Articles

Highly Regioselective and Stereoselective Silylformylation of Alkynes Under Mild Conditions Promoted by Dirhodium(II) Perfluorobutyrate

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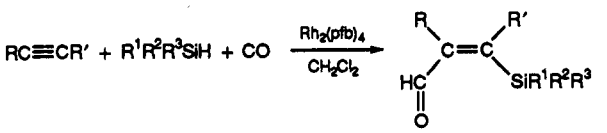
Addition to alkynes by organosilanes and carbon monoxide to form β-silylacrylaldehydes (silylformylation) occurs efficiently in the presence of dirhodium(II) perfluorobutrate, $Rh_2(pfb)_4$, with turnover numbers that exceed 300. Reactions take place at atmospheric pressure and 0 °C by controlled addition of the alkyne to the combination of organosilane and $Rh_2(pfb)_4$ or at 10 atm of CO without this control. Terminal alkynes are directed to silylformylation products in moderate to high yield with complete regiocontrol for carbonylation at the substituted carbon and with exceptional stereocontrol for the *Z* isomer (>10:1). Preferential silylformylation occurs with triethylsilane in competition with hydrosilylation, and this preference is greatly enhanced with the more reactive dimethylphenylsilane. With internal alkynes hydrosilylation is often dominant. At 1 atm of CO 3-butyn-2-one undergoes trimerization to 1,3,5-triacetylbenzene, and both CO and organosilane in combination with $Rh_2(pfb)_4$ are required, but at 10 atm of CO silylformylation occurs to the near exclusion of this trimerization reaction. Similar processes occur with methyl propynoate, but they are complicated by competitive hydrosilylation of the silylformylation product. The active catalyst for silylformylation is generated from $Rh_2(pfb)_4$ by CO association followed by hydrosilylation that generates trialkylsilyl perfluorobutyrate.

We have recently reported that dirhodium(II) perfluorobutyrate, $Rh_2(pfb)_4$, is an effective and efficient catalyst for the silylformylation of alkynes (eq 1).[1] These reactions



(1)

occur with a high degree of stereoselectivity (*Z*:*E* ≥ 10), they are regiospecific, and turnover numbers are greater than 300. Tolerance for other functional groups includes alcohols, ethers, and esters, and product yields following distillation are generally greater than 70%. Compared to other methods for silylformylation which employ rhodium carbonyl compounds,[2-7] particularly $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$, use of $Rh_2(pfb)_4$ appears to afford comparable or higher reactivity and selectivity. Additional results and the full experimental details for the silylformylation transformation are now described.

Dirhodium(II) acetate has been reported to catalyze olefin hydrogenation,[8] and several dirhodium(II) compounds are known to associate carbon monoxide.[9] However, since only low-valent rhodium compounds have previously been successful for silylformylation or for the analogous hydroformylation process,[10] we have investigated the role of dirhodium(II) perfluorobutyrate in these reactions. The results of this evaluation and their implications for the mechanism of $Rh_2(pfb)_4$-catalyzed silylformylation are reported.

Results and Discussion

Alkyne addition to the combination of trisubstituted organosilane, carbon monoxide, and 0.3–0.4 mol % of $Rh_2(pfb)_4$ in CH_2Cl_2 at 0 °C and atmospheric pressure results in the formation of silylformylation products in high yields, excellent regiocontrol, and predominant cis addition stereoselectivity (Table 1). Reported yields are those following distillation and, because some of the silylformylation products are thermally sensitive to isomerization, the *Z*:*E* isomer ratios of the isolated products may in certain cases be higher than those reported. The identity of *Z* and *E* isomers was obtained through chromatographic

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Table 1. Silylformylation of Alkynes Catalyzed by $Rh_2(pfb)_4$ at Atmospheric Pressure[a]

alkyne	organosilane	silylformylation product	yield, %[b]	*Z*:*E* isomer ratio	silylformylation: hydrosilylation
PhC≡CH	Et_3SiH	$Et_3SiCH{=}C(Ph)CHO$ (1)	82	10:1	>99:1
p-TolC≡CH[c]	Et_3SiH	$Et_3SiCH{=}C(p\text{-Tol})CHO$ (2)	24	13:1	38:62
	Me_2PhSiH	$Me_2PhSiCH{=}C(p\text{-Tol})CHO$ (3)	84	38:1	>99:1
p-*i*-BuC_6H_4C≡CH	Et_3SiH	$Et_3SiCH{=}C(p\text{-}i\text{-}BuC_6H_4)CHO$ (4)	28	10:1	91:9
	Me_2PhSiH	$Me_2PhSiCH{=}C(p\text{-}i\text{-}BuC_6H_4)CHO$ (5)	74	11:1	>99:1
6-MeONap-2-C≡CH[d]	Me_2PhSiH	$Me_2PhSiCH{=}C(2\text{-Nap-6-MeO})CHO$ (6)	95	11:1	>99:1
PhC≡CPh	Et_3SiH	$Et_3SiC(Ph){=}C(Ph)CHO$ (7)	95	32:1	71:29
PhC≡CCH_3	Et_3SiH	$Et_3SiC(CH_3){=}C(Ph)CHO$ (8)	72	40:1	56:44
	Me_2PhSiH	$Me_2PhSiC(CH_3){=}C(Ph)CHO$ (9)	83	12:1	14:86
n-HexC≡CH	Et_3SiH	$Et_3SiCH{=}C(n\text{-Hex})CHO$ (10)	45	36:1	40:60
	Me_2PhSiH	$Me_2PhSiCH{=}C(n\text{-Hex})CHO$ (11)	81	14:1	>99:1
$AcOCH_2C$≡CH	Et_3SiH	$Et_3SiCH{=}C(CH_2OAc)CHO$ (12)	71	29:1	96:4
$MeOCH_2C$≡CH	Et_3Si	$Et_3SiCH{=}C(CH_2OMe)CHO$ (13)	87	14:1	>99:1
$Me_2C(OH)C$≡CH	Et_3SiH	$Et_3SiCH{=}C(C(OH)Me_2)CHO$ (14)	41[e]	24:1	91:9

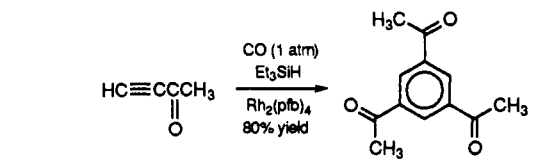
[a] Reactions performed on a 2.5-mmol scale by controlled addition (4–5 h) of the alkyne in 5 mL of dichloromethane to the same amount of silane and 0.3–0.4 mol % $Rh_2(pfb)_4$ in 25 mL of dichloromethane at 0 °C under an atmosphere of CO (ambient). [b] Yield of combined products obtained after chromatographic separation of catalyst and distillation of product under reduced pressure. [c] *p*-Tol = *p*-$CH_3C_6H_4$. [d] Nap = naphthalene. [e] Reaction only went to ~60% completion.

and spectroscopic correlations with model compounds[11] and with selected examples of the same products formed from silylformylation of acetylenes catalyzed by $Rh_4(CO)_{12}$.[2] The ^1H NMR signals for aldehyde protons are at higher chemical shift values for the *Z* isomer than for the *E* isomer of product 2-propenals. Silylformylation occurs in competition with hydrosilylation,[12] and relative rates for these competitive processes are determined primarily by the reactivity of the organosilane (Me_2PhSiH > Et_3SiH) and steric or electronic influences from the alkyne. Electron-donating substituents on the alkyne (compare PhC≡CH with para-substituted derivatives) effect significantly decreased reactivity toward silylformylation with Et_3SiH, but vastly improved results occur with the use of Me_2PhSiH.[3b] The opposite occurs with 1-phenyl-1-propyne, where use of Me_2PhSiH leads to a decrease in the relative yield of silylformylation products. As seen from the results in Table 1, hydrosilylation is more competitive in reactions with internal alkynes than with terminal alkynes.

