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C−Si Reductive Elimination from *cis*-Vinyl(silyl)platinum(II) Complexes

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The complexes *cis*-$Pt(CH{=}CH_2)(SiR_3)(PMe_2Ph)_2$ (SiR_3 = $SiPh_3$ (**3a**), $Si(C_6H_4Me\text{-}p)_3$ (**3b**), $Si(C_6H_4OMe\text{-}p)_3$ (**3c**), $SiMePh_2$ (**3d**), $SiFPh_2$ (**3e**)) have been prepared by the reactions of *trans*-$PtCl(SiR_3)(PMe_2Ph)_2$ with $Mg(CH{=}CH_2)_2$ in THF, followed by trans−cis isomerization of the resulting *trans*-alkenyl(silyl) complexes in solution promoted by CO. Complexes **3a**−**e** undergo C−Si reductive elimination in toluene-d_8 to give platinum(0) complexes coordinated with vinylsilanes. Kinetic data have suggested a direct reaction path without dissociation of the phosphine ligand.

Introduction

While the transition-metal-catalyzed silylation reactions of unsaturated hydrocarbons such as hydrosilylation, bis-silylation, and borylsilylation are generally assumed to involve C−Si reductive elimination as the product-forming step,[1] detailed information on this elementary process has been limited.[2−4] We have examined mechanisms of reductive elimination from *cis*-$PtR'(SiR_3)L_2$ type complexes (R′ = alkyl, aryl, alkynyl; L = PMe_2Ph) in solution.[4] Two types of mechanisms have been observed, depending on hybridization of the carbyl ligands (R′). When R′ is an alkyl group having an sp^3-hybridized carbon, the reductive elimination is a very slow process in neat solvents but is effectively accelerated by addition of diphenylacetylene to the system.[4e,f] The product alkylsilanes are eliminated from $[PtR'(SiR_3)(PhC{\equiv}CPh)L]$ intermediates formed by ligand exchange of L with diphenylacetylene. The reaction rates decrease according to the alkyl ligands in the order Me > Et > Pr > Bu.[4c] Although this order is the opposite of that commonly observed for C−C reductive elimination from group 10 metal alkyls, a recent theoretical study has suggested that a longer alkyl group causes higher steric repulsion between the alkyl and silyl ligands in the transition state, leading to a higher activation barrier for C−Si reductive elimination.[3a] On the other hand, reductive elimination from *cis*-$Pt(C{\equiv}CAr)(SiR_3)L_2$ type complexes bearing sp-hybridized alkynyl ligands proceeds directly from the four-coordinate species without dissociation of L.[4a] In this case, more electron-donating alkynyl and silyl ligands provide higher reductive elimination rates.

This paper reports the synthesis and thermolysis behavior of *cis*-$Pt(CH{=}CH_2)(SiR_3)L_2$ type complexes. These complexes bearing sp^2-hybridized ligands possess much higher reactivity than the alkyl and alkynyl analogues. The reductive elimination takes place directly from the four-coordinate species.

Results and Discussion

Synthesis of *cis*-$Pt(CH{=}CH_2)(SiR_3)(PMe_2Ph)_2$ (3a−e). *cis*-Alkyl(silyl) analogues of the title compounds have been synthesized in one pot by the treatment of *trans*-$PtCl(SiR_3)L_2$ with an excess amount of alkyllithium (R′Li), followed by methanolysis of the resulting $Li^+[Pt(R')_2(SiR_3)L]^-$ species.[4f] However, similar reactions using vinyllithium instead of alkyllithium provided complex mixtures. Accordingly, **3a**−**e** were synthesized by the two-step procedure shown in Scheme 1. The reactions of **1a**−**e** with divinylmagnesium took place instantly at room temperature to give trans complexes **2a**−**e**, which were isolated as analytically pure solids in 46−68% yields by recrystallization. Treatment of **2a**−**e** with CO in solution at low temperature resulted in trans−cis isomerization to give **3a**−**e** in quantitative yields. Since **3a**−**e** were too unstable to be isolated, they were characterized by NMR spectroscopy.

The trans isomers **2a**−**e** exhibited a singlet signal with ^{195}Pt satellites in the $^{31}P\{^1H\}$ NMR spectra; the $^1J_{PtP}$ values (2681−2790 Hz) were typical of platinum-

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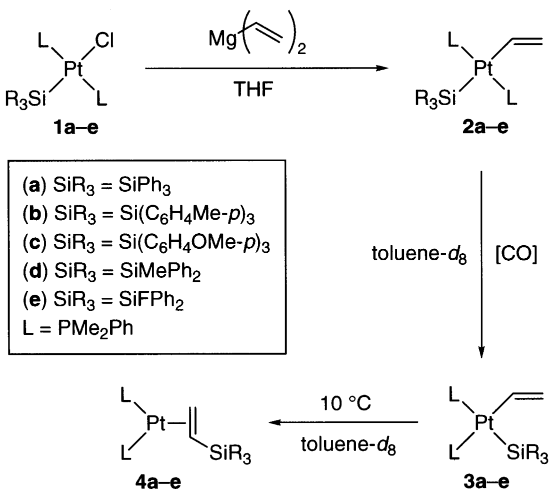
Scheme 1



(II) complexes coordinated with two phosphine ligands in mutually trans positions. The cis isomers **3a**–**e** exhibited two sets of doublets, reflecting the *cis*-bis(phosphine)platinum(II) structures with two additional ligands. One of the doublets involved ${}^1J_{PtP}$ couplings of 1988–2002 Hz, and this signal was assigned to the phosphine trans to the vinyl ligand. On the other hand, owing to the strong trans influence of silyl ligands, ${}^1J_{PtP}$ couplings observed for the other doublet were significantly smaller (1290–1382 Hz).

In the ${}^{13}C\{{}^1H\}$ NMR spectra, α- and β-vinylic carbon signals of trans isomers were observed, each being a triplet owing to the couplings with two equivalent phosphorus nuclei. On the other hand, α- and β-vinylic carbons of cis isomers exhibited doublet of doublets and doublet signals, respectively. The α-carbon involved large and small ${}^2J_{PC}$ couplings (89–96 and 15–17 Hz), consistent with trans and cis arrangements of phosphine ligands toward the vinyl ligand.

Reductive Elimination Reactions. The *cis*-vinyl(silyl) complexes **3a**–**e** underwent C–Si reductive elimination in solution to give platinum(0) complexes coordinated with vinylsilanes (**4a**–**e**) (Scheme 1). For example, when the reaction of **3a** in toluene-d_8 was followed by ${}^{31}P\{{}^1H\}$ NMR spectroscopy at 10 °C, the signals of **3a** at δ −13.7 and −5.2 gradually decreased over a period of several hours and were replaced by two sets of doublets at δ −6.7 (d, ${}^2J_{PP} = 49$ Hz, ${}^1J_{PtP} = 3538$ Hz) and −7.6 (d, ${}^2J_{PP} = 49$ Hz, ${}^1J_{PtP} = 3581$ Hz). The ${}^1J_{PtP}$ values thus observed were larger than those of **3a** (1990 and 1347 Hz), consistent with a platinum(0) complex. In the ${}^{13}C\{{}^1H\}$ NMR spectrum, vinylic carbon signals appeared as two sets of doublet of doublets with ${}^{195}Pt$ satellites at δ 27.3 (${}^2J_{PC} = 29$ and 4 Hz, ${}^1J_{PtC} = 216$ Hz) and 35.2 (${}^2J_{PC} = 32$ and 4 Hz, ${}^1J_{PtC} = 211$ Hz); the chemical shifts were significantly higher than those of **3a** (δ 117.6 and 158.7), showing the formation of the vinylsilane-coordinated complex **4a**. The reactions of **3b**–**e** proceeded similarly. All reactions obeyed first-order kinetics over 2 half-lives, giving **4a**–**e** quantitatively.

