127.8, 127.6, 126.5, 125.7, 50.1, 48.3, 34.0, 33.4, 29.8, 25.4, 7.8, 4.9. HRMS (EI) calcd. for C₂₇H₄₀NOSi [M+H]⁺ *m/z* 422.2879, found 422.2877.

***N,N*-Dibenzyl-7-(triethylsilyl)hept-6(*E*)-enamide**—¹H NMR (300 MHz) δ 7.39-7.14 (m, 10H), 6.00 (dt, *J* = 18.6, 6.0 Hz, 1H), 5.52 (d, *J* = 18.6 Hz, 1H), 4.60 (s, 2H), 4.44 (s, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.16-2.09 (m, 2H), 1.78-1.70 (m, 2H), 1.49-1.39 (m, 2H), 0.93-0.88 (m, 9H), 0.56-0.46 (m, 6H); ¹³C NMR (75 MHz) δ 173.8, 148.3, 137.7, 136.8, 129.2, 128.8, 128.5, 127.8, 127.6, 126.5, 126.2, 50.1, 48.2, 37.0, 33.3, 28.8, 25.2, 7.6, 3.7.

Compound 12, combined yield 98%, *Z/E* = 10:1.

(*Z*)-Triethyl(8-(oxiran-2-yl)oct-1-enyl)silane—¹H NMR (300 MHz) δ 6.37 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 2.92-2.89 (m, 1H), 2.75 (dd, *J* = 3.9, 4.8 Hz, 1H), 2.47 (dd, *J* = 2.7, 4.8 Hz, 1H), 2.13-2.06 (m, 2H), 1.54-1.34 (m, 10H), 0.96-0.90 (m, 9H), 0.64-0.55 (m, 6H); ¹³C NMR (75 MHz) δ 150.4, 125.3, 52.6, 47.4, 34.2, 32.7, 29.9, 29.6, 29.5, 26.1, 7.8, 4.9. HRMS (EI) calcd. for C₁₆H₃₂OSi [M]⁺ *m/z* 268.2222, found 268.2222.

(*E*)-Triethyl(8-(oxiran-2-yl)oct-1-enyl)silane—¹H NMR (300 MHz) δ 6.02 (dt, *J* = 18.9 Hz, 6.3 Hz, 1H), 5.53 (d, *J* = 18.9 Hz, 1H), 2.92-2.88 (m, 1H), 2.75 (dd, *J* = 3.9, 4.8 Hz, 1H), 2.47 (dd, *J* = 2.7, 4.8 Hz, 1H), 2.15-2.08 (m, 2H), 1.54-1.34 (m, 10H), 0.95-0.89 (m, 9H), 0.58-0.50 (m, 6H); ¹³C NMR (75 MHz) δ 148.8, 125.8, 52.6, 47.4, 37.2, 32.7, 29.5, 29.2, 28.9, 26.1, 7.6, 3.7.

Compound 14, combined yield 71%, *Z/E* = 7:1.

6-(Triethylsilyl)hex-5(*Z*)-en-2-one, 62% yield following PTLC separation. ¹H NMR (300 MHz) δ 6.31 (dt, *J* = 14.1, 7.2 Hz, 1H), 5.45 (d, *J* = 14.1 Hz, 1H), 2.53-2.48 (m, 2H), 2.40-2.34 (m, 2H), 2.15 (s, 3H), 1.49-1.42 (m, 2H), 0.96-0.90 (m, 9H), 0.65-0.57 (m, 6H); ¹³C NMR (75 MHz) δ 208.3, 147.9, 127.0, 43.8, 30.2, 28.3, 7.7, 4.8. HRMS (EI) calcd. for C₁₂H₂₄OSi [M]⁺ *m/z* 212.1596, found 212.1599.

