assumption that is fully supported by the observed differences ΔS (Table IV). Large deviations ΔS result in those solvents that are highly dipolar themselves such as ketones, nitriles, and nitrobenzene; therefore, the more dipolar tungsten complex is more strongly stabilized in the ground state, and a more pronounced hypsochromic shift is the result. On the other side, the most negative differences ΔS are observed in the aliphatic hydrocarbon solvents pentane and cyclohexane; these solvents are not dipolar, nor do they contain polarizable second-row-element heteroatoms such as Cl or S.

In summary, the unusual electronic structures and absorption spectra of the (olefin)carbonylmetal complexes $(TCNE)M(CO)_5$ have allowed us to quantify a specific solvatochromism that is based on the n- *and* π-donor capability of the medium toward an approximately[21,22c] planar π-acceptor system. The empirical parameters $E_{CT}(\pi)$ for aprotic solvents derived from this study may be of value for other π-electron-accepting organometallic compounds with planar ligand "decks" such as $(\eta^6\text{-arene})_2Fe^{2+}$[31] or for electron-poor square-planar complexes with d^8 metal centers. Another area of potential application is the electron-transfer reactivity of aromatics where (radical) ion-pair complexes with planar, coordinatively unsaturated π acceptors can occur as intermediates.[32]

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Stabilization of Iridium(I), -(III), and -(V) in an Oxygen-Donor Ligand Environment and the Selective Dehydrogenative Silylation and Hydrosilylation of Ethylene with $\{C(Ph_2P{=}O)_3\}Ir(ol)_2$

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Ir(I), -(III), and -(V) can be stabilized in an O-donor ligand environment, as shown by the preparation of $(triso)Ir(ol)_2$ (**1**; triso = tris(diphenyloxophosphoranyl)methanide; ol = C_2H_4 (**a**), cyclooctene (coe) (**b**)), $(triso)Ir(SiPh_3)H(C_2H_4)$ (**2**), and $(triso)Ir(H)_2(SiPh_2Me)_2$ (**3a**). **1a**,**b** are selective catalysts for the dehydrogenative silylation and hydrosilylation of ethylene with triphenylsilane and diphenylmethylsilane. Complex **2** is a rare example of an alkene silyl hydride and is a proposed catalytic intermediate.

Introduction

Interest in how the properties of organometallic compounds change on moving from the more common P- and C-donor sets to an O-donor set has increased in recent years.[1] Studies by Yermakov, Schwartz, and others[2] of site-isolated organometallic fragments supported on oxide surfaces show that an O-donor ligand environment leads to species with interesting catalytic properties. The cobalt ligand[3] $[CpCo(R_2PO)_3]^-$, the trisilanol[4] $[(Cy)_7Si_7O_{12}H_2]$, and the triphosphate[5] $[P_3O_9]^{3-}$ are tridentate O-ligands that can form rare examples of stable organometallic complexes. We felt that O-donor ligands[6] might provide for chemically robust catalysts, particularly for alkane conversion.

We show that the triso ligand (triso = tris(diphenyloxophosphoranyl)methanide) prepared by Grim et al.[7] binds to Ir(I), -(III), and -(V). Compounds of Ir(I) and Ir(III) are relatively common, but examples of Ir(V) are very rare, being limited to phosphine and cyclopentadienyl polyhydrides and related compounds. We also demonstrate that $(triso)Ir(ol)_2$ (**1**; ol = C_2H_4 (**a**); coe (**b**)) are the first homogeneous O-donor catalysts for the dehydrogenative silylation and hydrosilylation of ethylene. Some of this work has been reported in a communication.[6b]

Stoichiometric Reactions with Silanes

We recently reported the preparation of the O-donor alkene complex $(triso)Ir(C_2H_4)_2$ (**1a**), which is formed in

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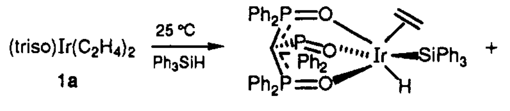
good yield from the reaction of C_2H_4 with (triso)Ir(coe)$_2$.[6c] Surprisingly, **1a** fails to oxidatively add methyl iodide, allyl bromide, or hydrogen, but it does react with triphenylsilane at 25 °C in CH_2Cl_2, ether, or $CDCl_3$ to give **2**, ethyltriphenylsilane, triphenylvinylsilane, and ethane (eq 1).