Rate constants for the reductive elimination from **3a** measured under several conditions are listed in runs 1–5 in Table 1. Unlike the reactions of *cis*-alkyl(silyl) analogues, the reaction of **3a** is not retarded by addition of free PMe_2Ph (1 equiv) to the system, showing the occurrence of a direct reductive elimination process without prior dissociation of PMe_2Ph (runs 1 and 2). Activation parameters estimated for a temperature range of 10.0–25.0 °C (runs 1–5) are as follows: $\Delta H^\ddagger = 20.0(4)$ kcal mol^{-1}, $\Delta S^\ddagger = -5(1)$ eu, $\Delta G^\ddagger = 21.5(4)$ kcal mol^{-1}. The activation energy ($\Delta G^\ddagger$) for **3a** is smaller than that previously observed for related methyl(silyl) and phenylethynyl(silyl) complexes: $PtMe(SiPh_3)(PhC{\equiv}CPh)(PMe_2Ph)$ (22.8 kcal mol^{-1}) and *cis*-$Pt(C{\equiv}CPh)(SiPh_3)(PMe_2Ph)_2$ (23.2 kcal mol^{-1}).[5]

Table 1. First-Order Rate Constants for Reductive Elimination from 3a–e[a]

run	complex	SiR3	CH=CHR′	temp (°C)	10^3k (s^{-1})
1	**3a**	$SiPh_3$	$CH{=}CH_2$	25.0	1.20(10)
2[b]	**3a**	$SiPh_3$	$CH{=}CH_2$	25.0	1.21(9)
3	**3a**	$SiPh_3$	$CH{=}CH_2$	20.0	0.633(5)
4	**3a**	$SiPh_3$	$CH{=}CH_2$	15.0	0.354(4)
5	**3a**	$SiPh_3$	$CH{=}CH_2$	10.0	0.188(2)
6	**3b**	$SiAr_3$[c]	$CH{=}CH_2$	10.0	0.352(4)
7	**3c**	$SiAr'_3$[d]	$CH{=}CH_2$	10.0	0.403(3)
8	**3d**	$SiMePh_2$	$CH{=}CH_2$	10.0	0.144(1)
9	**3e**	$SiFPh_2$	$CH{=}CH_2$	10.0	0.141(1)

[a] Conditions: in toluene-d_8, [complex]$_0$ = 30 mM. [b] The reaction was examined in the presence of PMe_2Ph (30 mM). [c] Ar = p-MeC_6H_4. [d] Ar′ = p-$MeOC_6H_4$.

Reductive elimination rates decreased according to silyl ligands in the order **3c** ($Si(C_6H_4OMe\text{-}p)_3$) > **3b** ($Si(C_6H_4Me\text{-}p)_3$) > **3a** ($SiPh_3$) > **3d** ($SiMePh_2$) ≈ **3e** ($SiFPh_2$) (runs 5–9). While the rate variation is small, the observed tendency suggests that the reactivity of vinyl(silyl)platinum complexes toward C–Si reductive elimination is dependent on the bulkiness of the silyl ligands. Thus, **3d**,**e**, having sterically similar but electronically different silyl ligands (i.e., $SiMePh_2$ and $SiFPh_2$), give almost the same reaction rates, and these complexes are less reactive than **3a**–**c** bearing bulkier silyl ligands. It is possible that steric repulsion between triarylsilyl ligands and PMe_2Ph ligands in **3a**–**c** facilitates the approach of the silyl ligand to the vinyl ligand during C–Si reductive elimination to cause the higher reaction rates. A similar phenomenon has been reported for C–C reductive elimination from group 10 metal complexes.[6] On the other hand, for **3a**–**c** having triarylsilyl ligands with almost the same sizes, the reductive elimination rate increases as the electron-donating ability of the aryl group increases (runs 5–7). A similar tendency has been observed for *cis*-$Pt(C{\equiv}CPh)(SiR_3)(PMe_2Ph)_2$ complexes ($SiR_3 = SiPh_3$, $Si(C_6H_4Me\text{-}p)_3$, $Si(C_6H_4OMe\text{-}p)_3$, $Si(C_6H_4CF_3\text{-}p)_3$).[4a]

Conclusion. The C–Si reductive elimination from *cis*-$Pt(CH{=}CH_2)(SiR_3)(PMe_2Ph)_2$ complexes (**3a**–**e**) has been found to take place directly from the four-coordinate species, as already found for *cis*-alkynyl(silyl) analogues.[4a] The reactivity is affected by both the

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(5) Kinetic parameters are as follows. $PtMe(SiPh_3)(PhC{\equiv}CPh)(PMe_2Ph)$: $\Delta H^\ddagger = 20.8$ kcal mol^{-1}, $\Delta S^\ddagger = -6.8$ eu, $\Delta G^\ddagger = 22.8$ kcal mol^{-1}, $k = 0.45 \times 10^{-3}$ s^{-1} at 35 °C. *cis*-$Pt(C{\equiv}CPh)(SiPh_3)(PMe_2Ph)_2$: $\Delta H^\ddagger = 26.4$ kcal mol^{-1}, $\Delta S^\ddagger = 10$ eu, $\Delta G^\ddagger = 23.2$ kcal mol^{-1}, $k = 0.283 \times 10^{-3}$ s^{-1} at 35 °C.

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electronic and steric factors of silyl ligands. Thus, the reaction proceeds more rapidly when the silyl ligand is bulkier. For the triarylsilyl complexes **3a**−**c**, more electron-donating groups provide higher reductive elimination rates.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of the deuterated solvents or to the ^{31}P and ^{195}Pt signals of external $\mathrm{H_3PO_4}$ and $\mathrm{K_2PtCl_6}$ standards. An ethereal solution of $\mathrm{Mg(CH{=}CH_2)_2}$ was prepared by the treatment of $\mathrm{Mg(CH{=}CH_2)Cl}$ with dioxane in $\mathrm{Et_2O}$, followed by removal of the resulting precipitate of $\mathrm{MgCl_2}$(dioxane) by filtration. Elemental analysis was performed on a Perkin-Elmer 2400II CHN Analyzer. The complexes *trans*-$\mathrm{PtCl(SiR_3)(PMe_2Ph)_2}$ (**1a**−**e**) were prepared according to literature procedures.[7]

Preparation of *trans*-$\mathrm{Pt(CH{=}CH_2)(SiPh_3)(PMe_2Ph)_2}$ (2a). To a solution of *trans*-$\mathrm{PtCl(SiPh_3)(PMe_2Ph)_2}$ (**1a**; 800 mg, 1.04 mmol) in THF (15 mL) was added a solution of $\mathrm{Mg(CH{=}CH_2)_2}$ in $\mathrm{Et_2O}$ (0.86 M, 1.3 mL, 1.12 mmol). The mixture was stirred for 30 min at room temperature and then cooled to −30 °C. Methanol (1 mL) was slowly added, and the solution was concentrated to dryness under vacuum. The resulting solid was extracted with benzene (5 mL × 2), filtered through a Celite pad to remove magnesium salts, and concentrated to dryness to give a yellow solid, which was washed with hexane containing a small amount of $\mathrm{Et_2O}$ and dried under vacuum. The crude product was dissolved in a minimum amount of $\mathrm{CH_2Cl_2}$, layered with hexane, and allowed to stand at −70 °C to give colorless crystals of **2a** (536 mg, 68%). Complexes **2b**−**e** were similarly prepared.