Use of 0.3 mol % $Rh_2(pfb)_4$), is optimal for reactions performed with phenylacetylene. With lower relative molar amounts of this catalyst, overall product yields decrease (42% at 0.2 mol % and 22% at 0.1 mol % $Rh_2(pfb)_4$), and hydrosilylation occurs in competition with silylformylation (up to 64% hydrosilylation at 0.1 mol % $Rh_2(pfb)_4$). Reactions performed with $Rh_2(OAc)_4$ in place of $Rh_2(pfb)_4$ were not as effective for silylformylation; with 1.0 mol % $Rh_2(OAc)_4$, silylformylation products accounted for only 70% of total products (84% yield, *Z*:*E* = 12:1).

At atmospheric pressure of CO, addition of the alkyne to the reaction solution at a controlled rate is critical to the success of the transformation. If the order of addition is reversed with the organosilane added under a CO atmosphere to the solution containing the catalyst and alkyne, overall product yields are low, and the relative percentages of hydrosilylation products increase significantly. These requirements are minimized when the reaction is performed under 10 atm pressure (Table 2), when neither the rate nor order of addition is an important consideration. Under these conditions product yields increase (compare Et_3SiH reactions with *p*-TolC≡CH, *p*-*i*-BuC_6H_4C≡CH, and *n*-HexC≡CH in Tables 1 and 2), as do the relative percentages of silylformylation products. Small amounts of hydrosilylation products result from the initial mixing of reagents at atmospheric pressure rather than from competition at 10 atm of CO.

Silylformylation catalyzed by $Rh_2(pfb)_4$ is tolerant of ether, ester, alcohol, and ketone functionalities. The absence of products from silane alcoholysis, especially from reactions with propargyl alcohol, is surprising in view of the facile catalysis of such reactions by $Rh_2(pfb)_4$ in the absence of CO.[13] With the relatively unreactive 3-butyn-2-one and methyl propynoate, silylformylation occurs under 10 atm of CO pressure, but product yields are low. However, at 1 atm of CO pressure the reaction takes on an entirely new course, producing cycloaddition trimers that are isolated in moderate to good yields (eqs 2 and 3).



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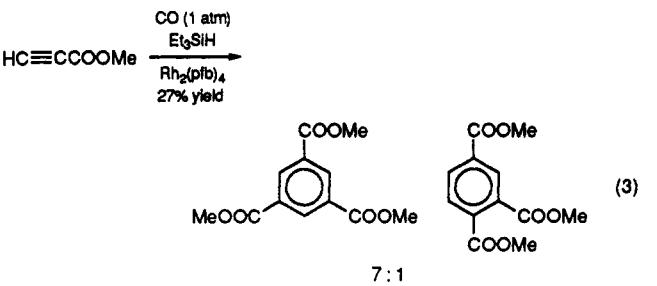

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The combination of $Rh_2(pfb)_4$, organosilane, and CO is essential to these trimerization reactions; without any one of these three components, the yield of the trisubstituted benzene is negligible. No attempt was made to optimize conditions for trimerization. However, similar trimerization reactions of alkyl- or arylacetylenes in the presence of $Rh_2(pfb)_4$ with or without CO and/or Et_3SiH did not occur in measurable yield.

In addition to the alkyne trimers formed from methyl propynoate (eq 3), the major reaction process was the

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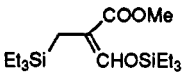
Table 2. Silylformylation of Alkynes with Et_3SiH Catalyzed by $Rh_2(pfb)_4$ at 10 Atm of CO Pressure[a]

alkyne	organosilane	silylformylation product	yield, %[b]	*Z*:*E* isomer ratio	silylformylation: hydrosilylation
PhC≡CH	Et_3SiH	$Et_3SiCH{=}C(Ph)CHO$ (**1**)	75	24:1	92:8
	Me_2PhSiH	$Me_2PhSiCH{=}C(Ph)CHO$ (**15**)	73	12:1	>99:1
p-TolC≡CH	Et_3SiH	$Et_3SiCH{=}C(p\text{-}Tol)CHO$ (**2**)	63	17:1	96:4
p-*i*-BuC_6H_4C≡CH	Et_3SiH	$Et_3SiCH{=}C(p\text{-}i\text{-}BuC_6H_4)CHO$ (**4**)	72	10:1	96:4
6-MeONap-2-C≡CH	Et_3SiH	$Me_2PhSiCH{=}C(2\text{-}Nap\text{-}6\text{-}MeO)CHO$ (**6**)	99	21:1	>99:1
n-HexC≡CH	Me_2PhSiH	$Et_3SiCH{=}C(n\text{-}Hex)CHO$ (**10**)	81	35:1	>99:1
$AcOCH_2C$≡CH	Et_3SiH	$Et_3SiCH{=}C(CH_2OAc)CHO$ (**12**)	51	22:1	>99:1
$MeOCH_2C$≡CH	Et_3SiH	$Et_3SiCH{=}C(CH_2OMe)CHO$ (**13**)	77	30:1	>99:1
$Me_2C(OH)C$≡CH	Et_3SiH	$Et_3SiCH{=}C(C(OH)Me_2)CHO$ (**14**)	66	36:1	>99:1
$HOCH_2C$≡CH	Et_3SiH	$Et_3SiCH{=}C(CH_2OH)CHO$ (**16**)	56	18:1	>99:1
CH_3COC≡CH	Et_3SiH	$Et_3SiCH{=}C(COCH_3)CHO$ (**17**)	24	1.1:1	>99:1
CH_3OOCC≡CH	Et_3SiH	$Et_3SiCH{=}C(COOMe)CHO$ (**18**)	20	1:1.3	>99:1

[a] Reactions performed at room temperature with 0.3 mol % $Rh_2(pfb)_4$ in a stainless steel autoclave with a Pyrex reaction vessel (50 mL) at a 2–10-mmol scale with an equivalent amount of alkyne and Et_3SiH. [b] Yield obtained after chromatographic separation of catalyst and distillation of product under reduced pressure.

formation of disilylated carbonylation product (**19**; *Z*/*E* = 6, 41% yield). Only a trace amount of the "normal"



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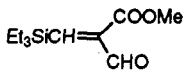

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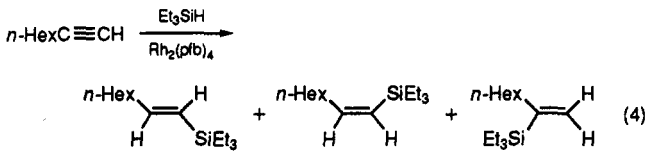
silylformylation product (**20**) was evident, and hydrosilylation products were minor constituents of the reaction mixture. Formally, **19** is the product of 1,4-hydrosilylation of **20**. Products similar to **19** were not evident from reactions performed under the same conditions with 3-butyn-2-one or with other alkynes employed in this investigation, and **19** was not formed from methyl propynoate and triethylsilane under 10 atm of CO pressure.

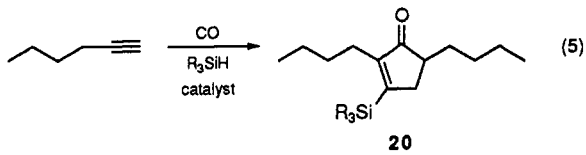
Dirhodium(II) perfluorobutyrate is a highly effective catalyst for the hydrosilylation of acetylenes,[12] and its outcome, like that for catalysis by rhodium carbonyl complexes,[14] is generally net trans addition, as opposed to cis addition which characterizes reactions with chloroplatinic acid.[15] Analyses of the hydrosilylation products formed during silylformylation reactions that employ $Rh_2(pfb)_4$, however, show predominant cis addition (e.g., eq 4), which suggests that the catalytically active species in reactions performed under carbon monoxide is different from that operating in the absence of CO.



without CO	13	73	14
with CO	67	21	12

(4)

The formation of a novel silylcarbocyclization product (**20**) from the combination of CO, R_3SiH, and two molecules of 1-hexyne (eq 5; R_3SiH = Et_3SiH, Me_2PhSiH) was recently reported from reactions catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $(t\text{-}BuNC)_4RhCo(CO)_4$ (optimal, 54% yield),[3,16] and from this discovery silylcarbocyclization of allyl propargylamines was formulated.[17] We have thoroughly examined the reaction mixtures from silylformylation of 1-alkynes catalyzed by $Rh_2(pfb)_4$ and find no evidence for such products from reactions performed at 10 atm of CO and only a trace amount (<1%) of a product having the expected mass spectral fragmentation from reactions with 1-octyne at atmospheric pressure. Addition of an acylmetal intermediate to an alkyne, which is formulated to account for the silylcarbocyclization transformation,[16] is clearly not an important process with $Rh_2(pfb)_4$ catalysis.