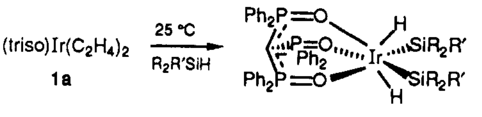


2

$$CH_3CH_2SiPh_3 + CH_2{=}CHSiPh_3 + CH_3CH_3 \qquad (1)$$

Alkene silyl hydrides are rare, and **2** is the only example with an O-donor ligand. Complex **2** is also significant because it seems to be an intermediate in alkene hydrosilylation. Apart from **2**, the only other examples are the $Fe(CO)_3(C_2H_4)H(SiPh_3)$ complex prepared by Bellachioma et al.,[8] Cp*Rh(C_2H_4)SiR_3(H) (Cp* = pentamethylcyclopentadienyl) by Ruiz et al.,[9] and CpRh(C_2H_4)SiR_3(H) by Duckett et al.,[10] and attempts to prepare the Cp*Ir analogue of **2** were unsuccessful.[9] The ^{1}H NMR spectrum of **2** shows two types of olefinic resonances at 3.3 and 2.3 ppm, reflecting the chirality at the metal center, and a hydride peak at −24.78 ppm. The olefinic carbons resonate at 31.6 ppm in the ^{13}C NMR spectrum, and the ^{31}P NMR spectrum (298 K) shows a broad singlet of unit intensity at 48.5 ppm and a singlet at 23.5 ppm of intensity 2. The IR spectrum shows ν(Ir–H) at 2132 cm^{-1} and ν(P=O) at 1154 and 1114 cm^{-1}.

Reaction of **1a** with the sterically small silanes Ph_2MeSiH and Et_3SiH at 25 °C (eq 2) yields **3a,b**, respectively, assigned on the basis of ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy. Double oxidative additions of this type are rare. Satisfactory analytical data could only be obtained for **3a**, the stablest complex of the series. The ^{1}H NMR spectra show the hydride resonances at −21.9 and −23.6 ppm, and the ^{31}P NMR spectra show resonances at 23.5 and 23.8 ppm for **3a,b**, respectively. We considered the nonclassical forms of **3**, (triso)Ir(η^2-R_3SiH)SiR_3(H) and (triso)Ir(η^2-H_2)(SiR_3)$_2$, but the absence both of Si satellites in the ^{1}H NMR spectra of **3a,b** and of H–D coupling in the ^{1}H NMR spectrum of (triso)IrH(SiEt$_3$)$_2$D (**3b**-*d*) make these formulations unlikely. The complex **3b**-*d* shows a secondary isotopic shift of 0.06 ppm from **3b**-d_0 as expected when compared to the shift observed in Re polyhydrides and related species.[11] IR spectroscopy shows weak ν(Ir–H) bands at 2144 cm^{-1} (**3a**) and 2143 cm^{-1} (**3b**) at energies similar to that observed for Cp*Ir(H)$_2$(SiEt$_3$)$_2$ (2135 cm^{-1}).[12] The only other Ir(V) silyl hydride known is Cp*IrH$_3$(SiMe$_3$).[13]



(2)

3a: R = Ph, R′ = Me
b: R, R′ = Et

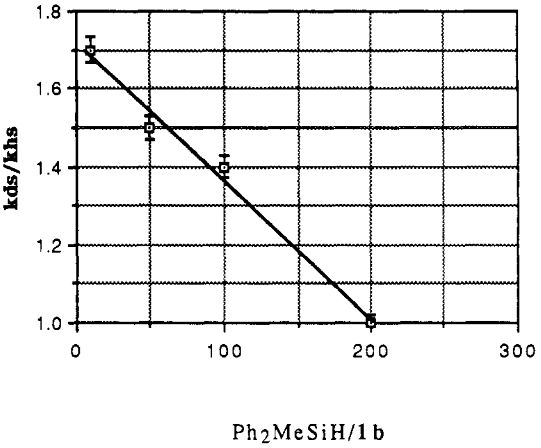


Figure 1. Effect of the silane:catalyst ratio on k_{ds}/k_{hs}.