6-(Triethylsilyl)hex-5(*E*)-en-2-one, 9% yield following PTLC separation. ¹H NMR (300 MHz) δ 6.01 (dt, *J* = 18.6, 6.3 Hz, 1H), 5.57 (d, *J* = 18.6 Hz, 1H), 2.56-2.52 (m, 2H), 2.43-2.36 (m, 2H), 2.15 (s, 3H), 1.49-1.42 (m, 2H), 0.93-0.88 (m, 9H), 0.57-0.49 (m, 6H); ¹³C NMR (75 MHz) δ 208.6, 146.3, 127.1, 42.9, 31.1, 30.2, 7.6, 3.6.

Compound 16, combined yield 71%, *Z/E* = 7:1.

(*Z*)-Benzyl(6-(*tert*-butyldimethylsilyloxy)hex-1-enyl)dimethylsilane—¹H NMR (300 MHz) δ 7.25-7.18 (m, 2H), 7.09-7.00 (m, 3H), 6.33 (dt, *J* = 14.1, 7.5 Hz, 1H), 5.44 (d, *J* = 14.1 Hz, 1H), 3.59 (t, *J* = 6.3 Hz, 1H), 2.15 (s, 2H), 2.09-2.02 (m, 2H), 1.53-1.46 (m, 2H), 1.41-1.35 (m, 2H), 0.90 (s, 9H), 0.09 (s, 6H), 0.04 (s, 6H); ¹³C NMR (75 MHz) δ 150.4, 140.4, 128.4, 128.3, 127.0, 124.1, 63.3, 33.7, 32.7, 26.9, 26.2, 26.1, 18.6, -1.4, -5.1. HRMS (EI) calcd. for C₂₁H₃₉Si₂ [M+H]⁺ *m/z* 363.2539, found 363.2541.

(*E*)-Benzyl(6-(*tert*-butyldimethylsilyloxy)hex-1-enyl)dimethylsilane—¹H NMR (300 MHz) δ 7.25-7.18 (m, 2H), 7.09-7.00 (m, 3H), 5.99 (dt, *J* = 18.9, 7.5 Hz, 1H), 5.58 (d, *J* = 18.9 Hz, 1H), 3.60 (t, *J* = 6.3 Hz, 1H), 2.10 (s, 2H), 2.12-2.08 (m, 2H), 1.53-1.47 (m, 2H),

1.45-1.40 (m, 2H), 0.05 (s, 9H), 0.01 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (75 MHz) δ 148.6, 140.4, 128.4, 128.2, 127.9, 124.0, 63.3, 36.7, 32.5, 26.4, 26.2, 18.6, -3.1, -5.0.

Compound 18, combined yield 71%, $Z/E = 7:1$.

(Z)-Benzyldimethyl(4-(2-methyl-1,3-dioxolan-2-yl)but-1-enyl)silane— ^1H NMR (300 MHz) δ 7.23-7.18 (m, 2H), 7.09-7.00 (m, 3H), 6.33 (dt, $J = 14.1, 7.2$ Hz, 1H), 5.45 (d, $J = 14.1$ Hz, 1H), 3.98-3.86 (m, 4H), 2.17 (s, 2H), 2.17-2.10 (m, 2H), 1.68-1.63 (m, 2H), 1.30 (s, 3H), 0.11 (s, 6H); ^{13}C NMR (75 MHz) δ 149.6, 140.3, 128.4, 128.3, 127.2, 124.1, 109.9, 64.9, 39.1, 28.7, 26.9, 24.1, -1.5. HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Si}$ $[\text{M}]^+$ m/z 290.1702, found 290.1704.

(E)-Benzyldimethyl(4-(2-methyl-1,3-dioxolan-2-yl)but-1-enyl)silane— ^1H NMR (300 MHz) δ 7.22- 7.17 (m, 2H), 7.08-6.97 (m, 3H), 6.02 (dt, $J = 18.6, 6.3$ Hz, 1H), 5.61 (d, $J = 18.6$ Hz, 1H), 3.97-3.88 (m, 4H), 2.25-2.17 (m, 2H), 2.10 (s, 2H), 1.75-1.70 (m, 2H), 1.32 (s, 3H), 0.01 (s, 6H); ^{13}C NMR (75 MHz) δ 148.1, 140.4, 128.5, 128.2, 127.7, 124.1, 110.0, 64.9, 38.2, 31.4, 26.4, 24.2, -3.1.