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The absence of silane alcoholysis products and the predominant trans stereoselectivity for hydrosilylation in reactions performed under carbon monoxide suggest that the active silylformylation catalyst is not $Rh_2(pfb)_4$. In order to better understand the role of $Rh_2(pfb)_4$ in these transformations, therefore, the course of the reaction was followed by ^{19}F NMR spectroscopy. Spectral data for standard compounds are reported in Table 3. Absorptions for the fluorine nuclei at the α-position are most sensitive to structural changes. Upon addition of carbon monoxide to $Rh_2(pfb)_4$ a new set of resonances (δ 59.40 and 49.68) appears as the principal dirhodium(II) form, presumably due to CO coordination with $Rh_2(pfb)_4$. Confirmation of this CO complex was obtained by IR spectroscopic analysis of the solution, which gave evidence for coordinated carbon monoxide from a strong absorption at 2043 cm^{-1}. Drago and co-workers have reported that $Rh_2(OAc)_4$ reversibly binds CO in dichloromethane with a carbonyl frequency of 2095 cm^{-1},[18] and a single crystal X-ray diffraction of $Rh_2(OAc)_4(CO)_2$ has revealed that both CO molecules are coordinated through their carbon atoms.[19] With addition of triethylsilane the ^{19}F NMR spectrum shows the emergence of absorptions at δ 95.83, 57.58, and 49.75, which are attributable to triethylsilyl perfluorobutyrate. The major component, however, with resonance absorptions at δ 95.73, 59.08, and 49.42, suggests a dirhodium species. Upon addition of phenylacetylene to this solution, resonance signals from triethylsilyl perfluorobutyrate increase at the expense of those that are characteristic of a

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Table 3. ^{19}F NMR Chemical Shifts of Reactants and Products

compd	δ, ppm[a]		
$Rh_2(OOCCF_2CF_2CF_3)_4$	95.86	59.28	49.64
$CF_2CF_2CF_2COOH$	95.89	56.71	49.76
$CF_3CF_2CF_2COOSiEt_3$	95.84	57.60	49.75

[a] Relative to $FCCl_3$; solvent is $CDCl_3$.

dirhodium species. Upon sitting overnight at room temperature in a closed tube, all of the perfluorobutyrates that had originally been bonded to dirhodium(II) are now observed as triethylsilyl perfluorobutyrate, which was subsequently characterized by chromatographic and spectral comparisons with the independently synthesized silyl ester. The conclusions that can be drawn from this spectral investigation are that carbon monoxide coordinates with $Rh_2(pfb)_4$ and that the addition of Et_3SiH initiates events that result in the formation of triethylsilyl perfluorobutyrate (eqs 6 and 7).

$$Rh_2(pfb)_4 + CO \rightleftharpoons Rh(pfb)_4RhCO \quad (6)$$

$$Rh(pfb)_4RhCO + Et_3SiH \rightarrow Rh_2(pfb)_3(CO)(H) + CF_3CF_2CF_2COOSiEt_3 \quad (7)$$

How many pfb ligands are retained by active catalyst(s) and whether CO and H are bound separately to rhodium or are bound as a formyl complex[20] were not established. Attempts to detect the hydride or formyl proton by NMR spectroscopy were unsuccessful. However, subsequent events involve alkyne association with coordinatively unsaturated rhodium, followed by silylation and completed by formylation, and these individual steps may be the same as those previously advanced for silylformylation catalyzed by $Co_2Rh_2(CO)_{12}$ and related bimetallic complexes.[3,16] Alternatively, the silylformylation reaction mechanism may involve a multistep sequence in which a distinct acylmetal intermediate is not included.

In support of organosilane coordination during the course of silylformylation, Et_3SiH forms a coordination complex with $Rh_2(pfb)_4$,[12] but its equilibrium constant (K_{eq} = 15) is much less than that for association with 1-octene (K_{eq} = 65), although it is comparable to that for phenylacetylene (K_{eq} = 18). Interference with R_3SiH coordination by the alkyne would inhibit silylformylation, and this interference may be the cause of the requirement for slow alkyne addition to the silane–catalyst–CO combination in reactions performed at 1 atm of CO.

Experimental Section

General Considerations. ^1H NMR spectra were obtained on a 300-MHz instrument, and ^{19}F NMR spectra were recorded from the same instrument operated at 282 MHz. Mass spectra were taken on a quadrupole GC/MS system operated at 70 eV, and IR spectra were obtained from a FT instrument. Rhodium(II) acetate was prepared from rhodium(III) chloride hydrate according to the established procedure.[21] Dichloromethane was distilled from P_2O_5 prior to use, and all alkynes were purified by distillation. Microanalyses were performed at Texas Analytical Laboratories, Inc. Hydrosilylation products were characterized through spectral and chromatographic comparisons with authentic samples.[12,22] Triethylsilyl perfluorobutyrate was prepared from perfluorobutyric acid and chlorotriethylsilane.

Rhodium(II) Perfluorobutyrate. Rhodium(II) acetate (500 mg, 1.13 mmol) was dissolved in 10 mL of heptafluorobutanoic acid and 1 mL of heptafluorobutanoic anhydride, and the resulting solution was heated to reflux under nitrogen for 1 h. Excess acid and anhydride were distilled using an oil bath, and the resulting aqua-green residue was suspended in 5 mL of hexane, cooled to 0 °C, and filtered. The isolated solid was dissolved in a minimum amount of boiling toluene and cooled to −20 °C overnight. The resulting aqua precipitate was collected by vacuum filtration and washed with ice-cold hexane to give a dark green solid which was dried in a vacuum oven at 90 °C to give 530 mg of a light green solid. The mother liquor was evaporated, and the residue was redissolved in a minimum volume of boiling toluene and cooled overnight at −20 °C to give, after drying, an additional 444 mg of light green solid which was found to be identical by HPLC analysis (methanol, μ-Bondapak-CN reverse phase column) to the first crop of crystals. A total of 974 mg (78% yield) of rhodium(II) perfluorobutyrate was obtained as a light green, hygroscopic solid which rapidly turns dark green upon exposure to moist air. The light green, nonhydrated material can be regenerated by heating under vacuum at 100 °C for 24 h. ^{19}F NMR (282 MHz, $CDCl_3$): δ 95.86 (t, J = 8.8 Hz, 3 F), 59.28 (q, J = 8.8 Hz, 2 F), 49.64 (m, 2 F).

Silylformation Procedure at 10 atm of CO. General Procedure. The 300-mL glass sleeve of a 300-mL autoclave was charged with the appropriate acetylene (10.0 mmol), organosilane (10.0 mmol), and anhydrous dichloromethane (100 mL). Rhodium(II) perfluorobutyrate (0.3–0.5 mol %) was added, and the glass vessel was placed in a stainless steel autoclave and purged with carbon monoxide three times (50–150 psig). The autoclave was then brought to 150 psig and stirred for 16 h at room temperature. After venting, the glass sleeve was removed from the autoclave, and the reaction solution was filtered through a 1-cm bead of neutral alumina to remove catalyst. The solvent was then evaporated under reduced pressure, and the residue was further purified by bulb-to-bulb distillation.

