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Preparation and C−Si Reductive Elimination Behavior of *cis*-Alkynyl(silyl)platinum(II) Complexes

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A series of *cis*-alkynyl(silyl)platinum(II) complexes, *cis*-Pt(C≡CAr)(SiAr′$_3$)(PMe$_2$Ph)$_2$ (**2**: Ar = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-NCC$_6$H$_4$; Ar′ = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$), have been prepared, and their thermolysis reactions in solution have been examined. Complexes **2** smoothly undergo C−Si reductive elimination in benzene-d_6 at around 35 °C to give the corresponding platinum(0) complexes coordinated with silylacetylenes, Pt(ArC≡CSiAr′$_3$)(PMe$_2$Ph)$_2$ (**3**). Kinetic examinations suggest a concerted reaction process that is operative directly from the four-coordinate complexes. The more electron-donating substituents on the Ar and Ar′ groups provide higher reductive elimination rates.

Introduction

Reductive elimination leading to C−Si bond formation has often been assumed as a product-forming step in transition-metal-catalyzed silylation of organic compounds.[1] However, mechanistic information about this elementary process has been limited.[2−4] In previous studies we prepared *cis*-alkyl(silyl)platinum(II) complexes (*cis*-PtR(SiPh$_3$)L$_2$: R = Me, Et, Pr, Bu; L = PMe$_2$Ph, PMePh$_2$) and examined their thermolysis reactions in solution by kinetic experiments.[4] Although the complexes are fairly stable in neat solvents, they readily undergo C−Si reductive elimination to give RSiPh$_3$ in the presence of alkynes or alkenes. Two types of processes are operative in the presence of diphenylacetylene. In the first process, RSiPh$_3$ is formed from a PtR(SiPh$_3$)(PhC≡CPh)L intermediate, generated by ligand displacement of *cis*-PtR(SiR$_3$)L$_2$ with diphenylacetylene. On the other hand, in the second process, the alkyl−silyl complexes are initially converted into *cis*-PtPh(SiRPh$_2$)L$_2$ by intramolecular exchange of the Pt−R group with the Si−Ph group, and the subsequent C−Si reductive elimination affords RSiPh$_3$ via the intermediate PtPh(SiRPh$_2$)(PhC≡CPh)L.

In this paper we examine the mechanism of C−Si reductive elimination from *cis*-Pt(C≡CAr)(SiAr′$_3$)(PMe$_2$Ph)$_2$ complexes. It has been documented that the mechanism of C−C reductive elimination from d^8 metal complexes is significantly affected by the nature of σ-carbyl ligands, especially by hybridization of the carbon atom bonded to metal.[5] For example, *cis*-dialkylpalladium(II) complexes (*cis*-PdR$_2$L$_2$: R = Me, Et) undergo C−C reductive elimination with prior dissociation of L,[6] whereas aryl−alkyl and alkenyl−alkyl analogues (*cis*-PdRR′L$_2$: R′ = Ph, PhCH=CH, etc.) provide the reductive elimination products (R−R′) without dissociation of L.[7] Similarly, we found in this study that the alkynyl(silyl)platinum(II) complexes undergo a C−Si reductive elimination process, clearly different from that previously observed for alkyl−silyl analogues. Thus, the reaction proceeds directly from the four-coordinate species without dissociation of phosphine.

Results

Preparation of *cis*-Pt(C≡CAr)(SiAr′$_3$)(PMe$_2$Ph)$_2$ (2). Scheme 1 summarizes synthetic routes to **2**. Unlike

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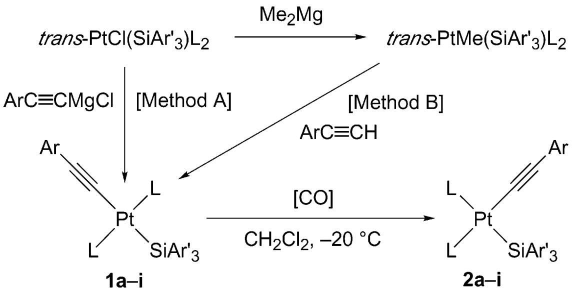
Table 1. Selected NMR Data for *cis*-Pt(C≡CAr)(SiAr′$_3$)(PMe$_2$Ph)$_2$ (2a−i)[a]

complex			^{13}C{^{1}H} NMR: δ (ppm) [J_{PC} (Hz)]		^{31}P{^{1}H} NMR: δ (ppm) [$^1J_{PtP}$ (Hz)] {$^2J_{SiP}$ (Hz)}[b]	
Ar	Ar′		Ar*C*≡CPt (C$^\beta$)	ArC≡*C*Pt (C$^\alpha$)	P trans to Si	P trans to C
Ph	Ph	**2a**	115.9 (dd) [32, 2]	113.7 (dd) [126, 21]	−6.1 (d) [1137] {177}	−14.2 (d) [2667] {0}
4-MeOC$_6$H$_4$	Ph	**2b**	115.5 (dd) [31, 2]	110.9 (dd) [127, 20]	−6.3 (d) [1137] {179}	−14.3 (d) [2663] {0}
4-MeC$_6$H$_4$	Ph	**2c**	115.9 (dd) [29, 2]	112.4 (dd) [127, 19]	−6.0 (d) [1134] {177}	−14.3 (d) [2665] {0}
4-ClC$_6$H$_4$	Ph	**2d**	114.7 (dd) [30, 3]	115.6 (dd) [126, 18]	−6.1 (d) [1139] {177}	−14.2 (d) [2664] {0}
4-BrC$_6$H$_4$	Ph	**2e**	114.8 (dd) [31, 5]	116.0 (dd) [128, 18]	−6.1 (d) [1139] {177}	−14.2 (d) [2667] {0}
4-NCC$_6$H$_4$	Ph	**2f**	115.3 (dd) [30, 4]	122.7 (dd) [125, 19]	−6.1 (d) [1146] {174}	−14.2 (d) [2664] {0}
Ph	4-MeOC$_6$H$_4$	**2g**	115.5 (dd) [31, 3]	113.9 (dd) [127, 20]	−5.6 (d) [1080] {176}	−13.5 (d) [2667] {0}
Ph	4-MeC$_6$H$_4$	**2h**	115.2 (dd) [33, 3]	113.8 (dd) [126, 21]	−5.8 (d) [1095] {176}	−14.2 (d) [2661] {0}
Ph	4-CF$_3$C$_6$H$_4$	**2i**	117.2 (dd) [30, 3]	111.7 (dd) [126, 20]	−6.2 (d) [1281] {208}	−14.7 (d) [2624] {0}

[a] NMR spectra were measured in CD$_2$Cl$_2$ at −20 °C (**2a**−**f**) or −30 °C (**2g**−**i**). [b] Doublet signals are due to the P−P coupling ($^2J_{PP}$ = 23 Hz).

Scheme 1[a]



complex	Ar	Ar'
1a, **2a**	Ph	Ph
1b, **2b**	4-MeOC$_6$H$_4$	Ph
1c, **2c**	4-MeC$_6$H$_4$	Ph
1d, **2d**	4-ClC$_6$H$_4$	Ph
1e, **2e**	4-BrC$_6$H$_4$	Ph
1f, **2f**	4-NCC$_6$H$_4$	Ph

complex	Ar	Ar'
1g, **2g**	Ph	4-MeOC$_6$H$_4$
1h, **2h**	Ph	4-MeC$_6$H$_4$
1i, **2i**	Ph	4-CF$_3$C$_6$H$_4$

[a] L = PMe$_2$Ph.