Compound 20, combined yield 95%, $Z/E = 9:1$.

(Z)-5-(Triethylsilyl)pent-4-enyl benzoate— ^1H NMR (300 MHz) δ 8.07-8.04 (m, 2H), 7.56-7.53 (m, 1H), 7.47-7.41 (m, 2H), 6.41 (dt, $J = 14.1, 7.2$ Hz, 1H), 5.48 (d, $J = 14.1$ Hz, 1H), 4.34 (t, $J = 6.3$ Hz, 2H), 2.32-2.25 (m, 2H), 1.91-1.82 (m, 2H), 0.95-0.90 (m, 9H), 0.65-0.57 (m, 6H); ^{13}C NMR (75 MHz) δ 166.9, 148.6, 133.1, 130.6, 129.8, 128.5, 126.8, 64.8, 30.8, 29.1, 7.7, 4.9. HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$ $[\text{M}]^+$ m/z 304.1859, found 304.1874.

(E)-(6-(Benzyloxy)hex-1-enyl)triethylsilane— ^1H NMR (300 MHz) δ 8.07-8.04 (m, 2H), 7.58-7.53 (m, 1H), 7.47-7.42 (m, 2H), 6.41 (dt, $J = 18.6, 6.3$ Hz, 1H), 5.62 (d, $J = 18.6$ Hz, 1H), 4.33 (t, $J = 6.6$ Hz, 2H), 2.33-2.26 (m, 2H), 1.94-1.84 (m, 2H), 0.97-0.90 (m, 9H), 0.58-0.50 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.9, 147.0, 133.1, 130.6, 129.8, 128.5, 127.3, 64.7, 33.5, 28.0, 7.6, 3.7.

Compound 22, combined yield 84%, $Z/E = 10:1$.

(Z)-(6-(Benzyloxy)hex-1-enyl)triethylsilane— ^1H NMR (300 MHz) δ 7.35-7.26 (m, 5H), 6.36 (dt, $J = 14.1, 7.5$ Hz, 1H), 5.40 (d, $J = 14.1$ Hz, 1H), 4.51 (s, 2H), 3.48 (t, $J = 6.6$ Hz, 2H), 2.16-2.09 (m, 2H), 1.67-1.60 (m, 2H), 1.49-1.44 (m, 2H), 0.96-0.90 (m, 9H), 0.64-0.55 (m, 6H); ^{13}C NMR (75 MHz) δ 150.1, 138.8, 128.6, 127.8, 127.7, 125.6, 73.1, 70.5, 34.0, 29.7, 26.6, 7.8, 4.9. HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{31}\text{OSi}$ $[\text{M}+\text{H}]^+$ m/z 303.2144, found 303.2160.

(E)-(6-(Benzyloxy)hex-1-enyl)triethylsilane— ^1H NMR (300 MHz) δ 7.35-7.26 (m, 5H), 6.02 (dt, $J = 18.6$ Hz, 6.3 Hz, 1H), 5.40 (d, $J = 18.6$ Hz, 1H), 4.51 (s, 2H), 3.48 (t, $J = 6.6$ Hz, 2H), 2.17-2.11 (m, 2H), 1.66-1.58 (m, 2H), 1.51-1.45 (m, 2H), 0.95-0.90 (m, 9H), 0.59-0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 148.5, 138.9, 128.6, 127.8, 127.7, 126.2, 73.0, 70.5, 37.0, 29.4, 25.6, 7.6, 3.7.

Compound 24, combined yield 88%, $Z/E = 8:1$.

(Z)-Triethyl(4-(4-fluorophenyl)but-1-enyl)silane— ^1H NMR (300 MHz) δ 7.15-7.10 (m, 2H), 6.99-6.94 (m, 2H), 6.39 (dt, $J = 14.1, 7.2$ Hz, 1H), 5.45 (d, $J = 14.1$ Hz, 1H), 2.66 (t, $J = 7.5$ Hz, 2H), 2.42-2.35 (m, 2H), 0.95-0.88 (m, 9H), 0.62-0.54 (m, 6H); ^{13}C NMR (75 MHz) δ 163.1, 159.9, 148.8, 137.65, 137.6, 130.0, 129.9, 126.5, 115.4, 115.1, 36.3, 35.5, 7.7, 4.9. HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{25}\text{FSi}$ $[\text{M}]^+$ m/z 246.1710, found 246.1715.