Silylformation of Ethynylbenzene with Triethylsilane. Ethynylbenzene (1.02 g, 10.0 mmol) was reacted with triethylsilane (1.16 g, 10.0 mmol) in the presence of 30 mg (0.028 mmol) of $Rh_2(pfb)_4$ according to the above procedure to give, after chromatography and bulb-to-bulb distillation at 80–85 °C (0.2 Torr), 1.85 g (75% overall yield) of a mixture consisting of 88% (*Z*)- and (*E*)-2-phenyl-3-(triethylsilyl)propenal (*Z*:*E* = 24:1) and 12% vinylsilanes.

2-Phenyl-3-(triethylsilyl)-2-propenal (1). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.03 (s, 1 H), 7.31–7.29 (m, 5 H), 7.13 (s, 1 H), 1.05–0.94 (m, 9 H), 0.88–0.73 (m, 6 H); *E* isomer, δ 9.68 (s, 1 H), 7.39–7.25 (m, 5 H), 6.96 (s, 1 H), 1.05–0.94 (m, 9 H), 0.88–0.73 (m, 6 H). IR (thin film): 1693 cm^{-1} (C=O). Mass spectrum (*m*/*e* (relative abundance)): *Z* isomer, 246 (2, M), 218 (19), 217 (100, M − 29), 189 (47), 175 (8), 171 (15), 161 (21), 131 (23), 115 (42), 105 (22), 87 (25), 75 (69), 59 (43); *E* isomer, 218 (10), 217 (56, M − 29), 189 (100), 171 (2), 161 (25), 131 (10), 115 (34), 105 (9), 87 (7), 75 (8). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00; Si, 11.40. Found: C, 73.21; H, 9.08; Si, 11.36.

Silylformylation of Ethynylbenzene with Dimethylphenylsilane. Ethynylbenzene (1.02 g, 10.0 mmol) was reacted under the above conditions with dimethylphenylsilane (1.36 g, 10.0 mmol) in the presence of 35 mg (0.033 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 80–90 °C, 1.95 g of a light yellow oil (73% overall yield) as a mixture consisting of 95% (*Z*)- and (*E*)-2-phenyl-3-(dimethylphenylsilyl)-2-propenal (*Z*:*E* = 12:1) and 5% vinylsilanes.

2-Phenyl-3-(dimethylphenylsilyl)-2-propenal (15). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.04 (s, 1 H), 7.60–7.41 (m, 3 H), 7.39–7.34 (m, 7 H), 7.24 (s, 1 H), 0.58 (s, 6 H); *E* isomer, δ 9.69 (s, 1 H), 7.45–7.30 (m, 10 H), 7.11 (s, 1 H), 0.17 (s, 6 H).

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IR (thin film): 1685 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 266 (32, M), 265 (53), 251 (85), 233 (18), 192 (16), 191 (30), 189 (78), 173 (11), 145 (35), 135 (75), 115 (100), 107 (21), 91 (15), 75 (47); *E* isomer, 266 (41, M), 265 (61), 251 (25), 233 (23), 192 (15), 191 (18), 189 (33), 173 (14), 145 (18), 135 (100), 115 (37), 107 (24), 91 (12), 75 (43).

Silylformation of 4-Ethynyltoluene with Triethylsilane. 4-Ethynyltoluene (0.65 g, 5.60 mmol) and triethylsilane (0.65 g, 5.60 mmol) were reacted under the above conditions in the presence of 20 mg (0.019 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 80–90 °C (0.2 Torr), 0.92 g (63% overall yield) of a light yellow oil as a mixture consisting of 95% (*Z*)- and (*E*)-2-(*p*-tolyl)-3-(triethylsilyl)-2-propenal (*Z*:*E* = 17:1) and 5% vinylsilanes.

2-(*p*-Tolyl)-3-(triethylsilyl)-2-propenal (2). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.02 (s, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.17 (d, *J* = 8.2 Hz, 2 H), 7.09 (s, 1 H), 2.36 (s, 3 H), 1.01 (t, *J* = 7.3 Hz, 9 H), 0.82 (q, *J* = 7.3 Hz, 6 H); *E* isomer, δ 9.67 (s, 1 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 7.03 (d, *J* = 8.3 Hz, 2 H), 6.92 (s, 1 H), 2.36 (s, 3 H), 1.01 (t, *J* = 7.3 Hz, 9 H), 0.82 (q, *J* = 7.3 Hz, 6 H). IR (thin film): 1689 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 260 (3, M), 231 (92, M – 29), 204 (22), 203 (100), 175 (24), 161 (17), 145 (21), 129 (17), 115 (33), 91 (11), 75 (54), 59 (38); *E* isomer, 231 (47, M – 29), 204 (18), 203 (100), 175 (19), 161 (8), 145 (7), 129 (14), 115 (9), 91 (4), 75 (6), 59 (12). Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29; Si, 10.78. Found: C, 73.83; H, 9.26; Si, 10.82.

Silylformylation of 4-Isobutyl-1-ethynylbenzene with Triethylsilane. *p*-Isobutylethynylbenzene (0.32 g, 0.20 mmol) and triethylsilane (0.23 g, 0.20 mmol) were reacted under the above conditions in the presence of 10 mg (0.009 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 80–85 °C (0.5 Torr), 0.44 g of a light yellow oil (72% overall yield) as a mixture of 96% (*Z*)- and (*E*)-2-(*p*-isobutylphenyl)-3-(triethylsilyl)-2-propenal (*Z*:*E* = 10:1) and 4% vinylsilanes.

2-(*p*-Isobutylphenyl)-3-(triethylsilyl)-2-propenal (4). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.02 (s, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.17 (d, *J* = 8.2 Hz, 2 H), 7.11 (s, 1 H), 2.48 (d, *J* = 7.1 Hz, 2 H), 1.87 (sept, *J* = 6.7 Hz, 1 H), 1.02 (d, *J* = 7.9 Hz, 9 H), 0.91 (d, *J* = 6.7 Hz, 6 H), 0.82 (q, *J* = 7.9 Hz, 6 H); *E* isomer, δ 9.68 (s, 1 H), 6.93 (s, 1 H), 2.48 (d, *J* = 7.1 Hz, 2 H), 1.87 (sept, *J* = 6.7 Hz, 1 H), 1.02 (t, *J* = 7.9 Hz, 9 H), 0.91 (d, *J* = 6.7 Hz, 6 H), 0.80 (q, *J* = 7.9 Hz, 6 H). IR (thin film): 1693 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomers, 302 (2, M), 274 (22), 273 (87), 246 (22), 245 (100), 128 (14), 115 (23), 87 (25), 75 (33), 59 (31); *E* isomer, 274 (12), 273 (49, M – 29), 246 (21), 245 (100), 128 (10), 115 (8), 87 (8), 75 (6), 59 (13). Anal. Calcd for $C_{19}H_{30}OSi$: C, 75.43; H, 9.99; Si, 9.28. Found: C, 75.36; H, 10.07; Si, 9.24.

Silylformylation of 2-Ethynyl-6-methoxynaphthalene with Dimethylphenylsilane. 2-Ethynyl-6-methoxynaphthalene (0.73 g, 3.99 mmol) and dimethylphenylsilane (0.55 g, 4.04 mmol) were reacted under the above conditions in the presence of 24 mg (0.23 mmol) of $Rh_2(pfb)_4$ to give 1.37 g (99% yield) of a yellow solid (mp 70–71 °C (hexane)) as a 11:1 mixture of (*Z*)- and (*E*)-2-(6-methoxynaphthyl)-3-(dimethylphenylsilyl)-2-propenal.

2-(6-Methoxynaphthyl)-3-(dimethylphenylsilyl)-2-propenal (6). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.12 (s, 1 H), 7.86–7.13 (m, 12 H), 3.93 (s, 3 H), 0.61 (s, 6 H); *E* isomer, δ 9.76 (s, 1 H), 7.86–7.13 (m, 12 H), 3.93 (s, 3 H), 0.33 (s, 6 H). IR (KBr): 1693 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 347 (33), 346 (100, M), 345 (45), 331 (54), 315 (10), 269 (72), 225 (18), 195 (52), 152 (15), 135 (91), 75 (18); *E* isomer, 347 (38), 346 (100, M), 331 (53), 315 (12), 269 (47), 225 (18), 195 (36), 152 (15), 135 (90), 75 (19). Anal. Calcd for $C_{22}H_{22}O_2Si$: C, 76.26; H, 6.40; Si, 8.11. Found: C, 7.17; H, 4.48; Si, 8.15.