Catalytic Reactions

Homogeneous hydrosilylation[14] (eq 3) and dehydrogenative silylation (eq 4) of olefins has been found for Fe,[15,16] Ru,[17] Rh,[18] and Ir[19] catalysts with P- or C-supporting ligands. We now find that the O-donor complex **1** is also active.

$$C_2H_4 + R_3SiH \rightarrow CH_3CH_2SiR_3 \qquad (3)$$

$$2C_2H_4 + R_3SiH \rightarrow CH_2{=}CHSiR_3 + CH_3CH_3 \qquad (4)$$

The O-donor complexes (triso)Ir(ol)$_2$ (**1a,b**) catalyze the dehydrogenative silylation and hydrosilylation of ethylene with triphenylsilane or diphenylmethylsilane in CH_2Cl_2. Remarkably, no other olefinic substrate but ethylene could be hydrosilylated. This type of behavior does not seem to have been observed previously. In the presence of **1a**, ethylene and triphenylsilane react at 25 °C over 1.5 h to give triphenylvinylsilane[20] (14 turnovers (TO), 9.3 TO/h) and ethyltriphenylsilane (4.0 TO, 2.7 TO/h). Catalytic activity is maintained in the presence of Hg, which suggests a heterogeneous catalyst is not involved.[21] The k_{ds}/k_{hs} ratio (k_{ds} = rate constant of dehydrogenative silylation; k_{hs} = rate constant of hydrosilylation) of 3.3 is unexceptional. The ratio is dependent on the ethylene concentration, as illustrated by the fact that k_{ds}/k_{hs} is 0.2 in the stoichiometric reaction of silane with **1a** where only 2 equiv of ethylene is present. The mass spectrum of ^{2}H NMR spectrum of the products formed by reaction of ethylene with Ph$_3$SiD show that the majority of the deuterium in the hydrosilylation product is present as Ph$_3$SiCH$_2$CH$_2$D; however, deuterium is also found in all vinyl positions of

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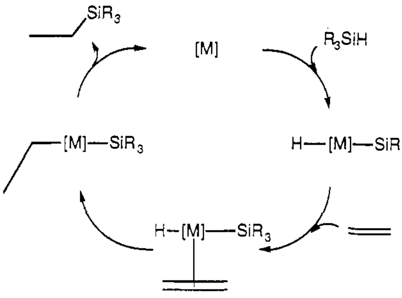
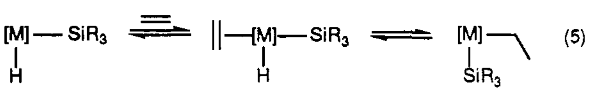
Scheme I. The Chalk-Harrod Mechanism for Hydrosilylation



the triphenylvinylsilane (4% d_1, <1% d_2) and in both ethyl positions of the ethyltriphenylsilane (5% d_1, <1% d_2). The low total deuterium incorporation into the product suggests that ethylene binding and insertion are reversible (eq 5) and that these reactions are much faster than that leading to the hydrosilylated product.



$$\underset{H}{[M]-SiR_3} \overset{=}{\rightleftharpoons} \underset{H}{\|-[M]-SiR_3} \rightleftharpoons \underset{SiR_3}{[M]\diagdown} \tag{5}$$

Diphenylmethylsilane reacts more rapidily with ethylene in the presence of **1a** than does triphenylsilane, but k_{ds}/k_{hs} ratios are lower. As found by others[17b,18c] for Rh and Ru catalysts, an increase in the silane:catalyst ratios favors formation of the saturated product (Figure 1).