(E)-Triethyl(4-(4-fluorophenyl)but-1-enyl)silane— ^1H NMR (300 MHz) δ 7.14-7.09 (m, 2H), 6.98-6.92 (m, 1H), 6.01 (dt, J = 18.9 Hz, 6.0 Hz, 1H), 5.56 (d, J = 18.9 Hz, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.44-2.37 (m, 2H), 0.93-0.88 (m, 9H), 0.57-0.49 (m, 6H); ^{13}C NMR (75 MHz) δ 163.0, 159.8, 147.3, 137.75, 137.71, 130.0, 129.9, 127.1, 115.3, 115.0, 39.0, 34.7, 7.6, 3.7.

Compound 26, combined yield 88%, Z/E = 7:1.

(Z)-(4-(2-Bromophenyl)but-1-enyl)triethylsilane— ^1H NMR (300 MHz) δ 7.55-7.52 (m, 1H), 7.24-7.21 (m, 2H), 7.09-7.03 (m, 1H), 6.43 (dt, J = 14.1, 7.2 Hz, 1H), 5.46 (d, J = 14.1 Hz, 1H), 2.81 (t, J = 7.5 Hz, 2H), 2.46-2.38 (m, 2H), 0.96-0.89 (m, 9H), 0.63-0.55 (m, 6H); ^{13}C NMR (75 MHz) δ 148.6, 141.3, 133.0, 130.7, 127.8, 127.6, 126.6, 124.6, 36.5, 34.4, 7.7, 4.8. HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{25}\text{BrSi}$ $[\text{M}]^+$ m/z 324.0909, found 324.0906.

(E)-(4-(2-Bromophenyl)but-1-enyl)triethylsilane— ^1H NMR (300 MHz) δ 7.52 (d, J = 7.8 Hz, 1H), 7.24-7.20 (m, 2H), 7.07-7.02 (m, 1H), 6.07 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.57 (d, J = 18.6 Hz, 1H), 2.84 (t, J = 7.5 Hz, 2H), 2.46-2.40 (m, 2H), 0.93-0.88 (m, 9H), 0.57-0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 147.0, 141.3, 132.9, 130.7, 127.7, 127.5, 127.2, 124.6, 37.2, 35.8, 7.6, 3.7.

Compound 28, combined yield 77%, Z/E = 8:1.

(Z)-Triethyl(4-hydroxyl-4-phenylbut-1-enyl)silane, 68% yield following PTLC separation. ^1H NMR (300 MHz) δ 7.38-7.26 (m, 5H), 6.41 (dt, J = 14.1, 7.2 Hz, 1H), 5.64 (d, J = 14.1 Hz, 1H), 4.77-4.73 (m, 1H), 2.61-2.55 (m, 2H), 2.03-2.00 (m, 1H), 0.96-0.91 (m, 9H), 0.66-0.58 (m, 6H); ^{13}C NMR (75 MHz) δ 145.1, 144.2, 129.9, 128.7, 127.8, 126.0, 74.1, 43.9, 7.7, 4.8. HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{26}\text{OSi}$ $[\text{M}]^+$ m/z 262.1753, found 262.1751.

(E)-Triethyl(4-hydroxyl-4-phenylbut-1-enyl)silane, 8% yield following PTLC separation. ^1H NMR (300 MHz) δ 7.36-7.24 (m, 5H), 6.01 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.71 (d, J = 18.6 Hz, 1H), 4.78-4.73 (m, 1H), 2.62-2.55 (m, 2H), 2.03-2.02 (m, 1H), 0.93-0.88 (m, 9H), 0.58-0.50 (m, 6H); ^{13}C NMR (75 MHz) δ 144.1, 143.7, 131.6, 128.6, 127.7, 126.0, 73.4, 47.4, 7.6, 3.6.