Silylformylation of 1-Octyne with Triethylsilane. 1-Octyne (1.10 g, 10.0 mmol) and triethylsilane (1.16 g, 10.0 mmol) were reacted in the presence of 35 mg (0.033 mmol) of $Rh_2(pfb)_4$ under the above conditions to give, after chromatography and bulb-to-bulb distillation at 70–75 °C (0.25 Torr), 2.05 g of a clear oil (81% yield) as a 35:1 mixture of (*Z*)- and (*E*)-2-(*n*-hexyl)-3-(triethylsilyl)-2-propenal.

(*Z*)-2-(*n*-Hexyl)-3-(triethylsilyl)-2-propenal (10). ^1H NMR (300 MHz, $CDCl_3$): δ 9.74 (s, 1 H), 6.97 (s, 1 H), 2.27 (t, *J* = 7.5 Hz, 2 H), 1.41–1.27 (m, 8 H), 0.97 (t, *J* = 7.9 Hz, 9 H), 0.88 (t, *J* = 6.7 Hz, 3 H), 0.72 (q, *J* = 7.9 Hz, 6 H). IR (thin film): 1686 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): 225 (34, M – 29), 197 (21), 155 (100), 127 (25), 103 (35), 86 (12), 75 (44), 59 (34). Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88; Si, 11.04. Found: C, 70.72; H, 11.93; Si, 11.10.

Silylformylation of 2-Propyn-1-yl Acetate with Triethylsilane. 2-Propyn-1-yl acetate (0.98 g, 10.0 mmol) and triethylsilane (1.16 g, 10.0 mmol) were reacted under the above conditions in the presence of 40 mg (0.037 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 60 °C (0.2 Torr), 1.73 g (71% yield) of a 21:1 mixture of (*Z*)- and (*E*)-2-formyl-3-(triethylsilyl)-2-propen-1-yl acetate.

2-Formyl-3-(triethylsilyl)-2-propen-1-yl Acetate (12). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 9.80 (s, 1 H), 6.97 (s, 1 H), 4.82 (s, 2 H), 2.12 (s, 3 H), 0.98 (t, *J* = 7.3 Hz, 9 H), 0.76 (*q*, *J* = 7.3 Hz, 6 H); *E* isomer, δ 9.49 (s, 1 H), 7.05 (s, 1 H), 4.67 (s, 2 H), 2.05 (s, 3 H), 0.98 (t, *J* = 7.3 Hz, 9 H), 0.76 (q, *J* = 7.3 Hz, 6 H). IR (thin film): 1748 cm^{-1} (ester C=O), 1683 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 213 (100, M – 29), 171 (95), 153 (60), 143 (53), 125 (23), 115 (46), 103 (47), 91 (100), 75 (82), 59 (58). Anal. Calcd for $C_{12}H_{22}O_3Si$: C, 59.46; H, 9.15; Si, 11.59. Found: C, 59.38; H, 9.23; Si, 11.60.

Silylformation of 1-Methoxy-2-propyne with Triethylsilane. 1-Methoxy-2-propyne (0.70 g, 10.0 mmol) and triethylsilane (1.16 g, 10.0 mmol) were reacted under the above conditions in the presence of 30 mg (0.028 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 70–80 °C (0.7 Torr), 1.65 g of a clear oil (77% yield) as a 30:1 mixture of (*Z*)- and (*E*)-2-(methoxymethyl)-3-(triethylsilyl)-2-propenal.

2-(Methoxymethyl)-3-(triethylsilyl)-2-propenal (13). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 9.81 (s, 1 H), 7.05 (s, 1 H), 4.16 (s, 2 H), 3.40 (s, 3 H), 0.98 (t, *J* = 7.6 Hz, 9 H), 0.75 (q, *J* = 7.6 Hz, 6 H); *E* isomer, δ 9.48 (s, 1 H), 6.91 (s, 1 H), 4.13 (s, 2 H), 3.35 (s, 3 H), 0.98 (t, *J* = 7.6 Hz, 9 H), 0.75 (q, *J* = 7.6 Hz, 6 H). IR (thin film): 1685 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 185 (14, M – 29), 157 (16), 155 (100), 153 (7), 127 (44), 125 (11), 105 (5), 99 (17), 89 (14), 77 (10), 61 (25), 59 (35); *E* isomer, 185 (100, M – 29), 157 (11), 155 (17), 153 (42), 127 (31), 125 (23), 105 (62), 99 (13), 89 (71), 77 (57), 61 (68), 59 (72). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34; Si, 13.10. Found: C, 61.32; H, 10.18; Si, 12.84.

Silylformylation of 2-Methyl-3-butyn-2-ol with Triethylsilane. 2-Methyl-3-butyn-2-ol (0.84 g, 10.0 mmol) and triethylsilane (1.16 g, 10.0 mmol) were reacted under the above conditions in the presence of 38 mg (0.036 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 60–65 °C (0.35 Torr), 1.51 g (66%) of (*Z*)-3-formyl-2-methyl-4-(triethylsilyl)-3-buten-1-ol.

(*Z*)-3-Formyl-2-methyl-4-(triethylsilyl)-3-buten-2-ol (14). ^1H NMR (300 MHz, $CDCl_3$): δ 9.79 (s, 1 H), 7.05 (s, 1 H), 3.20 (s, 1 H), 1.43 (s, 6 H), 0.98 (t, *J* = 7.9 Hz, 9 H), 0.74 (q, *J* = 7.9 Hz, 6 H). IR (thin film): 3450 cm^{-1} (O—H), 1687 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): 199 (14, M – 29), 171 (6), 153 (9), 131 (100), 125 (15), 103 (10), 75 (23). Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.11; H, 10.59; Si, 12.29. Found: C, 62.74; H, 11.04; Si, 12.24.

Silylformation of 2-Propyn-1-ol with Triethylsilane. 2-Propyn-1-ol (0.56 g, 10 mmol) and triethylsilane (1.16 g, 10 mmol) were reacted under the above conditions in the presence of 32 mg (0.030 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 70–80 °C (0.25 Torr), 1.16 g of a clear oil (58% yield) as an 18:1 mixture of (*Z*)- and (*E*)-2-(hydroxymethyl)-3-(triethylsilyl)-2-propenal.

2-(Hydroxymethyl)-3-(triethylsilyl)-2-propenal (16). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 9.82 (s, 1 H), 7.03 (s, 1 H), 4.39 (s, 2 H), (broad s, 1 H), 0.99 (t, *J* = 7.9 Hz, 9 H), 0.75 (q, *J*

= 7.9 Hz, 6 H); *E* isomer, δ 9.47 (s, 1 H), 6.84 (s, 1 H), 4.39 (s, 2 H), 2.30 (broad s, 1 H), 0.99 (t, *J* = 7.9 Hz, 9 H), 0.75 (q, *J* = 7.9 Hz, 6 H). IR (thin film): 3581 cm^{-1} (O—H), 1681 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 171 (43, M − 29), 143 (100), 125 (13), 115 (19), 91 (27), 75 (60), 63 (28); *E* isomer, 171 (26, M − 29), 143 (18), 125 (14), 115 (47), 91 (79), 75 (100), 63 (55). Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.94; H, 10.08; Si, 14.02. Found: C, 59.86; H, 10.12; Si, 14.09.

Silylformylation of 3-Butyn-2-one. 3-Butyn-2-one (0.68 g, 10.0 mmol) and triethylsilane (1.16 g, 10.0 mmol) were reacted under the above conditions in the presence of 35 mg (0.033 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 56–70 °C (0.20 Torr), 1.00 g (47% yield) of a 1:1.9 mixture of (*Z*)- and (*E*)-3-formyl-4-(triethylsilyl)-3-buten-2-one.