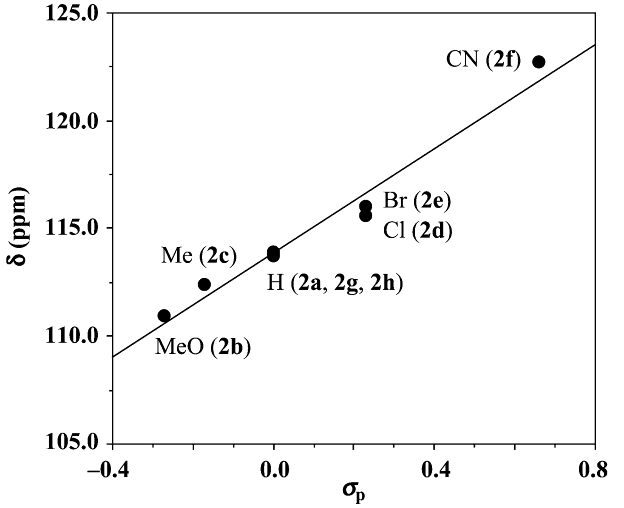


Figure 1. Dependence of the chemical shifts of α-acetylenic carbons in **2a**−**h** upon the σ_p values of para substituents on the Ar groups. The σ_p values were taken from ref 9.

the *cis*-alkyl−silyl analogues,[4] direct synthesis of **2** from *trans*-PtCl(SiAr′$_3$)L$_2$ by treatment with alkynyllithium instead gave a mixture of trans and cis isomers of the alkynyl−silyl complex (**1** and **2**, respectively). On the other hand, **2** was successfully prepared by trans to cis isomerization of **1**. This reaction proceeds smoothly in CH$_2$Cl$_2$ under a CO atmosphere at low temperature (−20 °C) without concomitant CO insertion and reductive elimination. The parent **1** can be prepared by either the reaction of *trans*-PtCl(SiAr′$_3$)L$_2$ with ArC≡CMgCl in THF (method A) or the treatment of *trans*-PtMe(SiAr′$_3$)L$_2$ with ArC≡CH in benzene (method B).[8] While the latter method requires a long reaction time (ca. 5 days), it forms methane as the only byproduct, making the workup procedure very simple.

The *cis*-alkynyl−silyl complexes bearing a variety of Ar and Ar′ groups (**2a**−**i**) were thus prepared and characterized by NMR spectroscopy and elemental analysis. Selected ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR data are listed in Table 1. The β-carbon signal of the alkynyl ligand appears as a doublet of doublets at around δ 115, irrespective of the sorts of Ar and Ar′ groups. On the other hand, the α-carbon signal is clearly shifted to a lower magnetic field as the more electron-withdrawing group is substituted at the para position of the Ar group; the chemical shifts for **2a**−**h** exhibit a good Hammett correlation (r = 0.985) with the σ_p values of substituents: $\delta_{C(\alpha)} = [12.1(9)]\sigma_p + 113.8(2)$ (Figure 1).

A clear tendency is also observed for the $^1J_{PtP}$ values of the phosphorus trans to silyl ligands. Thus, the coupling constant increases as the para substituent of the Ar′ group on silicon becomes more electron-withdrawing. The substituent effect is rationalized by the following equation for all complexes (r = 0.996): $^1J_{PtP} = [85(3)]\Sigma(1-3)\sigma_p + 1140(2)$ (Figure 2).

Reductive Elimination from 2. Complexes **2a**−**h** cleanly underwent C−Si reductive elimination in benzene-d_6 at 30−40 °C to give Pt(0) complexes coordinated with silylalkynes (**3a**−**h**) (Scheme 2), while **2i**, having the most electron-deficient silyl group, was exceptionally stable under the reaction conditions. ^{31}P{^{1}H} NMR spectra of the reaction solutions after thermolysis exhibited AB quartet signals with $^2J_{PP}$ values of 37−38 Hz and $^1J_{PtP}$ values of 3319−3570 Hz, the values of which are consistent with the formation of the Pt(0) alkyne complexes. Complexes **3a**−**h** were further characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (see Experimental Section).

The reductive elimination was followed by ^{1}H NMR spectroscopy using MeSiPh$_3$ as an internal standard. The rate constants (k_{obsd}) are listed in Table 2. All runs obeyed good first-order kinetics for at least 2 half-lives. Unlike the reactions of *cis*-alkyl−silyl analogues, the

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[8] Complexes **1a**−**f** were isolated by recrystallization and characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis. On the other hand, **1g**−**i** were employed as crude products in the synthesis of cis isomers, while their formation was confirmed by ^{31}P{^{1}H} NMR spectroscopy.

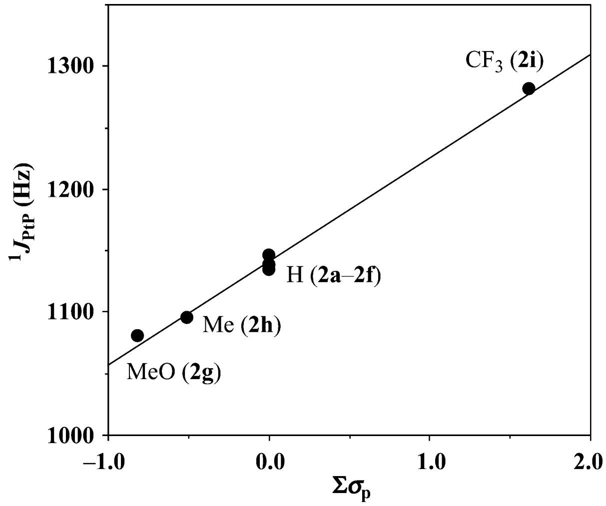
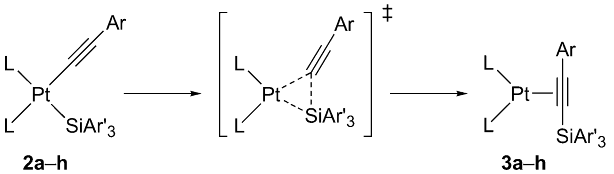


Figure 2. Dependence of the $^1J_{PtP}$ values for the phosphorus trans to silyl ligands in **2a**−**i** upon the sum of the σ_p values of para substituents on the $SiAr'_3$ groups. The σ_p values were taken from ref 9.

Scheme 2[a]



[a] L = PMe_2Ph.

Table 2. First-Order Rate Constants for Reductive Elimination from *cis*-Pt(C≡CAr)($SiAr'_3$)(PMe_2Ph)$_2$ (2a−i)[a]

run	Ar	Ar′	compd	temp	10^3k_{obsd} (s^{-1})
1	Ph	Ph	**2a**	30	0.128(8)
2	Ph	Ph	**2a**	35	0.283(2)
3[b]	Ph	Ph	**2a**	35	0.285(7)
4	Ph	Ph	**2a**	40	0.533(3)
5	Ph	Ph	**2a**	45	1.06(10)
6	4-$MeOC_6H_4$	Ph	**2b**	35	0.575(4)
7	4-MeC_6H_4	Ph	**2c**	35	0.422(3)
8	4-ClC_6H_4	Ph	**2d**	35	0.153(1)
9	4-BrC_6H_4	Ph	**2e**	35	0.147(1)
10	4-NCC_6H_4	Ph	**2f**	35	0.078(2)
11	Ph	4-$MeOC_6H_4$	**2g**	35	0.55(2)
12	Ph	4-MeC_6H_4	**2h**	35	0.468(3)
13	Ph	4-$CF_3C_6H_4$	**2i**	40	very slow

[a] All runs were examined in benzene-d_6 by ^1H NMR spectroscopy: $[\mathbf{2}]_0 = 0.03$ M. [b] PMe_2Ph (0.03 M) was added.

reaction of **2a** readily proceeds in the absence of alkyne promoters, and the reaction rate is not affected by addition of free PMe_2Ph to the system (1 equiv) (runs 2 and 3). The activation parameters estimated for the temperature range of 30−45 °C (runs 1−5) are as follows: $\Delta H^\ddagger = 26.4(7)$ kcal mol^{-1}, $\Delta S^\ddagger = 10(2)$ eu, $\Delta G^\ddagger = 23.2$ kcal mol^{-1}.

The reaction rate clearly decreases as the electron-withdrawing ability of the para substituent on the Ar group increases (runs 2, 6, and 7), according to the following Hammett equation ($r = 0.987$): $\log(k_Y/k_H) = [-0.95(8)]\sigma_p + 0.00(2)$ (Figure 3). Similarly, the presence of an electron-withdrawing substituent on the Ar′ group on silicon effectively decelerates the reductive elimination (runs 2 and 11−13).