2a. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.34 (virtual triplet, J = 3.3 Hz, $^{3}J_{\mathrm{PtH}}$ = 32.1 Hz, 12H, PMe), 5.17 (ddt, $^{3}J_{\mathrm{HH}}$ = 19.8 Hz, $^{2}J_{\mathrm{HH}}$ = 3.9 Hz, $^{4}J_{\mathrm{PH}}$ = 2.1 Hz, $^{3}J_{\mathrm{PtH}}$ = 44.4 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.15 (ddt, $^{3}J_{\mathrm{HH}}$ = 12.6 Hz, $^{2}J_{\mathrm{HH}}$ = 3.9 Hz, $^{4}J_{\mathrm{PH}}$ = 2.1 Hz, $^{3}J_{\mathrm{PtH}}$ = 87.3 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 7.1−7.6 (m, 26H, Ph and $\mathrm{PtC}H\mathrm{{=}CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 15.2 (virtual triplet, J = 20 Hz, $^{2}J_{\mathrm{PtC}}$ = 40 Hz, PMe), 123.3 (t, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $\mathrm{PtCH{=}}C\mathrm{H_2}$), 127.2 (s, SiPh), 127.3 (s, SiPh), 128.4 (virtual triplet, J = 5 Hz, PPh), 129.9 (s, PPh), 131.9 (virtual triplet, J = 5 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 137.0 (virtual triplet, J = 28 Hz, PPh), 137.5 (s, $^{3}J_{\mathrm{PtC}}$ = 16 Hz, SiPh), 148.3 (s, $^{2}J_{\mathrm{PtC}}$ = 25 Hz, SiPh), 171.8 (t, $^{2}J_{\mathrm{PC}}$ = 13 Hz, $^{1}J_{\mathrm{PtC}}$ = 512 Hz, $\mathrm{Pt}C\mathrm{H{=}CH_2}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −9.2 (s, $^{1}J_{\mathrm{PtP}}$ = 2756 Hz). Anal. Calcd for $\mathrm{C_{36}H_{40}P_2PtSi}$: C, 57.06; H, 5.32. Found: C, 56.97; H, 5.32.

2b (54% yield). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.33 (virtual triplet, J = 3.6 Hz, $^{3}J_{\mathrm{PtH}}$ = 32.1 Hz, 12H, PMe), 2.27 (s, 9H, Me), 5.14 (ddt, $^{3}J_{\mathrm{HH}}$ = 19.8 Hz, $^{2}J_{\mathrm{HH}}$ = 4.0 Hz, $^{4}J_{\mathrm{PH}}$ = 1.8 Hz, $^{3}J_{\mathrm{PtH}}$ = 43.8 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.12 (ddt, $^{3}J_{\mathrm{HH}}$ = 12.9 Hz, $^{2}J_{\mathrm{HH}}$ = 4.0 Hz, $^{4}J_{\mathrm{PH}}$ = 2.1 Hz, $^{3}J_{\mathrm{PtH}}$ = 86.4 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.92 (d, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, 6H, Ar), 7.0−7.5 (m, 11H, Ph and $\mathrm{PtC}H\mathrm{{=}CH_2}$), 7.41 (d, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, 6H, Ar). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 15.0 (virtual triplet, J = 20 Hz, $^{2}J_{\mathrm{PtC}}$ = 40 Hz, PMe), 21.3 (s, Me), 123.0 (t, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $\mathrm{PtCH{=}}C\mathrm{H_2}$), 127.9 (s, SiAr), 128.1 (virtual triplet, J = 5 Hz, PPh), 129.5 (s, PPh), 131.7 (virtual triplet, J = 6 Hz, $^{3}J_{\mathrm{PtC}}$ = 24 Hz, PPh), 136.5 (s, SiAr), 137.0 (virtual triplet, J = 30 Hz, PPh), 137.2 (s, $^{3}J_{\mathrm{PtC}}$ = 16 Hz, SiAr), 144.6 (t, $^{3}J_{\mathrm{PC}}$ = 2 Hz, $^{2}J_{\mathrm{PtC}}$ = 23 Hz, SiAr), 172.4 (t, $^{2}J_{\mathrm{PC}}$ = 14 Hz, $^{1}J_{\mathrm{PtC}}$ = 511 Hz, $\mathrm{Pt}C\mathrm{H{=}CH_2}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −9.2 (s, $^{1}J_{\mathrm{PtP}}$ = 2771 Hz). Anal. Calcd for $\mathrm{C_{39}H_{46}P_2PtSi}$: C, 58.56; H, 5.80. Found: C, 58.66; H, 5.80.

2c (46% yield). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.36 (virtual triplet, J = 3.4 Hz, $^{3}J_{\mathrm{PtH}}$ = 32.2 Hz, 12H, PMe), 3.75 (s, 9H, OMe), 5.18 (ddt, $^{3}J_{\mathrm{HH}}$ = 20.0 Hz, $^{2}J_{\mathrm{HH}}$ = 3.9 Hz, $^{4}J_{\mathrm{PH}}$ = 2.0 Hz, $^{3}J_{\mathrm{PtH}}$ = 43.9 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.16 (ddt, $^{3}J_{\mathrm{HH}}$ = 13.1 Hz, $^{2}J_{\mathrm{HH}}$ = 3.9 Hz, $^{4}J_{\mathrm{PH}}$ = 2.0 Hz, $^{3}J_{\mathrm{PtH}}$ = 86.4 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.69 (d, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 6H, Ar), 7.1−7.4 (m, 7H, Ph and $\mathrm{PtC}H\mathrm{{=}CH_2}$), 7.43 (d, $^{3}J_{\mathrm{HH}}$ = 8.7 Hz, 6H, Ar), 7.52 (m, 4H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 15.1 (virtual triplet, J = 20 Hz, $^{2}J_{\mathrm{PtC}}$ = 40 Hz, PMe), 55.2 (s, OMe), 112.8 (s, SiAr), 123.1 (t, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $\mathrm{PtCH{=}}C\mathrm{H_2}$), 128.2 (virtual triplet, J = 5 Hz, PPh), 129.6 (s, PPh), 131.8 (virtual triplet, J = 6 Hz, $^{3}J_{\mathrm{PtC}}$ = 24 Hz, PPh), 137.1 (virtual triplet, J = 28 Hz, PPh), 138.3 (s, $^{3}J_{\mathrm{PtC}}$ = 16 Hz, SiAr), 139.3 (t, $^{3}J_{\mathrm{PC}}$ = 2 Hz, $^{2}J_{\mathrm{PtC}}$ = 28 Hz, SiAr), 159.2 (s, SiAr), 172.6 (t, $^{2}J_{\mathrm{PC}}$ = 14 Hz, $^{1}J_{\mathrm{PtC}}$ = 511 Hz, $\mathrm{Pt}C\mathrm{H{=}CH_2}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −8.7 (s, $^{1}J_{\mathrm{PtP}}$ = 2775 Hz). Anal. Calcd for $\mathrm{C_{39}H_{46}O_3P_2PtSi}$: C, 55.25; H, 5.47. Found: C, 55.01; H, 5.47.