3-Formyl-4-(triethylsilyl)-3-buten-2-one (17). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.07 (s, 1 H), 7.53 (s, 1 H), 2.45 (s, 3 H), 1.00–0.96 (m, 9 H), 0.82–0.69 (m, 6 H); *E* isomer, δ 9.56 (s, 1 H), 7.09 (s, 1 H), 2.43 (s, 3 H), 1.00–0.96 (m, 9 H), 0.82–0.69 (m, 6 H). IR (thin film): 1698 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *E* isomer, 183 (100, M − 29), 155 (33), 129 (13), 127 (15), 91 (32), 63 (29); *Z* isomer, 183 (100, M − 29), 155 (87), 129 (26), 127 (26), 91 (31), 63 (23). Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49; Si, 13.23. Found: C, 62.13; H, 9.54; Si, 13.15.

Silylformylation of Methyl 2-Propynoate. Methyl 2-propynoate (0.84 g, 10 mmol) was reacted under the above conditions in the presence of 41 mg (0.038 mmol) of $Rh_2(pfb)_4$ to give, after chromatography and bulb-to-bulb distillation at 52–60 °C (0.1 Torr), 450 mg (20% yield) of a 1:1.3 mixture of methyl (*Z*)- and (*E*)-2-formyl-3-(triethylsilyl)-2-propenoate.

Methyl 2-Formyl-3-(triethylsilyl)-2-propenoate (18). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.06 (d, *J* = 1.5 Hz, 1 H), 7.67 (d, *J* = 1.5 Hz, 1 H), 3.87 (s, 3 H), 0.99–0.91 (m, 9 H), 0.81–0.70 (m, 6 H); *E* isomer, δ 9.68 (s, 1 H), 7.36 (s, 1 H), 3.86 (s, 3 H), 0.99–0.91 (m, 9 H), 0.81–0.70 (m, 6 H). IR (thin film): 1736 cm^{-1} (C=O), 1702 cm^{-1} (HC=O). Mass spectrum (*m/e* (relative abundance)): 199 (100, M − 29), 171 (27), 139 (11), 113 (12), 89 (28), 83 (11), 61 (26), 59 (34). Anal. Calcd for $C_{11}H_{20}O_3Si$: C, 57.86; H, 8.83; Si, 12.30. Found: C, 57.81; H, 8.88; Si, 12.23.

Silylformylation at Atmospheric Pressure of CO. General Procedure. A 50-mL two-necked round-bottom flask fitted with a septum and balloon adapter was charged with 10 mg (0.095 mmol) of rhodium(II) perfluorobutyrate. The reaction vessel was evacuated and refilled three times with carbon monoxide. Anhydrous dichloromethane (25 mL), which had been saturated with carbon monoxide, was added via syringe. The normally blue-green rhodium(II) perfluorobutyrate in dichloromethane became gray in the presence of carbon monoxide. The resulting solution was cooled to 0 °C, and triethylsilane (0.48 mL, 3.01 mmol) was added to the gray solution, which turned colorless when it was stirred over 10 min at 0 °C. Then, 3.0 mL of a 1.00 M solution of the acetylene in dichloromethane (3.0 mmol) was added to the reaction mixture at 0 °C by syringe pump. After addition was complete, the reaction mixture was warmed to room temperature and stirred at that temperature under an atmosphere of carbon monoxide for 16 h. The catalyst was removed by passing the reaction mixture through a short column of silica gel, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation.

Silylformylation of Ethynylbenzene at 1 atm of CO Using Triethylsilane. A 1.0 M solution of phenylacetylene in dichloromethane (10.0 mL, 10 mmol) was added at 1.0 mL/h to a solution of 1.16 g of triethylsilane (10.0 mmol) and 33 mg (0.031 mmol) of $Rh_2(pfb)_4$ in 100 mL of anhydrous dichloromethane under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 80–85 °C (0.2 Torr), 2.02 g (82% yield) of a 10:1 mixture of (*Z*)- and (*E*)-2-phenyl-3-(triethylsilyl)-2-propenal (1).

Silylformylation of 4-Ethynyltoluene at 1 atm of CO Using Triethylsilane. A 0.5 M solution of 4-ethynyltoluene (5 mL, 2.5 mmol) in dichloromethane was added at 1.0 mL/h to a solution of 0.29 g (2.5 mmol) of triethylsilane and 8 mg (0.007 mmol) of $Rh_2(pfb)_4$ under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 80–90 °C (0.2 Torr), 143 mg (24% overall yield) of a light yellow oil as a mixture consisting of 38% (*Z*)- and (*E*)-2-(*p*-tolyl)-3-(triethylsilyl)-2-propenal (2; *Z*:*E* = 13:1) and 62% vinylsilanes.

Silylformylation of 4-Ethynyltoluene at 1 atm of CO Using Dimethylphenylsilane. A 0.50 M solution of 4-ethynyltoluene (6.0 mL, 3.0 mmol) in dichloromethane was added at 1.0 mL/h to a solution of 0.35 g (3.0 mmol) of triethylsilane and 10 mg (0.009 mmol) of $Rh_2(pfb)_4$ in 25 mL of anhydrous dichloromethane under the above conditions to give, after chromatography and bulb-to-bulb distillation at 75–90 °C (0.2 Torr), 805 mg (84% yield) of a clear oil as a 38:1 mixture of (*Z*)- and (*E*)-2-(*p*-tolyl)-3-(dimethylphenylsilyl)-2-propenal.

2-(*p*-Tolyl)-3-(dimethylphenylsilyl)-2-propenal (3). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.03 (s, 1 H), 7.59–7.53 (m, 2 H), 7.39–7.33 (m, 3 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.21 (s, 1 H), 7.16 (d, *J* = 8.2 Hz, 2 H), 2.36 (s, 3 H), 0.57 (s, 6 H); *E* isomer, δ 9.68 (s, 1 H), 7.59–7.53 (m, 2 H), 7.39–7.33 (m, 3 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.16 (d, *J* = 8.2 Hz, 2 H), 7.06 (s, 1 H), 2.35 (s, 3 H), 0.18 (s, 6 H). IR (thin film): 1691 cm^{-1} (C=O). Mass spectrum (*m/e* relative abundance)): *Z* isomer, 280 (28, M), 265 (100), 247 (12), 205 (16), 203 (70), 159 (31), 135 (63), 129 (86), 105 (24), 75 (25); *E* isomer, 265 (75, M − 15), 247 (15), 205 (13), 203 (31), 159 (19), 135 (100), 105 (22), 75 (23). Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19; Si, 10.01. Found: C, 77.16; H, 7.23; Si, 9.95.

Silylformylation of 4-Isobutyl-1-ethynylbenzene at 1 atm of CO Using Triethylsilane. A 0.50 M solution of 4-isobutyl-1-ethynylbenzene (5.0 mL, 2.5 mmol) in dichloromethane was added at 1.0 mL/h to a solution of 0.29 g (2.5 mmol) of triethylsilane and 11 mg (0.010 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 80–85 °C and 0.5 Torr, 203 mg (28% overall yield) of a mixture consisting of 91% (*Z*)- and (*E*)-2-(*p*-isobutylphenyl)-3-(triethylsilyl)-2-propenal (4; *Z*:*E* = 10:1) and 9% vinylsilanes.

Silyformylation of 4-Isobutyl-1-ethynylbenzene at 1 atm of CO Using Dimethylphenylsilane. A 0.5 M solution of 4-isobutyl-1-ethynylbenzene (6.0 mL, 3.0 mmol) in dichloromethane was added at 1.19 mL/h to a solution of 0.41 g (3.0 mmol) and 10 mg (0.009 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 80–90 °C (0.2 Torr), 717 mg (74% yield) of a light yellow oil as a 11:1 mixture of (*Z*)- and (*E*)-2-(*p*-isobutylphenyl)-3-(dimethylphenylsilyl)-2-propenal.