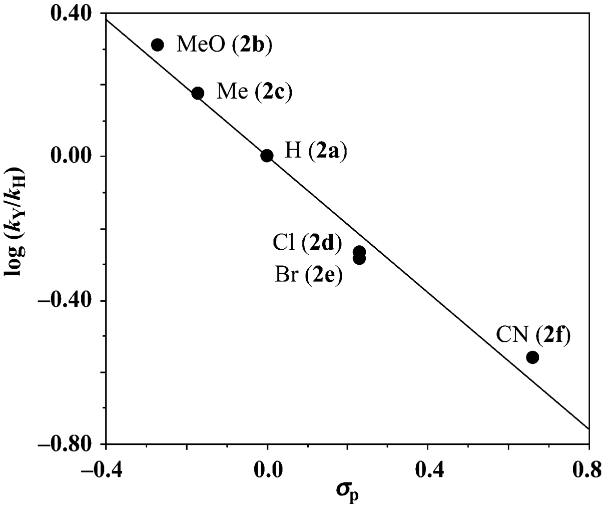


Figure 3. Hammett plot for the rate constants of runs 2, 6, and 7 in Table 2 against the σ_p values of para substituents on Ar groups. The σ_p values were taken from ref 9.

Discussion

The kinetic observations described above are fully consistent with the reductive elimination process given in Scheme 2, which is operative directly from the four-coordinated species **2** in a concerted manner. A similar type process has been proposed for C−C reductive elimination from *cis*-Pt(C≡CBu^t)(CMe=CH_2)(PPh_3)$_2$.[10] A clear substituent effect has been observed. Thus, the reductive elimination rate is effectively reduced by electron-withdrawing substituents on the Ar and Ar′ groups.[11]

Two types of mechanisms have been documented for C−C reductive elimination from d^8 metal complexes.[5] One involves simultaneous elimination of two σ-carbyl ligands with concomitant formation of a C−C bond via a three-center transition state. This mechanism has been assumed for dialkyl complexes bearing two sp^3-hybridized carbon ligands.[12] On the other hand, the other one is the so-called “migratory reductive elimination”, which has been proposed for diorgano complexes having sp^2- or sp-hybridized carbon ligands (e.g., aryl, alkenyl, CN).[7b,13,14] Thus, the C−C bond is formed by nucleophilic attack of one of the carbyl ligands upon the other carbyl ligand in a migration manner. Accordingly, the reductive elimination by this mechanism exhibits opposite substituent effects with respect to the two

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carbyl ligands; namely, the reaction is accelerated not only by increasing nucleophilicity of one of the ligands but also by increasing electrophilicity of the other ligand.

In the present C−Si reductive elimination, since the same tendency of substituent effect has been observed for both the alkynyl and silyl ligands, it is reasonable that the former type mechanism is operative with simultaneous weakening of the Pt−C and Pt−Si bonds.[15] In this case, electron-withdrawing substituents on the Ar and Ar′ groups must stabilize the ground-state species **2** via strengthening of the Pt−C≡CAr and Pt−SiAr′$_3$ bonds.[16] Although a bonding interaction between the acetylenic carbon and the silicon in the transition state is possibly enhanced by the electron-withdrawing substituents as well, the energy change in the transition state should be much smaller than that in the ground state, owing to incomplete formation of the C−Si bond. Hence, the substituent effects observed in this study are reasonably interpreted.

Experimental Section

General Procedure and Materials. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on JEOL A400 and Varian Mercury 300 spectrometers. Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^1H and ^{13}C NMR and to an external 85% H_3PO_4 standard for ^{31}P NMR. THF, Et_2O, benzene, and hexane were dried over sodium benzophenone ketyl and distilled just before using. CH_2Cl_2 was dried over CaH_2 and distilled just before using. Benzene-d_6 was dried over $LiAlH_4$, vacuum-transferred, and stored under a nitrogen atmosphere. *trans*-PtCl(SiAr$_3$)(PMe$_2$Ph)$_2$[17] and *trans*-PtMe(SiPh$_3$)(PMePh$_2$)$_2$[18] were prepared according to the literature. All other compounds used in this study were obtained from commercial sources and used without further purification.

Preparation of *trans*-Pt(C≡CAr)(SiAr′$_3$)(PMe$_2$Ph)$_2$ (1). The title compounds were prepared either by the reaction of *trans*-PtCl(SiAr′$_3$)(PMe$_2$Ph)$_2$ with ArC≡CMgCl in THF (method A) or by the reaction of *trans*-PtMe(SiAr′$_3$)(PMe$_2$Ph)$_2$ with ArC≡CH in benzene (method B). Typical procedures are as follows.

Method A. To a solution of *trans*-PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$ (500 mg, 0.65 mmol) in THF (8 mL) was added a THF solution of PhC≡CMgCl (1.44 M; 0.50 mL, 0.72 mmol) at room temperature. The mixture was stirred for 30 min and cooled to −20 °C. Methanol (1 mL) was added, and the solution was concentrated to dryness. The residue was extracted with benzene (4 mL × 3), and the extracts were filtered through a short Celite column. The filtrate was concentrated to dryness by pumping, and the residue was dissolved in CH_2Cl_2 (ca. 2 mL), slowly layered with Et_2O (20 mL), and allowed to stand at −20 °C for 1 day to give colorless crystals of **1a** (300 mg, 55% yield).

Method B. The complex *trans*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (500 mg, 0.67 mmol) was placed in a 25 mL Schlenk tube, and the system was purged with nitrogen gas. Benzene (8 mL) was added, and the mixture was stirred to dissolve the complex. PhC≡CH (0.43 mL, 3.9 mmol) was added, and the solution was stirred for 5 days at room temperature. $^{31}P\{^1H\}$ NMR analysis revealed complete conversion of the starting methyl complex (δ −3.6) into **1a** (δ −11.5). The volatile material was removed by pumping, and the resulting off-white solid of **1a** was purified similarly to method A (349 mg, 63% yield).

Complexes **1b**−**f** were synthesized by method B and **1g**−**i** by method A. The former complexes were isolated by recrystallization and characterized by NMR spectroscopy and elemental analysis as listed below. On the other hand, the latter complexes were employed in the synthesis of cis isomers without purification, but their formation was confirmed by $^{31}P\{^1H\}$ NMR analysis (CD_2Cl_2, −20 °C): **1g**, δ −10.7 ($^1J_{PtP}$ = 2604 Hz); **1h**, δ −12.0 ($^1J_{PtP}$ = 2403 Hz); **1i**, δ −12.2 ($^1J_{PtP}$ = 2374 Hz).

1a. ^1H NMR (CD_2Cl_2, −20 °C): δ 1.57 (virtual triplet, J = 3.2 Hz, $^3J_{PtH}$ = 31.7 Hz, 12H, PMe), 7.06−7.20 (m, 14H, Ph), 7.26−7.38 (m, 6H, Ph), 7.44 (m, 6H, Ph), 7.52 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 16.4 (virtual triplet, J = 20 Hz, $^2J_{PtC}$ = 42 Hz, PMe), 111.4 (s, $^2J_{PtC}$ = 198 Hz, Ph*C*≡C), 125.6 (s, Ph), 126.3 (t, $^2J_{PC}$ = 19 Hz, $^1J_{PtC}$ = 758 Hz, PhC≡*C*), 127.2 (s, SiPh), 127.5 (s, SiPh), 128.2 (virtual triplet, J = 5 Hz, PPh), 128.3 (s, Ph), 128.4 (s, $^3J_{PtC}$ = 23 Hz, Ph), 130.0 (s, PPh), 130.7 (s, Ph), 131.8 (virtual triplet, J = 6 Hz, PPh), 136.4 (virtual triplet, J = 28 Hz, $^2J_{PtP}$ = 28 Hz, PPh), 137.3 (s, $^3J_{PtC}$ = 17 Hz, SiPh), 145.7 (s, $^2J_{PtC}$ = 30 Hz, SiPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −11.4 (s, $^1J_{PtP}$ = 2551 Hz). Anal. Calcd for $C_{42}H_{42}P_2PtSi$: C, 60.64; H, 5.09. Found: C, 60.41; H, 4.90.