Compound 30, combined yield 96%, Z/E = 8:1.

(Z)-Triethyl(4-methoxy-4-phenylbut-1-enyl)silane, 85% yield following PTLC separation. ^1H NMR (300 MHz) δ 7.39-7.26 (m, 5H), 6.36 (dt, J = 14.4 Hz, 7.2 Hz, 1H), 5.50 (d, J = 14.4 Hz, 1H), 4.14 (t, J = 6.6 Hz, 1H), 3.22 (s, 3H), 2.67-2.59 (m, 2H), 2.49-2.40 (m, 2H), 0.93-0.88 (m, 9H), 0.61-0.53 (m, 6H); ^{13}C NMR (75 MHz) δ 145.6, 141.9, 128.6, 127.9, 127.8, 126.9, 84.2, 56.9, 42.5, 7.7, 4.8. HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{28}\text{OSi}$ $[\text{M}]^+$ m/z 276.1909, found 276.1907.

(E)-Triethyl(4-methoxy-4-phenylbut-1-enyl)silane, yield 10% following PTLC separation. ^1H NMR (300 MHz) δ 7.36-7.24 (m, 5H), 5.95 (dt, J = 18.6 Hz, 6.3 Hz, 1H), 5.55 (d, J = 18.6 Hz, 1H), 4.14 (t, J = 6.6 Hz, 1H), 3.22 (s, 3H), 2.67-2.59 (m, 2H), 2.49-2.40 (m, 2H), 0.90-0.85 (m, 9H), 0.54-0.46 (m, 6H); ^{13}C NMR (75 MHz) δ 144.1, 141.9, 129.3, 128.5, 127.7, 127.0, 84.0, 56.9, 45.9, 7.5, 3.6.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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FIGURE 1.
Proposed mechanism of Ir-catalyzed trialkylsilylation showing influence of ligand

TABLE 1Influence of promoters and reaction parameters on (*Z*)-selectivity and yield of **2**^a

entry	promoter	temp (°C)	solvent	yield (%) ^b	<i>Z:E</i> ^c
1	none	80	THF	<10	5:95 ^d
2	none	40	THF	16	4:1
3		40	THF	<5	nd ^e

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
4		40	THF	16	4:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
5		40	THF	<5	nd ^f
6		40	THF	<5	nd ^f

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
7		80	THF	91	2.5:1 ^f

8

40

THF

92

9:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
9		23	THF	<5	nd ^{e,f}

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
10		40	THF	60	5:1 ^g

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
11		40	DME	90	8:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
12		40	dioxane	88	7:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
14		40	THF	22	9:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
15		40	THF	21	10:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
16		40	THF	71	10:1

entry	promoter	temp (°C)	solvent	yield (%) ^b	Z:E ^c
17		40	THF	20	4:1

^aReaction conditions: [Ir(OMe)(cod)]₂ (5 mol%), dtbpy (10 mol%), promoter (3 equiv, if used) and Et₃SiH (3 equiv) in THF for 2 h.

^bCombined yield.

^cMeasured by crude ¹H NMR.

^dConducted for 15 h.

^end = not determined.

^fConducted for 24 h.

^gUsing 1.5 equivalents each of promoter and Et₃SiH.

TABLE 2

Trialkylsilylation of terminal alkenes^a

entry	alkene
1	3
2	5
3	7

entry	alkene
6	13

7	15
---	---

entry

alkene

8

17

9

19

entry	alkene
10	<chem>C=CCCCOCc1ccccc1</chem>
11	<chem>C=CCCCc1ccc(F)cc1</chem>
12	<chem>C=CCCCc1ccc(Br)cc1</chem>

entry	alkene
13	27
14	29
15	31

^aReaction conditions: [Ir(OMe)(cod)]₂ (5 mol%), dtbpy (10 mol%), 2-norbornene (3 equiv) and R₃SiH (3 equiv) in THF for 2h at 40°C.

^bCombined isolated yield.

^cMeasured by ¹H NMR.

^dna = not applicable.