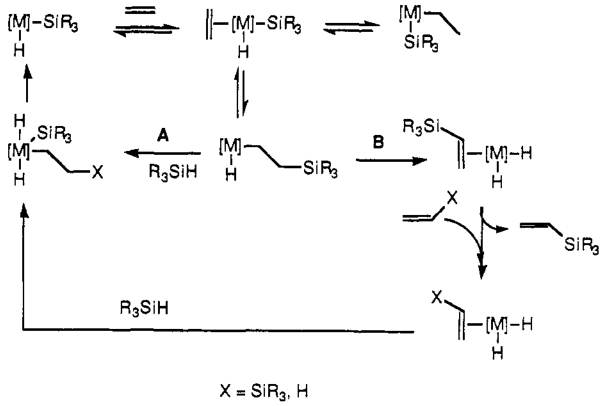
The rate of reaction with silane decreases with increasing silane:catalyst ratio. Reaction of Ph_2MeSiH with C_2D_4 showed that both vinyl-d_3 and ethyl-d_5 silanes were present; insertion and deinsertion of ethylene into the Ir–H bond is also rapid with Ph_2MeSiH. Polar coordinating solvents such as THF did not change the selectivity or rate of reaction.

Surprisingly, triethylsilane failed to react with ethylene in the presence of **1a**,**b**, leading to the formation of the Ir(V) complex **3b** only, possibly indicating that Et_3SiH is a better ligand than ethylene. Unlike other catalysts, **1a**,**b** are selective for ethylene. In contrast, styrene, 3,3-dimethyl-1-butene, methyl acrylate, cyclooctene, 1-heptene, and norbornylene all failed to react with triphenylsilane even in refluxing toluene to give either alkyl- or vinylsilanes. In the presence of silane, **1a** is an olefin isomerization catalyst for 1-heptene and allylbenzene at 25 °C; M–H insertion, therefore, occurs without formation of hydrosilylated product. In the absence of silane, **1a** does not isomerize allylbenzene unless heated to 60 °C.

Mechanism

The Chalk-Harrod mechanism[22] (Scheme I) for hydrosilylation is difficult to reconcile with the selectivity toward ethylene. We know that M–H insertion must be taking place for 1-heptene and allylbenzene because we see isomerization of these compounds. Although both allyl formation and M–H insertion are accepted pathways for olefin isomerization,[23] three observations support the idea that olefin isomerization in the presence of **1a** and silane occurs via the M–H insertion mechanism. First, olefin isomerization with **1a** does not take place in the absence of silane at 25 °C. Thus, a hydride source is necessary to promote isomerization. Second, olefin isomerization occurs in olefins lacking allyl protons. For example, *cis*-β-(triethylsilyl)styrene converts to *trans*-β-(triethylsilyl)styrene in the presence of **1a** and silane. Finally, deuterated olefin incorporates protons in the presence of **1a** and protiosilane. Thus, olefin isomerization occurs via M–H insertion and allylbenzene and 1-heptene isomerize but do not hydrosilylate. Consequently, if hydrosilylation occurs via Ir–H insertion, it is difficult for us to see how the ethyl silyl compound formed from ethylene is able to reductively eliminate to give product when the corresponding alkyl from allylbenzene or 1-heptene does not.

Scheme II. Proposed Mechanism for Hydrosilylation and Dehydrogenative Silylation of Ethylene with 1a,b



Since initial insertion into M–H does not lead to silylation products, a likely sequence leading to product involves initial insertion into the M–Si bond (Scheme II). Such an insertion has been previously proposed for dehydrogenative silylation,[18b] and olefin insertion into the M–Si bond has been demonstrated for Fe[15b,16] and Co[24] catalysts.

This route leads naturally to the dehydrogenative silylation product by β-elimination (B) and to the normal hydrosilylation product by reductive elimination (A). It is still difficult to see why only ethylene is capable of this insertion, but ethylene is uniquely unhindered. This might be the factor responsible for the observed selectivity.