1b. Yield 56%, colorless crystals. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.59 (virtual triplet, J = 3.4 Hz, $^3J_{PtH}$ = 31.7 Hz, 12H, PMe), 3.74 (s, 3H, MeO), 6.71 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 7.02 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 7.05−7.20 (m, 9H, Ph), 7.25−7.38 (m, 6H, Ph), 7.48 (d, 6H, $^3J_{HH}$ = 6.8 Hz, Ph), 7.56 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 16.9 (virtual triplet, J = 21 Hz, $^2J_{PtC}$ = 43 Hz, PMe), 55.7 (s, MeO), 111.4 (s, $^2J_{PtC}$ = 198 Hz, Ar*C*≡C), 114.0 (s, Ar), 121.4 (s, $^3J_{PtC}$ = 16 Hz, Ar), 124.0 (t, $^2J_{PC}$ = 19 Hz, ArC≡*C*), 127.4 (s, SiPh), 127.7 (s, SiPh), 128.4 (virtual triplet, J = 5 Hz, PPh), 130.2 (s, PPh), 132.1 (s, Ar), 132.2 (virtual triplet, J = 6 Hz, PPh), 137.0 (virtual triplet, J = 29 Hz, $^2J_{PtC}$ = 28 Hz, PPh), 137.6 (s, $^3J_{PtC}$ = 17 Hz, SiPh), 146.3 (s, $^2J_{PtC}$ = 30 Hz, SiPh), 158.1 (s, Ar). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −11.4 (s, $^1J_{PtP}$ = 2576 Hz). Anal. Calcd for $C_{43}H_{44}OP_2PtSi$: C, 59.92; H, 5.15. Found: C, 59.80; H, 5.19.

1c. Yield 74%, white solid. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.60 (virtual triplet, J = 3.4 Hz, $^3J_{PtH}$ = 31.2 Hz, 12H, PMe), 2.28 (s, 3H, Me), 7.01 (m, 4H, Ar), 7.06−7.25 (m, 9H, Ph), 7.25−7.40 (m, 6H, Ph), 7.45−7.63 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 16.8 (virtual triplet, J = 21 Hz, $^2J_{PtC}$ = 41 Hz, PMe), 21.6 (s, Me), 111.8 (s, $^2J_{PtC}$ = 197 Hz, Ar*C*≡C), 125.3 (t, $^2J_{PC}$ = 18 Hz, ArC≡*C*), 125.9 (s, $^3J_{PtC}$ = 18 Hz, Ar), 127.4 (s, SiPh), 127.7 (s, SiPh), 128.4 (virtual triplet, J = 5 Hz, PPh), 129.2 (s, Ar), 130.2 (s, PPh), 130.8 (s, Ar), 132.2 (virtual triplet, J = 6 Hz, PPh), 135.6 (s, Ar), 136.9 (virtual triplet, J = 28 Hz, $^2J_{PtC}$ = 28 Hz, PPh), 137.6 (s, $^3J_{PtC}$ = 18 Hz, SiPh), 146.3 (s, $^2J_{PtC}$ = 30 Hz, SiPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −11.4 (s, $^1J_{PtP}$ = 2572 Hz). Anal. Calcd for $C_{43}H_{44}P_2PtSi$: C, 61.05; H, 5.24. Found: C, 60.91; H, 5.10.

1d. Yield 75%, white solid. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.57 (virtual triplet, J = 3.4 Hz, $^3J_{PtH}$ = 31.7 Hz, 12H, PMe), 7.00 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.07−7.25 (m, 11H, Ar and Ph), 7.29 (m, 4H, Ph), 7.35 (m, 2H, Ph), 7.48 (m, 6H, Ph), 7.55 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 16.8 (virtual triplet, J = 21 Hz, $^2J_{PtC}$ = 41 Hz, PMe), 110.7 (s, Ar*C*≡C), 127.5 (s, SiPh), 127.7 (s, SiPh), 128.5 (virtual triplet, J = 5 Hz, PPh), 128.6 (s, Ar), 130.2 (s, PPh), 131.1 (s, Ar), 132.2 (virtual triplet, J = 7 Hz, PPh), 132.2 (s, Ar), 136.8 (virtual triplet, J = 28 Hz, $^2J_{PtC}$ = 28 Hz, PPh), 137.6 (s, $^3J_{PtC}$ = 17 Hz, SiPh), 146.1

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(14) Migratory reductive elimination has been proposed also for the reactions giving C−N, C−O, and C−S bonds. (a) Reference 11a. (b) Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504. (c) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. (d) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (e) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (f) Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

(15) This mechanism is consistent with the slightly positive activation entropy (10(2) eu) observed for **2a**.

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(s, $^2J_{PtC} = 28$ Hz, SiPh). One acetylenic carbon and one C_6H_4-Cl group carbon were not detected. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −11.3 (s, $^1J_{PtP} = 2573$ Hz). Anal. Calcd for $C_{42}H_{41}P_2PtSiCl$: C, 58.23; H, 4.77. Found: C, 58.28; H, 4.74.

1e. Yield 76%, white crystalline solid. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.56 (virtual triplet, $J = 3.7$ Hz, $^3J_{PtH} = 31.7$ Hz, 12H, PMe), 6.93 (d, $^3J_{HH} = 8.3$ Hz, 2H, Ar), 7.09 (m, 6H, Ph), 7.16 (m, 3H, Ph), 7.28 (m, 6H, Ar and Ph), 7.35 (m, 2H, Ph), 7.47 (m, 6H, Ph), 7.54 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 16.8 (virtual triplet, $J = 20$ Hz, $^2J_{PtC} = 43$ Hz, PMe), 110.7 (s, Ar*C*≡C), 119.2 (s, Ar), 127.5 (s, SiPh), 127.7 (s, SiPh), 128.5 (virtual triplet, $J = 5$ Hz, PPh), 130.2 (s, PPh), 131.5 (s, Ar), 132.1 (virtual triplet, $J = 7$ Hz, PPh), 132.5 (s, Ar), 136.8 (virtual triplet, $J = 28$ Hz, $^2J_{PtC} = 28$ Hz, PPh), 137.6 (s, $^3J_{PtC} = 17$ Hz, SiPh), 146.1 (s, $^2J_{PtC} = 28$ Hz, SiPh). One acetylenic carbon and one C_6H_4Br group carbon were not detected. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −11.3 (s, $^1J_{PtP} = 2573$ Hz). Anal. Calcd for $C_{42}H_{41}P_2PtSiBr$: C, 55.39; H, 4.54. Found: C, 55.18; H, 4.41.

1f. Yield 39%, pale yellow crystals. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.56 (virtual triplet, $J = 3.7$ Hz, $^3J_{PtH} = 31.7$ Hz, 12H, PMe), 7.10 (m, 8H, Ar and Ph), 7.17 (m, 3H, Ph), 7.29 (m, 4H, Ph), 7.36 (m, 2H, Ph), 7.42 (d, $^3J_{HH} = 8.3$ Hz, 2H, Ar), 7.47 (m, 6H, Ph), 7.54 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 16.8 (virtual triplet, $J = 21$ Hz, $^2J_{PtC} = 43$ Hz, PMe), 108.5 (s, Ar), 111.3 (s, $^2J_{PtC} = 194$ Hz, Ar*C*≡C), 119.9 (s, CN), 127.5 (s, SiPh), 127.9 (s, SiPh), 128.6 (virtual triplet, $J = 5$ Hz, PPh), 130.3 (s, PPh), 131.5 (s, Ar), 132.1 (virtual triplet, $J = 7$ Hz, PPh), 132.3 (s, Ar), 133.7 (s, $^3J_{PtC} = 20$ Hz, Ar), 135.7 (*t*, $^2J_{PC} = 18$ Hz, ArC≡*C*), 136.7 (virtual triplet, $J = 28$ Hz, $^2J_{PtC} = 28$ Hz, PPh), 137.6 (s, $^3J_{PtC} = 17$ Hz, SiPh), 146.0 (s, $^2J_{PtC} = 28$ Hz, SiPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −11.2 (s, $^1J_{PtP} = 2570$ Hz). Anal. Calcd for $C_{43}H_{41}NP_2PtSi$: C, 60.27; H, 4.82; N, 1.63. Found: C, 59.91; H, 4.67; N, 1.87.