2d (58% yield). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 0.33 (s, $^{3}J_{\mathrm{PtH}}$ = 15.0 Hz, 3H, SiMe), 1.47 (virtual triplet, J = 3.6 Hz, $^{3}J_{\mathrm{PtH}}$ = 32.4 Hz, 12H, PMe), 5.11 (ddt, $^{3}J_{\mathrm{HH}}$ = 19.8 Hz, $^{2}J_{\mathrm{HH}}$ = 3.6 Hz, $^{4}J_{\mathrm{PH}}$ = 2.1 Hz, $^{3}J_{\mathrm{PtH}}$ = 44.4 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.13 (ddt, $^{3}J_{\mathrm{HH}}$ = 13.2 Hz, $^{2}J_{\mathrm{HH}}$ = 3.9 Hz, $^{4}J_{\mathrm{PH}}$ = 1.8 Hz, $^{3}J_{\mathrm{PtH}}$ = 85.8 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 7.0−7.7 (m, 21H, Ph and $\mathrm{PtC}H\mathrm{{=}CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 4.4 (virtual triplet, J = 2 Hz, $^{2}J_{\mathrm{PtC}}$ = 38 Hz, SiMe), 15.5 (virtual triplet, J = 20 Hz, $^{2}J_{\mathrm{PtC}}$ = 40 Hz, PMe), 122.8 (t, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $\mathrm{PtCH{=}}C\mathrm{H_2}$), 126.7 (s, SiPh), 127.2 (s, SiPh), 128.3 (virtual triplet, J = 5 Hz, PPh), 129.8 (s, PPh), 131.8 (virtual triplet, J = 6 Hz, $^{3}J_{\mathrm{PtC}}$ = 25 Hz, PPh), 135.7 (s, $^{3}J_{\mathrm{PtC}}$ = 14 Hz, SiPh), 137.1 (virtual triplet, J = 28 Hz, PPh), 150.8 (s, $^{3}J_{\mathrm{PC}}$ = 2 Hz, $^{2}J_{\mathrm{PtC}}$ = 26 Hz, SiPh), 172.7 (t, $^{2}J_{\mathrm{PC}}$ = 14 Hz, $^{1}J_{\mathrm{PtC}}$ = 509 Hz, $\mathrm{Pt}C\mathrm{H{=}CH_2}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −7.6 (s, $^{1}J_{\mathrm{PtP}}$ = 2790 Hz). Anal. Calcd for $\mathrm{C_{31}H_{38}P_2PtSi}$: C, 53.52; H, 5.51. Found: C, 53.29; H, 5.56.

2e (51% yield). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.59 (virtual triplet, J = 3.6 Hz, $^{3}J_{\mathrm{PtH}}$ = 33.0 Hz, 12H, PMe), 4.49 (m, $^{3}J_{\mathrm{HH}}$ = 20.1 Hz, $^{2}J_{\mathrm{HH}}$ = 4.0 Hz, $^{3}J_{\mathrm{PtH}}$ = 43.8 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 6.10 (dddt, $^{3}J_{\mathrm{HH}}$ = 13.2 Hz, $^{2}J_{\mathrm{HH}}$ = 3.9 Hz, $^{4}J_{\mathrm{FH}}$ = 2.0 Hz, $^{4}J_{\mathrm{PH}}$ = 2.0 Hz, $^{3}J_{\mathrm{PtH}}$ = 85.2 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 7.2−7.4 (m, 13 H, Ph and $\mathrm{PtC}H\mathrm{{=}CH_2}$), 7.4−7.6 (m, 8H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 15.8 (virtual triplet, J = 21 Hz, $^{2}J_{\mathrm{PtC}}$ = 40 Hz, PMe), 123.7 (t, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $\mathrm{PtCH{=}}C\mathrm{H_2}$), 127.5 (s, SiPh), 128.2 (s, SiPh), 128.3 (virtual triplet, J = 5 Hz, PPh), 129.9 (s, PPh), 131.7 (virtual triplet, J = 6 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 135.4 (d, $^{3}J_{\mathrm{FC}}$ = 2 Hz, $^{3}J_{\mathrm{PtC}}$ = 14 Hz, SiPh), 136.2 (virtual triplet, J = 28 Hz, PPh), 147.6 (d, $^{2}J_{\mathrm{FC}}$ = 16 Hz, $^{2}J_{\mathrm{PtC}}$ = 28 Hz, SiPh), 172.0 (td, $^{2}J_{\mathrm{PC}}$ = 14 Hz, $^{3}J_{\mathrm{FC}}$ = 12 Hz, $^{1}J_{\mathrm{PtC}}$ = 508 Hz, $\mathrm{Pt}C\mathrm{H{=}CH_2}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −7.6 (d, $^{3}J_{\mathrm{FC}}$ = 10 Hz, $^{1}J_{\mathrm{PtP}}$ = 2681 Hz). Anal. Calcd for $\mathrm{C_{30}H_{35}FP_2PtSi}$: C, 51.50; H, 5.04. Found: C, 51.50; H, 5.47.

Generation and Characterization of *cis*-$\mathrm{Pt(CH{=}CH_2)(SiPh_3)(PMe_2Ph)_2}$ (2a). Complex **2a** (50 mg, 66 μmol) was dissolved in $\mathrm{CD_2Cl_2}$ (1.0 mL) in a 25 mL Schlenk flask. The reaction mixture was evacuated, placed under CO (1 atm) at −70 °C, and stirred at −30 °C for 1 h. The CO gas was removed at −70 °C under vacuum, and then $\mathrm{N_2}$ was introduced. A part of the solution (ca. 0.6 mL) was transferred into an NMR sample tube equipped with a rubber septum cap and examined by NMR spectroscopy at −30 °C, showing complete conversion of **2a** to **3a**. A similar procedure was used to generate **3b**−**e**. Complexes **3a**−**e** were too unstable to be isolated and were identified by ^{1}H, ^{31}C{^{1}H}, ^{31}P{^{1}H}, and ^{195}Pt{^{1}H} NMR spectroscopy.

3a. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −30 °C): δ 0.97 (d, $^{3}J_{\mathrm{PH}}$ = 8.3 Hz, $^{2}J_{\mathrm{PtH}}$ = 22.4 Hz, 6H, PMe), 1.32 (d, $^{2}J_{\mathrm{PH}}$ = 8.0 Hz, $^{3}J_{\mathrm{PtH}}$ = 17.6 Hz, 6H, PMe), 4.90 (dddd, $^{3}J_{\mathrm{HH}}$ = 19.5 Hz, $^{2}J_{\mathrm{HH}}$ = 4.4 Hz, $^{4}J_{\mathrm{PH}}$ = 8.8 and 4.4 Hz, $^{3}J_{\mathrm{PtH}}$ = 72.2 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 5.63 (dddd, $^{3}J_{\mathrm{HH}}$ = 12.7 Hz, $^{2}J_{\mathrm{HH}}$ = 4.4 Hz, $^{4}J_{\mathrm{PH}}$ = 18.1 and 3.9 Hz, $^{3}J_{\mathrm{PtH}}$ = 130.8 Hz, 1H, $\mathrm{PtCH{=}C}H_2$), 7.02 (m, 1H, $\mathrm{PtC}H\mathrm{{=}CH_2}$), 7.25−7.45 (m, 19H, Ph), 7.73 (d, $^{3}J_{\mathrm{HH}}$ = 6.3 Hz, 6H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, −30 °C): δ 12.2 (d, $^{1}J_{\mathrm{PC}}$ = 26 Hz, $^{2}J_{\mathrm{PtC}}$ = 26 Hz, PMe), 16.1 (dd, $^{1}J_{\mathrm{PC}}$ = 24 Hz, $^{3}J_{\mathrm{PC}}$ = 5 Hz, $^{2}J_{\mathrm{PtC}}$ = 30 Hz,

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(7) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343.