2-(*p*-Isobutylphenyl)-3-(dimethylphenylsilyl)-2-propenal (5). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.03 (s, 1 H), 7.61–7.42 (m, 2 H), 7.39–7.37 (m, 3 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.23 (s, 1 H), 7.14 (d, *J* = 8.2 Hz, 2 H), 2.48 (d, *J* = 7.3 Hz, 2 H), 1.95–1.78 (m, 1 H), 0.90 (d, *J* = 6.7 Hz, 6 H), 0.57 (s, 6 H); *E* isomer, δ 9.69 (s, 1 H), 7.61–7.42 (m, 2 H), 7.39–7.37 (m, 3 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.11 (s, 1 H), 7.01 (d, *J* = 8.2 Hz, 2 H), 2.47 (d, *J* = 7.3 Hz, 2 H), 1.96–1.78 (m, 1 H), 0.90 (d, *J* = 6.7 Hz, 6 H), 0.17 (s, 6 H). IR (thin film): 1693 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 322 (32, M), 307 (59), 279 (100), 265 (23), 245 (60), 205 (16), 171 (41), 135 (58); *E* isomer, 322 (30, M), 307 (28), 279 (100), 265 (23), 245 (29), 205 (15), 171 (18), 135 (79). Anal. Calcd for $C_{21}H_{28}OSi$: C, 78.23; H, 8.12; Si, 8.71. Found: C, 78.17; H, 8.21; Si, 8.66.

Silylformylation of Diphenylacetylene at 1 atm of CO Using Triethylsilane. A 0.87 M solution of diphenylacetylene (5 mL, 4.37 mm) was added at 1.0 mL/h to a solution of triethylsilane (0.51 g, 4.40 mmol) and 17 mg (0.016 mmol) of $Rh_2(pfb)_4$ in 50 mL of dichloromethane under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 80–85 °C and 0.1 Torr, 1.31 g (95% overall yield) of a mixture consisting of 71% (*Z*)- and (*E*)-2,3-diphenyl-3-(triethylsilyl)-2-propenal (*Z*:*E* = 32:1) and 29% vinylsilanes.

2,3-Diphenyl-3-(triethylsilyl)-2-propenal (7). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 10.27 (s, 1 H), 7.38–7.01 (m, 6 H),

6.86 (dd, J = 8.4, 1.6 Hz, 2 H), 6.76 (dd, J = 8.4, 1.6 Hz, 2 H), 0.98 (t, J = 7.9 Hz, 9 H), 0.75 (q, J = 7.9 Hz, 6 H); *E* isomer, δ 9.57 (s, 1 H), 7.38–7.01 (m, 6 H), 6.86 (dd, J = 8.4, 1.6 Hz, 2 H), 6.76 (dd, J = 8.4, 1.6 Hz, 2 H), 6.76 (dd, J = 8.4, 1.6 Hz, 2 H), 0.98 (t, J = 7.9 Hz, 9 H), 0.75 (q, J = 7.9 Hz, 6 H). IR (thin film): 1683 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 294 (18, M – 29), 265 (100), 237 (25), 207 (20), 163 (14), 135 (21), 107 (27); *E* isomer, 294 (27, M – 29), 265 (100), 237 (32), 207 (17), 163 (16), 135 (27), 107 (30). Anal. Calcd for $C_{21}H_{26}OSi$: C, 78.21; H, 8.13; Si, 8.71. Found: C, 77.98; H, 8.19; Si, 8.68.

Silylformylation of 1-Phenyl-1-propyne at 1 atm of CO with Triethylesilane. A 1.0 M solution of 1-phenyl-1-propyne (3.0 mL, 3.0 mmol) in dichloromethane was added at 0.79 mL/h to a solution of 0.35 g (3.0 mmol) of triethylsilane and 17 mg (0.016 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above conditions to give, after chromatography and bulb-to-bulb distillation at 75–80 °C (0.25 Torr), 540 mg (72% overall yield) of a light yellow oil as a mixture of 44% 1- and 2-(triethylsilyl)-1-phenyl-1-propene in a 2:1 molar ratio and 56% (*Z*)-2-phenyl-3-(triethylsilyl)-2-butenal.

(*Z*)-2-Phenyl-3-(triethylsilyl)-2-butenal (8). ^1H NMR (300 MHz, $CDCl_3$): δ 10.01 9s, 1 H), 7.42–7.32 (m, 3 H), 7.03 (dt, J = 6.8, 1.6 Hz, 2 H), 1.92 (s, 3 H), 1.03 (t, J = 8.3 Hz, 9 H), 0.86 (q, J = 8.3 Hz, 6 H). IR (thin film): 1686 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): 231 (100, M – 29), 203 (82), 175 (20), 143 (13), 129 (41), 128 (27), 115 (28), 89 (23), 87 (24), 75 (34), 59 (46). Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29; Si, 10.77. Found: C, 73.68; H, 9.34; Si, 10.72.

Silylformylation of 1-Phenyl-1-propyne at 1 atm of CO Using Dimethylphenylsilane. A 1.0 M solution of 1-phenyl-1-propyne (3.0 mL, 3.0 mmol) in dichloromethane was added at 0.79 mL/h to a solution of 0.41 g (3.0 mmol) and 10 mg (0.009 mmol) of $Rh_2(pfb)_4$ under the above conditions to give, after chromatography and bulb-to-bulb distillation at 75–85 °C (0.25 Torr), 639 mg (83% overall yield) of a clear oil consisting of a mixture of 14% isomeric aldehydes in the ratio of 12.5:1 of (*Z*)-2-phenyl-3-(dimethylphenylsilyl)-2-butenal and (*E*)-2-phenyl-3-(dimethylphenylsilyl)-2-butenal, respectively.

2-Phenyl-3-(dimethylphenylsilyl)-2-butenal (9).[2] ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 9.96 (s, 1 H), 7.60–6.86 (m, 10 H), 1.97 (s, 3 H), 0.60 (s, 6 H), *E* isomer, δ 9.98 (s, 1 H), 7.60–6.86 (m, 10 H), 1.63 (s, 3 H), 0.32 (s, 6 H). IR (thin film): 1691 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 280 (1, M), 265 (100, M – 15), 203 (34), 187 (22), 159 (32), 135 (54), 129 (29), 105 (17), 75 (18); *E* isomer, 280 (2, M), 265 (100, M – 15), 203 (75), 187 (9), 159 (24), 135 (54), 129 (39), 105 (18), 75 (15).

Silylformylation of 1-Octyne at 1 atm of CO Using Triethylsilane. A 1.0 M solution of 1-octyne in dichloromethane (3.0 mL, 3.0 mmol) was added at 1.19 mL/h to a solution of 0.35 g (3.0 mmol) of triethylsilane and 12 mg (0.011 mmol) of $Rh_2(pfb)_4$ in 25 mL of anhydrous dichloromethane under the above conditions to give, after chromatography and bulb-to-bulb distillation at 75–80 °C (0.25 Torr), 319 mg (45% overall yield) of a clear oil as a mixture of 60% vinylsilanes and 40% (*Z*)-2-(*n*-hexyl)-3-(triethylsilyl)-2-propenal (**10**).

Silylformylation of 1-Octyne at 1 Atm of CO with Dimethylphenylsilane. A 1.0 M solution of 1-octyne in dichloromethane (3.0 mL, 3.0 mmol) was added at 0.79 mL/h to a solution of 0.41 g (3.0 mmol) of dimethylphenylsilane and 11 mg (0.010 mmol) of $Rh_2(pfb)_4$ in 25 mL of anhydrous dichloromethane under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 78–82 °C (0.20 Torr), 669 mg (81%) of a 14:1 mixture of (*Z*)- and (*E*)-2-(*n*-hexyl)-3-(dimethylphenylsilyl)-2-propenal.