Preparation of *cis*-Pt(C≡CAr)(SiAr′$_3$)(PMe$_2$Ph)$_2$ (2). A typical procedure is reported for **2a**. The trans isomer **1a** (130 mg, 0.156 mmol) was placed in a 25 mL Schlenk tube and dissolved in CH_2Cl_2 (4 mL) at room temperature. The solution was cooled to −20 °C and saturated with CO by bubbling. The system was allowed to stand for 4 h at the same temperature, and the conversion of **1a** was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. The solution was concentrated to dryness by pumping to yield a yellow solid, which was washed with cold Et_2O and dried under vacuum. The crude product was dissolved in CH_2Cl_2 (ca. 0.4 mL) at −20 °C, layered carefully with Et_2O (2 mL), and allowed to stand at −70 °C to give pale yellow crystals of **2a** (76.1 mg, 59% yield). This product contained 0.5 equiv of Et_2O in the crystal, as confirmed by ^1H NMR spectroscopy.

2a. ^1H NMR (CD_2Cl_2, −20 °C): δ 0.97 (d, $^2J_{PH} = 8.8$ Hz, $^3J_{PtH} = 28.3$ Hz, 6H, PMe), 1.60 (d, $^2J_{PH} = 9.3$ Hz, $^3J_{PtH} = 16.6$ Hz, 6H, PMe), 6.53 (m, 2H, Ph), 6.94 (m, 3H, Ph), 7.12−7.43 (m, 19H, Ph), 7.65 (m, 6H, Ph); 1.08 (t, $^3J_{HH} = 6.8$ Hz, 3H, 0.5·Et_2O), 3.35 (q, $^3J_{HH} = 6.8$ Hz, 2H, 0.5 Et_2O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 14.7 (d, $^1J_{PC} = 26$ Hz, $^2J_{PtC} = 26$ Hz, PMe), 16.1 (dd, $J_{PC} = 35$ and 5 Hz, $^2J_{PtC} = 35$ Hz, PMe), 113.7 (dd, $^2J_{PC} = 126$ and 21 Hz, $^1J_{PtC} = 1082$ Hz, PhC≡*C*), 115.9 (dd, $^3J_{PC} = 32$ and 2 Hz, $^2J_{PtC} = 318$ Hz, Ph*C*≡C), 125.3 (s, Ph), 127.1 (s, SiPh), 127.4 (s, SiPh), 127.7 (s, Ph), 128.3 (s, $^3J_{PtC} = 24$ Hz, Ph), 128.5 (d, $^3J_{PC} = 10$ Hz, PPh), 128.7 (d, $^3J_{PC} = 11$ Hz, PPh), 129.6 (s, PPh), 130.5 (s, PPh), 130.9 (d, $^2J_{PC} = 10$ Hz, PPh), 131.4 (d, $^2J_{PC} = 12$ Hz, $^3J_{PtC} = 23$ Hz, PPh), 137.1 (s, $^3J_{PtC} = 20$ Hz, SiPh), 137.2 (d, PPh), 137.7 (dd, $J_{PC} = 52$ and 5 Hz, PPh), 145.5 (d, $^3J_{PC} = 7$ Hz, $^2J_{PtC} = 43$ Hz, SiPh); 15.5 (s, Et_2O), 66.1 (s, Et_2O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −14.2 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 2667$ Hz), −6.1 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 1137$ Hz, $^2J_{SiP} = 177$ Hz). Anal. Calcd for $C_{42}H_{42}P_2PtSi \cdot 0.5C_4H_{10}O$: C, 60.82; H, 5.45. Found: C, 60.60; H, 5.33.

2b. Yield 48%, pale yellow crystals. ^1H NMR (CD_2Cl_2, −20 °C): δ 1.03 (d, $^2J_{PH} = 8.8$ Hz, $^3J_{PtH} = 28.3$ Hz, 6H, PMe), 1.67 (d, $^2J_{PH} = 8.8$ Hz, $^3J_{PtH} = 16.6$ Hz, 6H, PMe), 3.68 (s, 3H, MeO), 6.49 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ar), 6.55 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ar), 7.17−7.48 (m, 19H, Ph), 7.70 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 14.7 (d, $^1J_{PC} = 28$ Hz, $^2J_{PtC} = 26$ Hz, PMe), 16.2 (dd, $J_{PC} = 36$ and 5 Hz, $^2J_{PtC} = 35$ Hz, PMe), 55.3 (s, OMe), 110.9 (dd, $^2J_{PC} = 127$ and 20 Hz, ArC≡*C*), 113.0 (s, Ar), 115.5 (dd, $^3J_{PC} = 31$ and 2 Hz, Ar*C*≡C), 120.8 (s, Ar), 127.1 (s, SiPh), 127.4 (s, SiPh), 128.5 (d, $^3J_{PC} = 10$ Hz, PPh), 128.6 (d, $^3J_{PC} = 11$ Hz, PPh), 129.6 (s, PPh), 130.4 (s, PPh), 130.9 (d, $^2J_{PC} = 10$ Hz, PPh), 131.5 (d, $^2J_{PC} = 12$ Hz, $^3J_{PtC} = 23$ Hz, PPh), 132.1 (s, Ar), 137.2 (s, $^3J_{PtC} = 20$ Hz, SiPh), 137.4 (d, PPh), 137.8 (dd, $J_{PC} = 52$ and 5 Hz, PPh), 145.6 (d, $^3J_{PC} = 5$ Hz, $^2J_{PtC} = 45$ Hz, SiPh), 157.4 (s, Ar). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −14.3 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 2663$ Hz), −6.3 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 1137$ Hz, $^2J_{SiP} = 179$ Hz). Anal. Calcd for $C_{43}H_{44}OP_2PtSi$: C, 59.92; H, 5.15. Found: C, 59.66; H, 4.88.

2c. Yield 65%, pale yellow crystals. ^1H NMR (CD_2Cl_2, −20 °C): δ 1.03 (d, $^2J_{PH} = 9.3$ Hz, $^3J_{PtH} = 28.3$ Hz, 6H, PMe), 1.67 (d, $^2J_{PH} = 8.8$ Hz, $^3J_{PtH} = 16.6$ Hz, 6H, PMe), 2.18 (s, 3H, Me), 6.51 (d, $^3J_{HH} = 7.6$ Hz, 2H, Ar), 6.85 (d, $^3J_{HH} = 7.6$ Hz, 2H, Ar), 7.15−7.50 (m, 19H, Ph), 7.71 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 14.7 (d, $^1J_{PC} = 28$ Hz, $^2J_{PtC} = 26$ Hz, PMe), 16.2 (dd, $J_{PC} = 36$ and 5 Hz, $^2J_{PtC} = 36$ Hz, PMe), 21.3 (s, Me), 112.4 (dd, $^2J_{PC} = 127$ and 19 Hz, ArC≡*C*), 115.9 (dd, $^3J_{PC} = 29$ and 2 Hz, $^2J_{PtC} = 317$ Hz, Ar*C*≡C), 125.3 (s, $^3J_{PtC} = 24$ Hz, Ar), 127.1 (s, SiPh), 127.4 (s, SiPh), 128.4 (s, Ar), 128.5 (d, $^3J_{PC} = 10$ Hz, PPh), 128.6 (d, $^3J_{PC} = 10$ Hz, PPh), 129.6 (s, PPh), 130.4 (s, PPh), 130.7 (s, Ar), 130.9 (d, $^2J_{PC} = 10$ Hz, PPh), 131.4 (d, $^2J_{PC} = 12$ Hz, $^3J_{PtC} = 23$ Hz, PPh), 135.2 (s, Ar), 137.2 (s, $^3J_{PtC} = 20$ Hz, SiPh), 137.2 (d, $^1J_{PC} = 60$ Hz, PPh), 137.8 (dd, $J_{PC} = 51$ and 5 Hz, PPh), 145.7 (d, $^3J_{PC} = 6$ Hz, $^2J_{PtC} = 46$ Hz, SiPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −14.1 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 2665$ Hz), −6.0 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 1134$ Hz, $^2J_{SiP} = 177$ Hz). Anal. Calcd for $C_{43}H_{44}P_2PtSi$: C, 61.05; H, 5.24. Found: C, 60.85; H, 5.13.