PMe), 117.6 (d, $^3J_{PC}$ = 8 Hz, $^2J_{PtC}$ = 20 Hz, PtCH=*C*H$_2$), 126.8 (s, SiPh), 127.0 (s, SiPh), 128.1 (d, $^3J_{PC}$ = 8 Hz, PPh), 128.4 (d, $^3J_{PC}$ = 10 Hz, PPh), 129.2 (s, PPh), 129.6 (s, PPh), 130.7 (d, $^2J_{PC}$ = 10 Hz, PPh), 130.8 (d, $^2J_{PC}$ = 12 Hz, PPh), 137.1 (s, $^2J_{PtC}$ = 21 Hz, SiPh), 137.5 (d, $^1J_{PC}$ = 34 Hz, PPh), 139.4 (dd, $^1J_{PC}$ = 43 Hz, $^3J_{PC}$ = 3 Hz, PPh), 145.0 (d, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 50 Hz, SiPh), 158.7 (dd, $^2J_{PC}$ = 94 and 15 Hz, $^1J_{PtC}$ = 672 Hz, Pt*C*H=CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −13.7 (d, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 1988 Hz), −5.2 (d, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 1342 Hz, $^2J_{SiP}$ = 180 Hz). ^{195}Pt{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −4821 (dd, $^1J_{PPt}$ = 1990 and 1347 Hz, $^1J_{PtSi}$ = 1408 Hz).

3b. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C): δ 0.94 (d, $^3J_{PH}$ = 8.4 Hz, $^2J_{PtH}$ = 22.2 Hz, 6H, PMe), 1.28 (d, $^3J_{PH}$ = 8.1 Hz, $^2J_{PtH}$ = 17.4 Hz, 6H, PMe), 2.29 (s, 9H, Me), 4.89 (dddd, $^3J_{HH}$ = 19.8 Hz, $^2J_{HH}$ = 4.5 Hz, $^4J_{PH}$ = 8.4 and 4.2 Hz, $^3J_{PtH}$ = 72.6 Hz, 1H, PtCH=C*H*$_2$), 5.61 (dddd, $^3J_{HH}$ = 13.2 Hz, $^2J_{HH}$ = 4.5 Hz, $^4J_{PH}$ = 17.7 and 4.2 Hz, $^3J_{PtH}$ = 132.6 Hz, 1H, PtCH=C*H*$_2$), 6.94 (m, 1H, PtC*H*=CH$_2$), 7.06 (d, $^3J_{HH}$ = 7.8 Hz, 6H, Ar), 7.0−7.5 (m, 10H, Ph), 7.55 (d, $^3J_{HH}$ = 7.8 Hz, 6H, Ar). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ 11.8 (d, $^1J_{PC}$ = 27 Hz, $^2J_{PtC}$ = 25 Hz, PMe), 15.7 (dd, $^1J_{PC}$ = 28 Hz, $^3J_{PC}$ = 4 Hz, $^2J_{PtC}$ = 30 Hz, PMe), 21.2 (s, Me), 116.8 (d, $^3J_{PC}$ = 9 Hz, PtCH=*C*H$_2$), 127.5 (s, SiAr), 127.9 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.0 (d, $^3J_{PC}$ = 10 Hz, PPh), 128.9 (s, PPh), 129.4 (s, PPh), 130.4 (d, $^2J_{PC}$ = 10 Hz, PPh), 130.6 (d, $^2J_{PC}$ = 11 Hz, PPh), 136.4 (s, SiAr), 136.9 (s, $^2J_{PtC}$ = 21 Hz, SiAr), 137.4 (d, $^1J_{PtC}$ = 35 Hz, PPh), 139.5 (dd, $^1J_{PC}$ = 44 Hz, $^3J_{PC}$ = 5 Hz, PPh), 141.3 (dd, $^3J_{PC}$ = 6 and 2 Hz, $^1J_{PC}$ = 54 Hz, SiAr), 159.4 (dd, $^2J_{PC}$ = 94 and 17 Hz, $^1J_{PtC}$ = 668 Hz, Pt*C*H=CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −14.6 (d, $^2J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 1995 Hz), −5.7 (d, $^2J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 1313 Hz). ^{195}Pt{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −4763 (dd, $^1J_{PPt}$ = 2003 and 1316 Hz, $^1J_{PtSi}$ = 1395 Hz).

3c. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C): δ 0.98 (d, $^3J_{PH}$ = 8.1 Hz, $^2J_{PtH}$ = 22.2 Hz, 6H, PMe), 1.33 (d, $^3J_{PH}$ = 8.1 Hz, $^2J_{PtH}$ = 16.2 Hz, 6H, PMe), 3.77 (s, 9H, OMe), 4.92 (dddd, $^3J_{HH}$ = 19.2 Hz, $^2J_{HH}$ = 4.5 Hz, $^4J_{PH}$ = 8.7 and 4.5 Hz, $^3J_{PtH}$ = 73.8 Hz, 1H, PtCH=C*H*$_2$), 5.66 (dddd, $^3J_{HH}$ = 13.5 Hz, $^2J_{HH}$ = 4.5 Hz, $^4J_{PH}$ = 17.1 and 4.5 Hz, $^3J_{PtH}$ = 132.9 Hz, 1H, PtCH=C*H*$_2$), 6.82 (d, $^3J_{HH}$ = 8.7 Hz, 6H, Ar), 7.01 (m, 1H, PtC*H*=CH$_2$), 7.15−7.5 (m, 10H, Ph), 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 6H, Ar). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ 12.1 (d, $^1J_{PC}$ = 27 Hz, $^2J_{PtC}$ = 25 Hz, PMe), 15.9 (dd, $^1J_{PC}$ = 30 Hz, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 31 Hz, PMe), 54.8 (s, OMe), 112.2 (s, SiAr), 116.9 (d, $^3J_{PC}$ = 9 Hz, PtCH=*C*H$_2$), 128.1 (d. $^3J_{PC}$ = 9 Hz, PPh), 128.2 (d, $^3J_{PC}$ = 9 Hz, PPh), 129.1 (s, PPh), 129.5 (s, PPh). 130.6 (d, $^2J_{PC}$ = 10 Hz, PPh), 130.8 (d, $^2J_{PC}$ = 11 Hz, PPh), 136.0 (dd, $^3J_{PC}$ = 6 and 2 Hz, $^2J_{PtC}$ = 53 Hz, SiAr), 137.6 (d, $^1J_{PC}$ = 34 Hz, PPh), 138.2 (d, $^2J_{PtC}$ = 21 Hz, SiAr), 139.5 (dd, $^1J_{PC}$ = 43 Hz, $^3J_{PC}$ = 5 Hz, PPh), 158.7 (s, SiAr), 159.5 (dd, $^2J_{PC}$ = 94 and 16 Hz, $^1J_{PtC}$ = 684 Hz, Pt*C*H=CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −13.5 (d, $^2J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 1994 Hz), −5.2 (d, $^2J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 1290 Hz). ^{195}Pt{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −4757 (dd, $^1J_{PPt}$ = 2006 and 1299 Hz, $^1J_{PtSi}$ = 1378 Hz).