A reviewer suggested that the fact that ΔH(hydrogenation) and therefore presumably ΔH(hydrosilylation) is higher for ethylene than for 1-hexene or styrene might alter the relative rates of reductive elimination and β-elimination the latter being heavily favored for olefins other than ethylene. Both 3,3-dimethyl-1-butene and norbornylene, however, have higher ΔH(hydrogenation) values than ethylene, but neither hydrosilylate. In addition, 3,3-dimethyl-1-butene should give an alkyl with steric and electronic properties very similar to those of ethylene. Hence, this suggestion remains possible but seems unlikely.

It might be thought that ethylene promotes hydrosilylation by acting as an incoming ligand to favor insertion of the olefin into the M–Si bond. We tested this idea by studying a mixture of ethylene and styrene. Only the ethylene was hydrosilylated; the styrene remained unchanged.

Conclusion

The O-donor ligand environment of triso not only stabilizes Ir(I), -(III), and -(V) but also promotes catalytic activity in dehydrogenative silylation and hydrosilylation reactions. Silanes oxidatively add to (triso)Ir$(C_2H_4)_2$ (**1a**) to yield (triso)Ir$(SiPh_3)H(C_2H_4)$ (**2**) and (triso)Ir$(H)_2(SiR_3)_2$ (**3a**,**b**). Surprisingly, **1a**,**b**, **2**, and **3a** catalyze the hydrosilylation of ethylene only. Other olefins can be isomerized but not hydrosilylated. Although all alkenes insert into

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the Ir–H bond, it does not seem that this leads to the hydrosilylated product. Rather, insertion into the Ir–Si bond, which seems only to happen for ethylene, leads to either the saturated or dehydrogenated silylation product, depending on the concentration of ethylene and the silane:catalyst ratio. Alkene silyl hydride complexes of type **2** are rare and may be intermediates in hydrosilylation.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere with use of standard Schlenk techniques. NMR spectra were recorded on a Bruker WM-250 or a Bruker WM-500 spectrometer at 298 K unless otherwise indicated. ^{31}P{^{1}H} NMR spectra were recorded with 85% H_3PO_4 as the reference. IR spectra were recorded on a Nicolet 5-SX FT spectrometer. Combustion analyses were performed by Galbraith Laboratories or Desert Analytics.

Tetrahydrofuran (THF), ether, toluene, benzene, and hexane were distilled from sodium benzophenone ketyl, and dichloromethane was distilled from calcium hydride. Complexes **1a,b** were prepared as previously described.[6c] Triphenylsilane-*d* (Si–D) was prepared by refluxing the corresponding chlorosilane with lithium aluminum deuteride in ether for 8 h.

(Tris(diphenyloxophosphoranyl)methanido)(η^2-ethylene)(triphenylsilyl)hydridoiridium(III) (2). To a CH_2Cl_2 (20 mL) solution of **1a** (150 mg, 0.17 mmol) was added triphenylsilane (50 mg, 0.19 mmol) and the mixture stirred at 20 °C for 30 min. Solvent was removed in vacuo; the residue was dissolved in ether (20 mL) and the solution filtered over Celite. The ether solution was reduced ca. 5 mL and hexane added to afford a yellow precipitate. Recrystallizing from benzene–hexane and drying in vacuo yielded **2** (80 mg, 42% yield): ^{1}H NMR (toluene-d_8, 250 MHz) δ 7.95–7.70 (m, 18 H, Ph), 7.0–6.8 (m, 27 H, Ph), 3.31 (m, 2 H, ethylene), 2.30 (m, 2 H, ethylene), –24.78 (s, 1 H, Ir-*H*); ^{13}C NMR ($CDCl_3$, 62.98 MHz) δ 31.57 (olefin); ^{31}P NMR ($CDCl_3$, 202.45 MHz) 48.5 ppm (broad, 1 P), 23.5 (s, 2 P); IR (neat) 2132 (Ir–H), 1154 (m), 1114 (s), (P=O) cm^{-1}. Anal. Calcd for $C_{57}H_{50}P_3O_3SiIr$: C, 62.45; H, 4.59. Found: C, 62.47; H, 4.89.