2d. Yield 73%, pale yellow crystals. ^1H NMR (CD_2Cl_2, −20 °C): δ 1.04 (d, $^2J_{PH} = 9.2$ Hz, $^3J_{PtH} = 28.0$ Hz, 6H, PMe), 1.64 (d, $^2J_{PH} = 8.4$ Hz, $^3J_{PtH} = 17.2$ Hz, 6H, PMe), 6.47 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ar), 6.97 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ar), 7.18−7.48 (m, 19H, Ph), 7.70 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 14.7 (d, $^1J_{PC} = 26$ Hz, $^2J_{PtC} = 26$ Hz, PMe), 16.1 (dd, $J_{PC} = 36$ and 4 Hz, $^2J_{PtC} = 36$ Hz, PMe), 114.7 (dd, $^3J_{PC} = 30$ and 3 Hz, Ar*C*≡C), 115.6 (dd, $^2J_{PC} = 126$ and 18 Hz, ArC≡*C*), 126.9 (s, $^3J_{PtC} = 24$ Hz, Ar), 127.2 (s, SiPh), 127.5 (s, SiPh), 127.8 (s, Ar), 128.6 (d, $^3J_{PC} = 8$ Hz, PPh), 128.7 (d, $^3J_{PC} = 10$ Hz, PPh), 129.7 (s, PPh), 130.5 (s, PPh), 131.0 (d, $^2J_{PC} = 10$ Hz, $^3J_{PtC} = 27$ Hz, PPh), 131.4 (d, $^2J_{PC} = 12$ Hz, $^3J_{PtC} = 23$ Hz, PPh), 132.2 (s, Ar), 132.2 (s, Ar), 137.1 (s, $^3J_{PtC} = 20$ Hz, SiPh), 137.2 (d, PPh), 137.6 (dd, $J_{PC} = 51$ and 5 Hz, PPh), 145.4 (d, $^3J_{PC} = 5$ Hz, $^2J_{PtC} = 45$ Hz, SiPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −14.2 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 2664$ Hz), −6.1 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 1139$ Hz, $^2J_{SiP} = 177$ Hz). Anal. Calcd for $C_{42}H_{41}P_2PtSiCl$: C, 58.23; H, 4.77. Found: C, 58.03; H, 4.64.

2e. Yield 59%, pale yellow crystals. ^1H NMR (CD_2Cl_2, −20 °C): δ 1.03 (d, $^2J_{PH} = 9.2$ Hz, $^3J_{PtH} = 28.6$ Hz, 6H, PMe), 1.63 (d, $^2J_{PH} = 8.4$ Hz, $^3J_{PtH} = 16.8$ Hz, 6H, PMe), 6.39 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ar), 7.11 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ar), 7.18−7.47 (m, 19H, Ph), 7.68 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 14.7 (d, $^1J_{PC} = 28$ Hz, $^2J_{PtC} = 23$ Hz, PMe), 16.1 (dd, $J_{PC} = 36$ and 5 Hz, $^2J_{PtC} = 36$ Hz, PMe), 114.8 (dd, $^3J_{PC} = 31$ and 5 Hz, Ar*C*≡C), 116.0 (dd, $^2J_{PC} = 128$ and 18 Hz, ArC≡*C*), 118.7 (s, Ar), 127.1 (s, SiPh), 127.5 (s, SiPh), 128.5 (d, $^3J_{PC} = 8$ Hz, PPh), 128.7 (d, $^3J_{PC} = 10$ Hz, PPh), 129.7 (s, PPh), 130.5 (s, PPh), 130.7 (s, Ar), 130.9 (d, $^2J_{PC} = 10$ Hz, PPh), 131.4 (d, $^2J_{PC} = 12$ Hz, $^3J_{PtC} = 23$ Hz, PPh), 132.5 (s, Ar), 137.1 (s, $^3J_{PtC} = 20$ Hz, SiPh), 137.2 (d, PPh), 137.6 (dd, $J_{PC} = 51$ and 5 Hz, PPh), 145.4 (d, $^3J_{PC} = 5$ Hz, $^2J_{PtC} = 46$ Hz, SiPh). One C_6H_4Br group carbon was not detected. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −14.2 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 2667$ Hz), −6.1 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 1139$ Hz, $^2J_{SiP} = 177$ Hz). Anal. Calcd for $C_{42}H_{41}P_2PtSiBr \cdot 0.5CH_2Cl_2$: C, 53.55; H, 4.44. Found: C, 53.12; H, 4.14.

2f. Yield 70%, yellow crystals. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 1.06 (d, $^2J_{PH}$ = 8.8 Hz, $^3J_{PtH}$ = 28.0 Hz, 6H, PMe), 1.62 (d, $^2J_{PH}$ = 8.3 Hz, $^3J_{PtH}$ = 16.1 Hz, 6H, PMe), 6.57 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ar), 7.15−7.50 (m, 21H, Ph), 7.68 (m, 6H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 14.7 (d, $^1J_{PC}$ = 28 Hz, $^2J_{PtC}$ = 23 Hz, PMe), 16.1 (dd, J_{PC} = 36 and 5 Hz, $^2J_{PtC}$ = 36 Hz, PMe), 107.6 (s, Ar), 115.3 (dd, $^3J_{PC}$ = 30 and 4 Hz, Ar*C*≡C), 119.9 (s, CN), 122.7 (dd, $^2J_{PC}$ = 126 and 19 Hz, ArC≡*C*), 127.2 (s, SiPh), 127.6 (s, SiPh), 128.6 (d, $^3J_{PC}$ = 8 Hz, PPh), 128.8 (d, $^3J_{PC}$ = 10 Hz, PPh), 129.8 (s, PPh), 130.6 (s, PPh), 131.0 (d, $^2J_{PC}$ = 10 Hz, PPh), 131.2 (s, Ar), 131.5 (d, $^2J_{PC}$ = 12 Hz, PPh), 131.5 (s, Ar), 133.1 (s, $^3J_{PtC}$ = 22 Hz, Ar), 137.0 (d, PPh), 137.1 (s, $^3J_{PtC}$ = 18 Hz, SiPh), 137.5 (dd, J_{PC} = 51 and 4 Hz, PPh), 145.1 (d, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 45 Hz, SiPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −14.2 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 2664 Hz), −6.1 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 1146 Hz, $^2J_{SiP}$ = 174 Hz). Anal. Calcd for $C_{43}H_{41}NP_2PtSi$: C, 60.27; H, 4.82; N, 1.63. Found: C, 59.95; H, 4.67; N, 1.78.