3d. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C): δ 0.51 (s, $^3J_{PtH}$ = 26.4 Hz, 3H, SiMe), 1.07 (d, $^2J_{PtH}$ = 8.1 Hz, $^3J_{PtH}$ = 23.4 Hz, 6H, PMe), 1.38 (d, $^2J_{PtH}$ = 8.1 Hz, $^3J_{PtH}$ = 16.8 Hz, 6H, PMe), 4.97 (dddd, $^3J_{HH}$ = 19.5 Hz, $^2J_{HH}$ = 4.4 Hz, $^4J_{PH}$ = 8.4 and 4.4 Hz, $^3J_{PtH}$ = 74.4 Hz, 1H, PtCH=C*H*$_2$), 5.88 (dddd, $^3J_{HH}$ = 13.2 Hz, $^2J_{HH}$ = 4.4 Hz, $^4J_{PH}$ = 18.0 and 4.4 Hz, $^3J_{PtH}$ = 147.1 Hz, 1H, PtCH=C*H*$_2$), 7.1−7.7 (m, 26 H, Ph and PtC*H*=CH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ 2.3 (dd, $^3J_{PC}$ = 4 and 2 Hz, $^2J_{PtC}$ = 64 Hz, SiMe), 12.6 (dd, $^1J_{PC}$ = 26 Hz, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 24 Hz, PMe), 16.5 (dd, $^1J_{PC}$ = 30 Hz, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 35 Hz, PMe), 118.1 (d, $^3J_{PC}$ = 8 Hz, PtCH=*C*H$_2$), 126.7 (s, SiPh), 126.9 (s. SiPh), 128.1 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.2 (d, $^3J_{PC}$ = 9 Hz, PPh), 129.2 (s, PPh), 129.4 (s, PPh), 130.6 (d, $^2J_{PC}$ = 11 Hz, PPh), 130.7 (d, $^2J_{PC}$ = 12 Hz, PPh), 135.7 (d, $^4J_{PC}$ = 1 Hz, $^2J_{PtC}$ = 20 Hz, SiPh), 137.9 (dd, $^1J_{PC}$ = 34 Hz, $^3J_{PC}$ = 2 Hz, PPh), 139.4 (dd, $^1J_{PC}$ = 44 Hz, $^3J_{PC}$ = 7 Hz, PPh), 147.8 (dd, $^3J_{PC}$ = 7 and 3 Hz, $^2J_{PtC}$ = 49 Hz, SiPh), 159.0 (dd, $^2J_{PC}$ = 96 and 15 Hz, $^1J_{PtC}$ = 683 Hz, Pt*C*H=CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −13.0 (d, $^2J_{PP}$ = 18 Hz, $^1J_{PtP}$ = 2002 Hz), −5.6 (d, $^2J_{PP}$ = 18 Hz, $^1J_{PtP}$ = 1292 Hz). ^{195}Pt{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −4828 (dd, $^1J_{PPt}$ = 2004 and 1294 Hz, $^1J_{PtSi}$ = 1324 Hz).

3e. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C): δ 1.36 (d, $^3J_{PH}$ = 8.1 Hz, $^2J_{PtH}$ = 18.0 Hz, 6H, PMe), 1.65 (d, $^3J_{PH}$ = 8.7 Hz, $^2J_{PtH}$ = 25.5 Hz, 6H, PMe), 4.94 (dddd, $^3J_{HH}$ = 19.5 Hz, $^2J_{HH}$ = 4.5 Hz, $^4J_{PH}$ = 8.4 and 4.5 Hz, $^3J_{PtH}$ = 70.8 Hz, 1H, PtCH=C*H*$_2$), 6.12 (dddd, $^3J_{HH}$ = 12.9 Hz, $^2J_{HH}$ = 4.5 Hz, $^4J_{PH}$ = 16.5 and 4.5 Hz, $^3J_{PtH}$ = 133.8 Hz, 1H, PtCH=C*H*$_2$), 7.16 (m, 1H, PtC*H*=CH$_2$), 7.25−7.7 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ 12.9 (dd, $^1J_{PC}$ = 27 Hz, $^4J_{FC}$ = 2 Hz, $^2J_{PtC}$ = 26 Hz, PMe), 17.8 (ddd, $^1J_{PC}$ = 32 Hz, $^3J_{PC}$ = 4 Hz, $^4J_{FC}$ = 4 Hz, $^2J_{PtC}$ = 39 Hz, PMe), 123.2 (d, $^3J_{PC}$ = 7 Hz, $^2J_{PtC}$ = 27 Hz, PtCH=*C*H$_2$), 127.1 (s, SiPh), 128.0 (s, SiPh), 128.2 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.4 (d, $^3J_{PC}$ = 10 Hz, PPh), 129.5 (s, PPh), 129.6 (s, PPh), 130.5 (d, $^2J_{PC}$ = 12 Hz, PPh), 130.7 (d, $^2J_{PC}$ = 11 Hz, PPh), 135.5 (d, $^3J_{FC}$ = 2 Hz, $^2J_{PtC}$ = 15 Hz, SiPh), 137.4 (d, $^1J_{PC}$ = 35 Hz, PPh), 138.9 (dd, $^1J_{PC}$ = 45 Hz, $^3J_{PC}$ = 4 Hz, PPh), 143.6 (dd, $^2J_{FC}$ = 16 Hz, $^3J_{PC}$ = 10 Hz, $^2J_{PtC}$ = 100 Hz, SiPh), 154.4 (dd, $^2J_{PC}$ = 89 and 15 Hz, $^1J_{PtC}$ = 652 Hz, Pt*C*H=CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −8.0 (dd, $^2J_{PP}$ = 20 Hz, $^3J_{FP}$ = 21 Hz, $^1J_{PtP}$ = 1994 Hz), −5.0 (dd, $^2J_{PP}$ = 20 Hz, $^3J_{FP}$ = 57 Hz, $^1J_{PtP}$ = 1382 Hz). ^{195}Pt{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ −4729 (ddd, $^1J_{PPt}$ = 2004 and 1397 Hz, $^2J_{FPt}$ = 379 Hz, $^1J_{PtSi}$ = 1512 Hz).

Kinetic Experiments. A typical procedure is as follows. Complex **2a** (22.7 mg, 30.0 μmol) was placed in a Schlenk tube and dissolved in toluene-d_8 (1.0 mL) at room temperature. The system was evacuated at −70 °C and filled with CO (1 atm), and the mixture was stirred at −30 °C for 1 h to produce **3a**. The CO gas was removed at −70 °C under vacuum and replaced with N$_2$ gas (1 atm). A part of the solution (ca. 0.6 mL) was transferred into an NMR sample tube equipped with a rubber septum cap. The amounts of **3a** and **4a** at intervals were determined by ^{31}P{^{1}H} NMR spectroscopy. The conversion of **3a** to **4a** proceeded quantitatively without any notable side reaction. All kinetic runs given in Table 1 were similarly carried out. Complexes **4a**−**e** were identified by ^{1}H, ^{31}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