In an NMR tube, **1a** (13 mg, 0.015 mmol), triphenylsilane (8 mg, 0.03 mmol), and CD_2Cl_2 (0.7 mL) were added and spectra observed. ^{1}H NMR spectroscopy showed the formation of ethane, **2**, triphenylvinylsilane, and ethyltriphenylsilane.

(Tris(diphenyloxophosphoranyl)methanido)bis(diphenylmethylsilyl)dihydridoiridium(V) (3a). A dry Schlenk tube was charged with **1a** (0.17 mmol, 150 mg), benzene (15 mL), and diphenylmethylsilane (138 μL, 0.68 mmol) and the mixture stirred at 25 °C for 2.5 h. Benzene was removed in vacuo and the residue extracted into CH_2Cl_2 (10 mL). Hexane was added to afford a white precipitate, which was filtered and dried in vacuo. Recrystallization from CH_2Cl_2 and hexane yielded **3a** (100 mg, 48% yield): ^{1}H NMR (C_6D_6, 250 MHz) δ 8.0 (br, 4 H, Ph), 7.64–7.61 (m, 16 H, Ph) 7.06–7.03 (m, 13 H, Ph), 7.02–6.7 (m, 17 H, Ph), 0.88 (s, 6 H, Me) –20.96 (s, 2 H, Ir-*H*); ^{13}C NMR (62.98 MHz, C_6D_6) δ 6.03 (Me); ^{31}P NMR (202.45 MHz, toluene-d_8) 23.6 ppm; IR (C_6D_6) 2144 (Ir–H), 1157, 1114 (P=O) cm^{-1}. Anal. Calcd for $C_{63}H_{58}IrO_3P_3Si_2{\cdot}2CH_2Cl_2$: C, 56.81; H, 4.55; P, 6.76. Found: C, 56.58; H, 4.59; P, 6.89.

(Tris(diphenyloxophosphoranyl)methanido)bis(triethylsilyl)dihydridoiridium(V) (3b). A dry Schlenk tube was charged with **1a** (0.05 mmol, 43 mg), ether (25 mL), and triethylsilane (32 μL, 0.2 mmol) and stirred at 25 °C for 2 h. Solvent was removed in vacuo, hexane (20 mL) added, and the solution filtered over Celite. Hexane was removed in vacuo to give an oil assigned as **3b**: ^{1}H NMR (CD_3Cl, 250 MHz) δ 7.74–7.56 (m, 12 H, Ph); 7.26–6.93 (m, 18 H, Ph), 0.96–0.81 (m, 30 H, Et), –23.60 (q, 2 H, Ir-*H*, J_{P-H} = 2 Hz); ^{13}C NMR (C_6D_6, 62.98 MHz) δ 137.1 (J_{P-C} = 113 Hz, *C*–P), 133.3 (J_{P-C} = 10 Hz, Ph), 130.5 (*p* Ph) 127.4 (J_{P-C} = 14 Hz, Ph), 11.3 (Et); 4.1 (Et); ^{31}P NMR (C_6D_6, 202.45 MHz) 23.8 ppm; IR (neat) 2143 (Ir–H), 1156, 1115 (P=O) cm^{-1}.

Dehydrogenative Silylation of Ethylene. With Triphenylsilane. Ethylene (20 mL/min) was bubbled through a CH_2Cl_2 (20 mL) solution of **1a** (22 mg, 0.025 mmol) and triphenylsilane (133 mg, 0.51 mmol) at 25 °C for 1.5 h. The solvent was removed in vacuo and the residue chromatographed (hexane/silica) to yield (determined by NMR, $CHBr_3$ standard) triphenylvinylsilane[20] (0.35 mmol, 14 TO) and triphenylethylsilane (0.09 mmol, 4.0 TO).