2-Hexyl-3-(dimethylphenylsilyl)-2-propenal (11). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 9.77 (s, 1 H), 7.53–7.49 (m, 2 H), 7.37–7.34 (m, 3 H), 6.74 (s, 1 H), 2.30 (t, J = 7.4 Hz, 2 H), 1.45–1.28 (m, 8 H), 0.89 (t, J = 6.7 Hz, 3 H), 0.50 (s, 6 H); *E* isomer, δ 9.41 (s, 1 H), 7.60–7.75 (m, 2 H), 7.37–7.34 (m, 3 H), 6.74 (s, 1 H), 2.30 (t, J = 7.4 Hz, 2 H), 1.45–1.28 (m, 8 H), 0.89 (t, J = 6.7 Hz), 0.33 (s, 6 H). IR (thin film): 1686 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *Z* isomer, 259 (28, M – 15), 203 (18), 189 (100), 137 (60), 135 (39), 129 (25), 127 (49), 105 (20), 75 (51), 61 (30); *E* isomer, 274 (1, M), 259 (5, M – 15), 203 (85), 189 (100), 137 (41), 135 (90), 129 (44), 127 (23), 105 (21), 75 (69), 61 (21). Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55; Si, 10.23. Found: C, 74.31; H, 9.60; Si, 10.24.

Silylformylation of 2-Propyn-1-yl Acetate at 1 atm of CO Using Triethylsilane. A 0.5 M solution of 2-propyn-1-yl acetate in dichloromethane (6 mL, 3.0 mmol) was added at 1.19 mL/h to a solution of 0.35 g (3.0 mmol) of triethylsilane and 10 mg (0.009 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above conditions to give, after chromatography and bulb-to-bulb distillation at 60 °C (0.2 Torr), 512 mg of a clear oil (71% overall yield) as a mixture consisting of 96% (*Z*)- and (*E*)-2-formyl-3-(triethylsilyl)-2-propenyl acetate (**12**; *Z*:*E* = 21.1) and 4% vinylsilanes.

Silylformylation of 1-Methoxy-2-propyne at 1 atm of CO Using Triethylsilane. A 1.0 M solution of methyl propargyl ether in dichloromethane (2.5 mL, 2.5 mmol) was added at 1.0 mL/h to a solution of 0.29 g (2.5 mmol) of triethylsilane and 15 mg (0.014 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above conditions to give, after chromatography had bulb-to-bulb distillation at 70–80 °C (0.7 Torr), 464 mg (87%) of a clear oil as a 14:1 mixture of (*Z*)- and (*E*)-2-(methoxymethyl)-3-(triethylsilyl)-2-propenal (**13**).

Silylformylation of 2-Methyl-3-butyn-2-ol at 1 atm of CO Using Triethylsilane. A 1.0 M solution of 2-methyl-3-butyn-2-ol in dichloromethane (2.5 mL, 2.5 mmol) was added at 0.8 mL/h to a solution of 0.29 g (2.5 mmol) of triethylsilane and 13 mg (0.012 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above reaction conditions to give, after chromatography and bulb-to-bulb distillation at 60–65 °C (0.4 Torr), 217 mg (41% overall yield) of a mixture of 91% (*Z*)- and (*E*)-3-formyl-2-methyl-4-(triethylsilyl)-3-buten-2-ol (**14**; *Z*:*E* = 24:1) and 9% vinylsilanes.

Trimerization of 3-Butyn-2-one. A 0.5 M solution of 3-butyn-2-one in dichloromethane (5 mL, 2.5 mmol) was added at 1.19 mL/h to a solution of 0.29 g (2.5 mmol) of triethylsilane and 18 mg (0.017 mmol) of $Rh_2(pfb)_4$ in 25 mL of dichloromethane under the above reaction conditions to give 410 mg (80%) of 1,3,5-triacetylbenzene as a light brown solid, which was recrystallized from ethyl acetate to give a white solid, mp 164–166 °C (lit.[23] mp 163 °C).

Silylformylation of Methyl 2-Propynoate at 1 atm of CO Using Triethylsilane. A 0.50 M solution of methyl 2-propynoate (6.0 mL, 3.0 mmol) in dichloromethane was added at 1.19 mL/h to a solution of 0.35 g (3.0 mmol) of triethylsilane and 15 mg (0.014 mmol) of $Rh_2(pfb)_4$ in 25 mL of anhydrous dichloromethane under the above conditions to give 272 mg of a crude solid. This solid was washed with 10 mL of cold hexane and filtered to give 40 mg of trimethyl 1,3,5-benzenetricarboxylate, mp 141–144 °C (lit.[24] mp 146 °C). The hexane filtrate was evaporated under reduced pressure to give 186 mg of a clear oil which consisted of a mixture of trimethyl 1,2,4-benzenetricarboxylate (14%), hexamethyldisiloxane (10%), and a 6:1 mixture of methyl (*Z*)- and (*E*)-2-((triethylsilyl)methyl)-3-(triethylsiloxy)-2-propenoate (48%). The remaining 28% of the mixture was composed of vinylsilanes and unidentified oligomers.

Methyl 2-((Triethylsilyl)methyl)-3-(triethylsiloxy)-2-propenoate (19). ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer, δ 7.44 (s, 1 H), 3.69 (s, 3 H), 1.71 (s, 2 H), 0.99 (t, J = 7.9 Hz, 9 H), 0.93 (t, J = 7.9 Hz, 9 H), 0.74 (q, J = 7.9 Hz, 6 H), 0.50 (q, J = 7.9 Hz, 6 H); *E* isomer, δ 6.55 (s, 1 H), 3.71 (s, 3 H), 1.54 (s, 2 H), 0.99 (t, J = 7.9 Hz, 9 H), 0.93 (t, J = 7.9 H, 9 H), 0.74 (q, J = 7.9 Hz, 6 H), 0.50 (q, J = 7.9 Hz, 6 H). IR (thin film): 1714 cm^{-1} (C=O). Mass spectrum (*m/e* (relative abundance)): *E* isomer, 344 (3, M), 329 (17), 316 (26), 315 (100), 219 (9), 213 (16), 169 (19), 115 (26), 113 (12), 87 (77), 59 (89); *Z* isomer, 344 (2, M), 329 (19), 316 (26), 315 (100), 219 (9), 213 (16), 169 (20), 115 (26), 113 (12), 87 (77), 59 (89). Anal. Calcd for $C_{17}H_{36}O_3Si_2$: C, 59.25; H, 10.53; Si, 16.30. Found: C, 59.18; H, 10.50; Si, 16.24.

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IR Study of the Carbonyl Complex of $Rh_2(pfb)_4$. Rhodium(II) perfluorobutyrate (15 mg, 0.014 mmol) was placed in a 100-mL Schlenk tube and covered with 10 mL of hexane. Carbon monoxide was bubbled into the tube, resulting in the gradual dissolution of the $Rh_2(pfb)_4$. The IR spectrum of this olive brown solution was taken, which gave, after subtraction for solvent and dissolved carbon monoxide, a signal at 2043 cm^{-1}.

^{19}F NMR Study of the Reaction of $Rh_2(pfb)_4$ with 4-Ethynyltoluene. Rhodium(II) perfluorobutyrate (19 mg, 0.018 mg) was dissolved in 0.75 mL of $CDCl_3$ and placed in a 5-mm NMR tube. After the initial spectrum was taken, CO was carefully bubbled through the tube, resulting in an olive brown solution. ^{19}F NMR of this mixture now showed additional signals at 59.40 and 49.57 ppm relative to $CDCl_3$. The addition of 10 equiv of triethylsilane by syringe under an atmosphere of CO produces new signals at δ 95.73, 57.58, 59.08, and 49.42. After 2 equiv of phenylacetylene was added by syringe under an atmosphere of CO, the ^{19}F NMR spectrum showed signals at δ 95.78, 95.67, 59.03, 49.73, and 49.37 ppm. After this mixture stood overnight under an atmosphere of carbon monoxide, the ^{19}F NMR spectrum exhibited only three signals, at δ 95.84, 57.58 and 49.76, which were identical with the signals obtained from the ^{19}F NMR spectrum of the triethylsilyl ester of perfluorobutyric acid.

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