4a. ^{1}H NMR (toluene-d_8, 20 °C): δ 1.06 (d, $^2J_{PH}$ = 6.9 Hz, $^3J_{PtH}$ = 30.0 Hz, 3H, PMe), 1.12 (d, $^2J_{PH}$ = 6.9 Hz, $^3J_{PtH}$ = 27.6 Hz, 3H, PMe), 1.28 (d, $^2J_{PH}$ = 7.2 Hz, $^3J_{PtH}$ = 31.2 Hz, 3H, PMe), 1.39 (d, $^2J_{PH}$ = 7.2 Hz, $^3J_{PtH}$ = 31.8 Hz, 3H, PMe), 2.11 (m, 1H, SiC*H*=CH$_2$), 2.45 (m, 2H, SiCH=C*H*$_2$), 6.95−7.35 (m, 19H, Ph), 7.85 (m, 6H, Ph). ^{13}C{^{1}H} NMR (toluene-d_8, 20 °C): δ 18.4 (dd, $^1J_{PC}$ = 24 Hz, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 45 Hz, PMe), 19.6 (m, PMe), 27.3 (dd, $^2J_{PC}$ = 29 and 4 Hz, $^1J_{PtC}$ = 216 Hz, Si*C*H=CH$_2$), 35.2 (dd, $^2J_{PC}$ = 32 and 4 Hz, $^1J_{PtC}$ = 211 Hz, SiCH=*C*H$_2$), 127.6 (s, SiPh), 128.0 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.2 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.6 (s, SiPh), 128.7 (d, $^2J_{PC}$ = 2 Hz, PPh), 128.8 (d, $^2J_{PC}$ = 2 Hz, PPh), 130.7 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 21 Hz, PPh), 130.8 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 20 Hz, PPh), 136.9 (s, SiPh), 139.3 (d, $^4J_{PC}$ = 3 Hz, $^3J_{PtC}$ = 14 Hz, SiPh), 141.9 (dd, $^1J_{PC}$ = 34 Hz, $^3J_{PC}$ = 4 Hz, PPh), 142.5 (dd, $^1J_{PC}$ = 35 Hz, $^3J_{PC}$ = 4 Hz, PPh). ^{31}P{^{1}H} NMR (toluene-d_8, 20 °C): δ −7.6 (d, $^2J_{PP}$ = 49 Hz, $^1J_{PtP}$ = 3581 Hz), −6.7 (d, $^2J_{PP}$ = 49 Hz, $^1J_{PtP}$ = 3538 Hz).

4b. ^{1}H NMR (toluene-d_8, 20 °C): δ 1.11 (d, $^2J_{PH}$ = 6.9 Hz, $^3J_{PtH}$ = 30.0 Hz, 3H, PMe), 1.17 (d, $^2J_{PH}$ = 6.6 Hz, $^3J_{PtH}$ = 28.2 Hz, 3H, PMe), 1.30 (d, $^2J_{PH}$ = 7.2 Hz, $^3J_{PtH}$ = 30.6 Hz, 3H, PMe), 1.39 (d, $^2J_{PH}$ = 6.9 Hz, $^3J_{PtH}$ = 31.8 Hz, 3H, PMe), 2.16 (m, 1H, SiC*H*=CH$_2$), 2.18 (s, 9H, Me), 2.50 (m, 2H, SiCH=C*H*$_2$), 6.95−7.15 (m, 12H, Ph and Ar), 7.22−7.38 (m, 4H, Ph), 7.82 (d, $^3J_{HH}$ = 7.8 Hz, 6H, Ar). ^{13}C{^{1}H} NMR (toluene-d_8, 20 °C): δ 18.6 (dd, $^1J_{PC}$ = 24 Hz, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 44 Hz, PMe), 19.7 (m, PMe), 21.5 (s, Me), 28.2 (dd, $^2J_{PC}$ = 29 and 4 Hz, $^1J_{PtC}$ = 213 Hz, Si*C*H=CH$_2$), 35.4 (dd, $^2J_{PC}$ = 32 and 5 Hz, $^1J_{PtC}$ = 208 Hz, SiCH=*C*H$_2$), 127.9 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.1 (d, $^3J_{PC}$ = 9 Hz, PPh), 128.4 (s, SiAr), 128.6 (d, $^2J_{PC}$ = 2 Hz, PPh), 128.8 (d, $^2J_{PC}$ = 2 Hz, PPh), 130.8 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 21 Hz, PPh), 130.8 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 20 Hz, PPh), 136.2 (d, $^4J_{PC}$ = 3 Hz, $^3J_{PtC}$ = 14 Hz, SiAr), 137.0 (s, SiAr), 137.8 (s, SiAr), 142.0 (dd, $^{1}J_{\mathrm{PC}}$ = 34 Hz, $^{3}J_{\mathrm{PC}}$ = 4 Hz, PPh), 142.8 (dd, $^{1}J_{\mathrm{PC}}$ = 35 Hz, $^{3}J_{\mathrm{PC}}$ = 3 Hz, PPh). ^{31}P{^{1}H} NMR (toluene-d_8, 20 °C): δ −7.6 (d, $^{2}J_{\mathrm{PP}}$ = 51 Hz, $^{1}J_{\mathrm{PtP}}$ = 3577 Hz), −6.6 (d, $^{2}J_{\mathrm{PP}}$ = 51 Hz, $^{1}J_{\mathrm{PtP}}$ = 3544 Hz).

4c. ^{1}H NMR (toluene-d_8, 20 °C): δ 1.13 (d, $^{2}J_{\mathrm{PH}}$ = 7.2 Hz, $^{3}J_{\mathrm{PtH}}$ = 30.0 Hz, 3H, PMe), 1.18 (d, $^{2}J_{\mathrm{PH}}$ = 6.9 Hz, $^{3}J_{\mathrm{PtH}}$ = 27.6 Hz, 3H, PMe), 1.30 (d, $^{2}J_{\mathrm{PH}}$ = 7.5 Hz, $^{3}J_{\mathrm{PtH}}$ = 30.6 Hz, 3H, PMe), 1.43 (d, $^{2}J_{\mathrm{PH}}$ = 7.5 Hz, $^{3}J_{\mathrm{PtH}}$ = 31.2 Hz, 3H, PMe), 2.21 (m, 1H, SiC*H*=CH$_2$), 2.51 (m, 2H, SiCH=C*H*$_2$), 3.38 (s, 9H, OMe), 6.80 (d, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz, 6H, Ar), 6.98−7.14 (m, 6H, Ph), 7.24−7.38 (m, 4H, Ph), 7.81 (d, $^{3}J_{\mathrm{HH}}$ = 8.4 Hz, 6H, Ar). ^{13}C{^{1}H} NMR (toluene-d_8, 20 °C): δ 18.5 (dd, $^{1}J_{\mathrm{PC}}$ = 24 Hz, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $^{2}J_{\mathrm{PtC}}$ = 44 Hz, PMe), 19.8 (m, PMe), 28.7 (dd, $^{2}J_{\mathrm{PC}}$ = 30 and 5 Hz, $^{1}J_{\mathrm{PtC}}$ = 214 Hz, Si*C*H=CH$_2$), 35.4 (dd, $^{2}J_{\mathrm{PC}}$ = 33 and 5 Hz, $^{1}J_{\mathrm{PtC}}$ = 210 Hz, SiCH=*C*H$_2$), 54.4 (s, OMe), 113.4 (s, SiAr), 128.0 (d, $^{3}J_{\mathrm{PC}}$ = 9 Hz, PPh), 128.2 (d, $^{3}J_{\mathrm{PC}}$ = 9 Hz, PPh), 128.7 (d, $^{2}J_{\mathrm{PC}}$ = 2 Hz, PPh), 128.8 (d, $^{2}J_{\mathrm{PC}}$ = 2 Hz, PPh), 130.7 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 21 Hz, PPh), 130.9 (d, $^{2}J_{\mathrm{PC}}$ = 13 Hz, $^{3}J_{\mathrm{PtC}}$ = 21 Hz, PPh), 130.8 (d, $^{4}J_{\mathrm{PC}}$ = 3 Hz, SiAr), 138.3 (s, SiAr), 142.0 (dd, $^{1}J_{\mathrm{PC}}$ = 35 Hz, $^{3}J_{\mathrm{PC}}$ = 2 Hz, PPh), 142.7 (dd, $^{1}J_{\mathrm{PC}}$ = 36 Hz, $^{3}J_{\mathrm{PC}}$ = 3 Hz, PPh), 160.6 (s, SiAr). ^{31}P{^{1}H} NMR (toluene-d_8, 20 °C): δ −7.7 (d, $^{2}J_{\mathrm{PP}}$ = 51 Hz, $^{1}J_{\mathrm{PtP}}$ = 3568 Hz), −6.4 (d, $^{2}J_{\mathrm{PP}}$ = 51 Hz, $^{1}J_{\mathrm{PtP}}$ = 3544 Hz).