2g. Yield 55%, pale yellow crystals. ^{1}H NMR (CD_2Cl_2, −30 °C): δ 1.05 (d, $^2J_{PH}$ = 8.8 Hz, $^3J_{PtH}$ = 28.0 Hz, 6H, PMe), 1.67 (d, $^2J_{PH}$ = 8.0 Hz, $^3J_{PtH}$ = 16.0 Hz, 6H, PMe), 3.75 (s, 9H, OMe), 6.66 (d, $^3J_{HH}$ = 6.8 Hz, 2H, Ph), 6.79 (d, $^3J_{HH}$ = 7.2 Hz, 6H, Ar), 7.03 (m, 3H, Ph), 7.20−7.65 (m, 16H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −30 °C): δ 14.6 (d, $^1J_{PC}$ = 28 Hz, $^2J_{PtC}$ = 23 Hz, PMe), 16.0 (dd, J_{PC} = 35 and 4 Hz, $^2J_{PtC}$ = 40 Hz, PMe), 55.1 (s, OMe), 112.5 (s, SiAr), 113.9 (dd, $^2J_{PC}$ = 127 and 20 Hz, PhC≡*C*), 115.5 (dd, $^3J_{PC}$ = 31 and 3 Hz, Ph*C*≡C), 125.2 (s, Ph), 127.6 (s, Ph), 128.3 (s, $^3J_{PtC}$ = 24 Hz, Ph), 128.4 (d, $^3J_{PC}$ = 8 Hz, PPh), 128.6 (d, $^3J_{PC}$ = 10 Hz, PPh), 129.4 (s, PPh), 130.4 (s, PPh), 130.7 (d, $^2J_{PC}$ = 10 Hz, PPh), 130.8 (s, Ph), 131.4 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 136.5 (d, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 46 Hz, SiAr), 137.3 (dd, J_{PC} = 41 and 5 Hz, PPh), 137.4 (d, PPh), 138.2 (s, $^3J_{PtC}$ = 18 Hz, SiAr), 159.0 (s, SiAr). ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C): δ −13.5 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 2667 Hz), −5.6 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 1080 Hz, $^2J_{SiP}$ = 176 Hz). Anal. Calcd for $C_{45}H_{48}O_3P_2PtSi$: C, 58.62; H, 5.25. Found: C, 58.58; H, 5.23.

2h. Yield 77%, white crystalline solid. ^{1}H NMR (CD_2Cl_2, −30 °C): δ 1.05 (d, $^2J_{PH}$ = 8.8 Hz, $^3J_{PtH}$ = 27.3 Hz, 6H, PMe), 1.66 (d, $^2J_{PH}$ = 7.3 Hz, $^3J_{PtH}$ = 16.6 Hz, 6H, PMe), 2.31 (s, 9H, Me), 6.56 (d, $^3J_{HH}$ = 6.3 Hz, 2H, Ar), 6.95−7.65 (m, 25H, Ar and Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −30 °C): δ 14.5 (d, $^1J_{PC}$ = 26 Hz, $^2J_{PtC}$ = 26 Hz, PMe), 15.9 (dd, J_{PC} = 35 and 5 Hz, $^2J_{PtC}$ = 40 Hz, PMe), 21.4 (s, Me), 113.8 (dd, $^2J_{PC}$ = 126 and 21 Hz, PhC≡*C*), 115.2 (dd, $^3J_{PC}$ = 33 and 3 Hz, Ph*C*≡C), 125.2 (s, Ph), 127.6 (s, Ph), 127.8 (s, SiPh), 128.4 (d, $^3J_{PC}$ = 8 Hz, PPh), 128.6 (d, $^3J_{PC}$ = 10 Hz, PPh), 129.4 (s, PPh), 130.4 (s, PPh), 130.6 (d, $^2J_{PC}$ = 9 Hz, PPh), 130.9 (s, Ph), 131.4 (d, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 22 Hz, PPh), 137.0 (s, SiAr), 137.0 (s, $^3J_{PtC}$ = 20 Hz, SiAr), 137.2 (d, PPh), 137.8 (dd, J_{PC} = 51 and 5 Hz, PPh), 142.0 (d, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 46 Hz, SiAr). One Ph carbon was not detected. ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C): δ −14.2 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 2661 Hz), −5.8 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 1095 Hz, $^2J_{SiP}$ = 176 Hz). Anal. Calcd for $C_{45}H_{48}P_2PtSi$: C, 61.84; H, 5.54. Found: C, 61.22; H, 5.16.

2i. Yield 78%, pale yellow crystals. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 1.11 (d, $^2J_{PH}$ = 8.8 Hz, $^3J_{PtH}$ = 28.8 Hz, 6H, PMe), 1.80 (d, $^2J_{PH}$ = 8.8 Hz, $^3J_{PtH}$ = 18.4 Hz, 6H, PMe), 6.45 (m, 2H, Ar), 7.00 (m, 3H, Ph), 7.25−7.51 (m, 16H, Ph), 7.65 (m, 6H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 15.0 (d, $^1J_{PC}$ = 30 Hz, $^2J_{PtC}$ = 27 Hz, PMe), 16.6 (dd, J_{PC} = 35 and 5 Hz, $^2J_{PtC}$ = 36 Hz, PMe), 111.7 (dd, $^2J_{PC}$ = 126 and 20 Hz, PhC≡*C*), 117.2 (dd, $^3J_{PC}$ = 30 and 3 Hz, $^2J_{PtC}$ = 309 Hz, Ph*C*≡C), 123.7 (q, $^3J_{FC}$ = 3 Hz, SiAr), 125.8 (s, Ph), 127.9 (s, Ph), 128.9 (d, $^3J_{PC}$ = 10 Hz, PPh), 129.1 (q, $^3J_{FC}$ = 31 Hz, SiAr), 130.2 (s, PPh), 130.5 (s, Ph), 130.8 (s, PPh), 131.0 (d, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 131.3 (d, $^2J_{PC}$ = 13 Hz, $^3J_{PtC}$ = 21 Hz, PPh), 136.7 (dd, J_{PC} = 52 and 3 Hz, PPh), 136.8 (d, $^1J_{PC}$ = 38 Hz, PPh), 137.3 (s, $^3J_{PtC}$ = 20 Hz, SiAr), 149.7 (d, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 45 Hz, SiAr). One Ph group carbon was not detected. ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −14.7 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 2624 Hz), −6.2 (d, $^2J_{PP}$ = 23 Hz, $^1J_{PtP}$ = 1281 Hz, $^2J_{SiP}$ = 208 Hz). Anal. Calcd for $C_{45}H_{39}P_2PtSiF_9$: C, 52.18; H, 3.79. Found: C, 51.93; H, 3.72.

Kinetic Study of Reductive Elimination. A typical procedure (run 2 in Table 1) is as follows. Complex **2a** (15.0 mg, 18.0 mmol) and $MeSiPh_3$ (1.7 mg, 6.2 mmol) as an internal standard were placed in an NMR sample tube with a rubber septum cap, and the system was purged with nitrogen gas at room temperature. Benzene-d_6 (0.60 mL) was added, and the sample tube was placed in an NMR sample probe controlled to 35.0(1) °C. The time course of the reductive elimination was followed by measuring the relative peak integration of the methyl proton signals of the product Pt(PhC≡CSiPh$_3$)(PMe$_2$Ph)$_2$ (**3a**) (δ 0.93) and $MeSiPh_3$ (δ 0.73).

Complex **3a** was isolated and characterized by NMR spectroscopy and elemental analysis. Thus, the solution of **2a** (50 mg, 60 mmol) in benzene (2 mL) was heated at 45 °C for 3 h. The solution was concentrated to dryness. Et_2O (0.5 mL) and pentane (5 mL) were added, and the resulting pale yellow suspension was stirred at room temperature for 1 h. The precipitate was collected by filtration and dried under vacuum (23 mg, 46% yield).

3a. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.24 (d, $^2J_{PH}$ = 6.8 Hz, $^3J_{PtH}$ = 28.8 Hz, 6H, PMe), 1.54 (d, $^2J_{PH}$ = 6.8 Hz, $^3J_{PtH}$ = 30.4 Hz, 6H, PMe), 6.96 (m, 5H, Ph), 7.20−7.38 (m, 15H, Ph), 7.50−7.62 (m, 4H, Ph), 7.69 (m, 6H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 19.6 (dd, J_{PC} = 23 and 8 Hz, $^2J_{PtC}$ = 46 Hz, PMe), 20.5 (dd, J_{PC} = 22 and 10 Hz, $^2J_{PtC}$ = 50 Hz, PMe), 115.9 (d, $^2J_{PC}$ = 43 Hz, Ph*C*≡C), 126.1 (s, Ph), 127.8 (s, Ph), 128.0 (s, SiPh), 128.5 (d, $^3J_{PC}$ = 8 Hz, PPh), 129.4 (d, $^4J_{PC}$ = 5 Hz, $^3J_{PtC}$ = 26 Hz, SiPh), 129.5 (s, SiPh, PPh, and Ph), 131.4 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 131.6 (d, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 136.5 (s, SiPh), 137.5 (s, Ph), 141.4 (dd, J_{PC} = 34 and 8 Hz, PPh), 141.7 (dd, J_{PC} = 48 and 8 Hz, PPh), 154.6 (dd, $^2J_{PC}$ = 51 and 5 Hz, C≡*C*Si). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ −12.5 (d, $^2J_{PP}$ = 37 Hz, $^1J_{PtP}$ = 3337 Hz), −12.8 (d, $^2J_{PP}$ = 37 Hz, $^1J_{PtP}$ = 3563 Hz). Anal. Calcd for $C_{42}H_{42}P_2PtSi$: C, 60.64; H, 5.09. Found: C, 60.54; H, 5.02.