With Diphenylmethylsilane. Ethylene (20 mL/min) was bubbled through a CH_2Cl_2 (25 mL) solution of **1b** (12 mg, 0.012 mmol) and diphenylmethylsilane (81 μL, 0.42 mmol) at 25 °C for 50 min. Solvent was removed in vacuo. Diphenylmethylvinylsilane (0.18 mmol, 15 TO, 20 TO/h); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.68 (m, Ph), 7.31 (m, Ph), 6.49 (dd, 1 H, J_{cis} = 15 Hz, J_{trans} = 20 Hz, C*H*Si), 6.20 (dd, 1 H, J_{gem} = 4 Hz, H trans to Si), 5.82 (dd, 1 H, H cis to Si), 0.66 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$, 62.98 MHz) δ 136.1, 135.8, 134.7, 129.7, 129.2, 127.9, –4.1 (Me)) and diphenylethylmethylsilane (0.14 mmol, 11, TO, 14 TO/h; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 768 (m, Ph), 7.31 (m, Ph), 1.08 (m, 5 H, Et), 0.58 (s, 3 H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.98 MHz) δ 135.2 (Ph), 134.4 (Ph), 129.0 (Ph), 127.8 (Ph), 7.5 (Et), 6.0 (Et), –5.0 (Me)) were obtained. The products can be removed from the catalyst by distillation (130 °C, ca. 0.1 Torr).

Ratio Study. Ethylene (20 mL/min) was bubbled through a CH_2Cl_2 (20 mL) solution of **1b** (15 mg, 0.015 mmol) containing various amounts of diphenylmethylsilane (10† quiv, 50† equiv, 100† equiv, 200 equiv; 0.15 mmol, 0.8 mmol, 1.5 mmol, 3 mmol; 30 μL, 155 μL, 270 μL, 0.58 mL) at 25 °C for 2 h. The solvent was removed in vacuo. Product ratios were determined by ^{1}H NMR spectroscopy (250 MHz, $CDCl_3$): k_{ds}/k_{hs} = 1.62, 1.5, 1.4, 1. The symbol † denotes that the reaction was run to complete conversion of silane.

Reaction in THF. Ethylene (20 mL/min) was bubbled through a THF (20 mL) solution of **1b** (10 mg, 0.01 mmol) and diphenylmethylsilane (196 μL, 1 mmol) at 25 °C for 2.25 h. Solvent was removed in vacuo. Diphenylmethylvinylsilane (0.43 mmol, 43 TO, 20 TO/h) and diphenylethylmethylsilane (0.31 mmol, 31 TO, 14 TO/h) were obtained.

Labeling Studies. (a) Ethylene (20 mL/min) was bubbled through an ether (50 mL) solution of **1** (25 mg, 0.03 mmol) and triphenylsilane-*d* (890 mg, 3.4 mmol) at 25 °C for 8.5 h. The solvent was removed in vacuo. Conditions allowed for complete conversion of starting material (k_{ds}/k_{hs} = 1.9). ^{2}H NMR (C_6H_6, 76.77 MHz): δ 6.64 (m), 6.11 (m), 5.81 (m), triphenylvinylsilane; δ 1.24 (m), 1.05 (broad), ethyltriphenylsilane. GC–MS showed parent ions for triphenylvinylsilane (d_0, 95%, d_1, 4%; d_2, <1%), ethyltriphenylsilane (d_0, 94%, d_1, 5%; d_2, <1%).

(b) Ethylene-d_4 (20 mL/min) was bubbled through a CH_2Cl_2 (30 mL) solution of diphenylmethylsilane (34 μL, 0.32 mmol) and **1b** (7 mg, 0.007 mmol) for 35 min. Solvent was removed in vacuo. ^{2}H NMR (C_6H_6, 76.77 MHz): δ 6.38 (s), 6.01 (s), 5.68 (s), vinylsilane; δ 0.85 (s), ethylsilane.

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