4d. ^{1}H NMR (toluene-d_8, 20 °C): δ 0.55 (s, 3H, SiMe), 1.19 (d, $^{2}J_{\mathrm{PH}}$ = 7.2 Hz, $^{3}J_{\mathrm{PtH}}$ = 30.0 Hz, 3H, PMe), 1.21 (d, $^{2}J_{\mathrm{PH}}$ = 6.9 Hz, $^{3}J_{\mathrm{PtH}}$ = 32.4 Hz, 3H, PMe), 1.30 (d, $^{2}J_{\mathrm{PH}}$ = 7.5 Hz, $^{3}J_{\mathrm{PtH}}$ = 30.6 Hz, 3H, PMe), 1.40 (d, $^{2}J_{\mathrm{PH}}$ = 7.5 Hz, $^{3}J_{\mathrm{PtH}}$ = 31.8 Hz, 3H, PMe), 2.1−2.5 (m, 3H, SiC*H*=C*H*$_2$), 6.95−7.36 (m, 12H, Ph), 7.4−7.6 (m, 4H, Ph), 7.54−7.86 (m, 4H, Ph). ^{13}C{^{1}H} NMR (toluene-d_8, 20 °C): δ −0.96 (d, $^{4}J_{\mathrm{PC}}$ = 2 Hz, $^{3}J_{\mathrm{PtC}}$ = 22 Hz, SiMe), 18.5 (dd, $^{1}J_{\mathrm{PC}}$ = 25 Hz, $^{3}J_{\mathrm{PC}}$ = 4 Hz, $^{2}J_{\mathrm{PtC}}$ = 44 Hz, PMe), 19.6 (m, PMe), 29.7 (dd, $^{2}J_{\mathrm{PC}}$ = 29 and 5 Hz, $^{1}J_{\mathrm{PtC}}$ = 206 Hz, Si*C*H=CH$_2$), 35.2 (dd, $^{2}J_{\mathrm{PC}}$ = 33 and 5 Hz, $^{1}J_{\mathrm{PtC}}$ = 208 Hz, SiCH=*C*H$_2$), 127.5 (s, SiPh), 127.7 (s, SiPh), 128.1 (s, PPh), 128.2 (s, PPh), 128.8 (s, SiPh), 129.5 (s, SiPh), 130.7 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 22 Hz, PPh), 131.0 (d, $^{2}J_{\mathrm{PC}}$ = 13 Hz, $^{3}J_{\mathrm{PtC}}$ = 21 Hz, PPh), 135.2 (s, SiPh), 135.6 (s, SiPh), 135.6 (s, $^{3}J_{\mathrm{PtC}}$ = 14 Hz, SiPh), 141.5 (dd, $^{1}J_{\mathrm{PC}}$ = 32 Hz, $^{3}J_{\mathrm{PC}}$ = 3 Hz, PPh), 142.3 (dd, $^{1}J_{\mathrm{PC}}$ = 24 Hz, $^{3}J_{\mathrm{PC}}$ = 3 Hz, PPh). ^{31}P{^{1}H} NMR (toluene-d_8, 20 °C): δ −7.5 (d, $^{2}J_{\mathrm{PP}}$ = 51 Hz, $^{1}J_{\mathrm{PtP}}$ = 3573 Hz), −6.2 (d, $^{2}J_{\mathrm{PP}}$ = 51 Hz, $^{1}J_{\mathrm{PtP}}$ = 3544 Hz).

4e. ^{1}H NMR (toluene-d_8, 20 °C): δ 1.23 (d, $^{2}J_{\mathrm{PH}}$ = 7.2 Hz, $^{3}J_{\mathrm{PtH}}$ = 31.8 Hz, 3H, PMe), 1.33 (d, $^{2}J_{\mathrm{PH}}$ = 6.9 Hz, $^{3}J_{\mathrm{PtH}}$ = 32.4 Hz, 3H, PMe), 1.50 (d, $^{2}J_{\mathrm{PH}}$ = 6.6 Hz, $^{3}J_{\mathrm{PtH}}$ = 29.2 Hz, 6H, PMe), 2.1−2.5 (m, 3H, SiC*H*=C*H*$_2$), 6.95−7.36 (m, 12H, Ph), 7.4−7.6 (m, 4H, Ph), 7.54−7.86 (m, 4H, Ph). ^{13}C{^{1}H} NMR (toluene-d_8, 20 °C): δ 18.0−19.8 (m, PMe), 27.3 (dd, $^{2}J_{\mathrm{PC}}$ = 22 Hz, $^{2}J_{\mathrm{FC}}$ = 19 Hz, $^{1}J_{\mathrm{PtC}}$ = 176 Hz, Si*C*H=CH$_2$), 34.5 (dd, $^{2}J_{\mathrm{PC}}$ = 28 and 3 Hz, $^{1}J_{\mathrm{PtC}}$ = 227 Hz, SiCH=*C*H$_2$), 127.4 (s, SiPh), 127.9 (s, SiPh), 128.0 (s, PPh), 128.1 (s, PPh), 128.8 (s, PPh), 128.9 (s, PPh), 129.4 (s, SiPh), 129.6 (s, SiPh), 130.7 (s, $^{3}J_{\mathrm{PtC}}$ = 21 Hz, PPh), 130.8 (s, $^{3}J_{\mathrm{PtC}}$ = 21 Hz, PPh), 135.5 (d, $^{3}J_{\mathrm{FC}}$ = 2 Hz, SiPh), 135.8 (d, $^{3}J_{\mathrm{FC}}$ = 1 Hz, SiPh), 136.7 (d, $^{2}J_{\mathrm{FC}}$ = 19 Hz, SiPh), 141.4 (d, $^{1}J_{\mathrm{PC}}$ = 40 Hz, PPh), 142.4 (d, $^{1}J_{\mathrm{PC}}$ = 38 Hz, PPh). ^{31}P{^{1}H} NMR (toluene-d_8, 20 °C): δ −7.7 (d, $^{2}J_{\mathrm{PP}}$ = 47 Hz, $^{4}J_{\mathrm{FP}}$ = 16 Hz, $^{1}J_{\mathrm{PtP}}$ = 3734 Hz), −7.1 (d, $^{2}J_{\mathrm{PP}}$ = 47 Hz, $^{1}J_{\mathrm{PtP}}$ = 3450 Hz).

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