The reductive elimination products **3b**−**h** were not isolated, while their formation was confirmed by ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectroscopy.

3b. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.23 (d, $^2J_{PH}$ = 6.8 Hz, $^3J_{PtH}$ = 27.8 Hz, 6H, PMe), 1.56 (d, $^2J_{PH}$ = 7.3 Hz, $^3J_{PtH}$ = 29.8 Hz, 6H, PMe), 3.68 (s, 3H, OMe), 6.46 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 6.82 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 7.10−7.75 (m, 25H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 19.8 (dd, J_{PC} = 22 and 10 Hz, $^2J_{PtC}$ = 45 Hz, PMe), 20.5 (dd, J_{PC} = 22 and 10 Hz, $^2J_{PtC}$ = 45 Hz, PMe), 55.6 (s, OMe), 114.0 (s, Ar), 114.3 (d, $^2J_{PC}$ = 50 Hz, Ar*C*≡C), 128.0 (s, SiPh), 128.4 (d, $^3J_{PC}$ = 8 Hz, PPh), 129.5 (s, SiPh), 129.5 (d, $^4J_{PC}$ = 5 Hz, $^3J_{PtC}$ = 26 Hz, SiPh), 129.6 (s, PPh), 131.4 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 131.6 (d, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 131.6 (s, Ar), 136.5 (s, SiPh), 137.7 (s, Ar), 141.5 (dd, J_{PC} = 34 and 8 Hz, PPh), 141.7 (dd, J_{PC} = 48 and 8 Hz, PPh), 158.1 (s, Ar), 154.0 (d, $^2J_{PC}$ = 51 Hz, C≡*C*Si). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ −12.4 (d, $^2J_{PP}$ = 38 Hz, $^1J_{PtP}$ = 3319 Hz), −12.7 (d, $^2J_{PP}$ = 38 Hz, $^1J_{PtP}$ = 3570 Hz).

3c. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.23 (d, $^2J_{PH}$ = 6.8 Hz, $^3J_{PtH}$ = 28.3 Hz, 6H, PMe), 1.55 (d, $^2J_{PH}$ = 7.3 Hz, $^3J_{PtH}$ = 29.3 Hz, 6H, PMe), 2.20 (s, 3H, Me), 6.77 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 6.83 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 7.20−7.75 (m, 25H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 19.7 (dd, J_{PC} = 22 and 10 Hz, $^2J_{PtC}$ = 45 Hz, PMe), 20.5 (dd, J_{PC} = 20 and 12 Hz, $^2J_{PtC}$ = 48 Hz, PMe), 21.4 (s, Me), 114.9 (d, $^2J_{PC}$ = 50 Hz, Ar*C*≡C), 128.0 (s, SiPh), 128.5 (d, $^3J_{PC}$ = 8 Hz, PPh), 128.6 (s, Ar), 129.5 (s, SiPh, PPh and Ar), 129.8 (d, $^4J_{PC}$ = 5 Hz, $^3J_{PtC}$ = 26 Hz, SiPh), 131.5 (d, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 131.7 (d, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 23 Hz, PPh), 136.0 (s, Ar), 136.5 (s, SiPh), 137.7 (s, Ar), 141.4 (dd, J_{PC} = 34 and 8 Hz, PPh), 141.8 (dd, J_{PC} = 48 and 8 Hz, PPh), 154.3 (d, $^2J_{PC}$ = 50 Hz, C≡*C*Si). ^{31}P{^{1}H}

NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −11.9 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3571 Hz), −12.2 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3302 Hz).

3d. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.27 (d, $^{2}J_{\mathrm{PH}}$ = 6.8 Hz, $^{3}J_{\mathrm{PtH}}$ = 28.8 Hz, 6H, PMe), 1.54 (d, $^{2}J_{\mathrm{PH}}$ = 7.3 Hz, $^{3}J_{\mathrm{PtH}}$ = 29.3 Hz, 6H, PMe), 6.80 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 2H, Ar), 6.90 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 2H, Ar), 7.10−7.75 (m, 25H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 19.7 (dd, J_{PC} = 25 and 7 Hz, $^{2}J_{\mathrm{PtC}}$ = 43 Hz, PMe), 20.5 (dd, J_{PC} = 23 and 8 Hz, $^{2}J_{\mathrm{PtC}}$ = 45 Hz, PMe), 117.7 (d, $^{2}J_{\mathrm{PC}}$ = 45 Hz, Ar*C*≡C), 127.9 (s, Ar), 128.1 (s, SiPh), 128.6 (d, $^{3}J_{\mathrm{PC}}$ = 8 Hz, PPh), 129.6 (s, SiPh, PPh, and Ar), 130.9 (d, $^{4}J_{\mathrm{PC}}$ = 5 Hz, $^{3}J_{\mathrm{PtC}}$ = 26 Hz, SiPh), 130.9 (s, Ar), 131.4 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 131.6 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 20 Hz, PPh), 136.4 (s, SiPh), 137.3 (s, Ar), 141.2 (dd, J_{PC} = 46 and 7 Hz, PPh), 141.5 (dd, J_{PC} = 45 and 7 Hz, PPh), 153.5 (d, $^{2}J_{\mathrm{PC}}$ = 51 Hz, C≡*C*Si). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −12.7 (d, $^{2}J_{\mathrm{PP}}$ = 37 Hz, $^{1}J_{\mathrm{PtP}}$ = 3341 Hz), −13.1 (d, $^{2}J_{\mathrm{PP}}$ = 37 Hz, $^{1}J_{\mathrm{PtP}}$ = 3555 Hz).

3e. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.26 (d, $^{2}J_{\mathrm{PH}}$ = 6.8 Hz, $^{3}J_{\mathrm{PtH}}$ = 28.8 Hz, 6H, PMe), 1.53 (d, $^{2}J_{\mathrm{PH}}$ = 7.3 Hz, $^{3}J_{\mathrm{PtH}}$ = 29.8 Hz, 6H, PMe), 6.72 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 2H, Ar), 7.02 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 2H, Ar), 7.10−7.75 (m, 25H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 19.7 (dd, J_{PC} = 25 and 7 Hz, $^{2}J_{\mathrm{PtC}}$ = 43 Hz, PMe), 20.5 (dd, J_{PC} = 23 and 8 Hz, $^{2}J_{\mathrm{PtC}}$ = 45 Hz, PMe), 118.2 (d, $^{2}J_{\mathrm{PC}}$ = 43 Hz, Ar*C*≡C), 119.5 (s, Ar), 128.0 (s, SiPh), 128.5 (d, $^{3}J_{\mathrm{PC}}$ = 8 Hz, PPh), 129.6 (s, SiPh and PPh), 130.5 (d, $^{4}J_{\mathrm{PC}}$ = 5 Hz, $^{3}J_{\mathrm{PtC}}$ = 26 Hz, SiPh), 130.8 (s, Ar), 130.9 (s, Ar), 131.4 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 131.6 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 136.4 (s, SiPh), 137.2 (s, Ar), 141.3 (dd, J_{PC} = 40 and 8 Hz, PPh), 141.6 (dd, J_{PC} = 48 and 8 Hz, PPh), 153.5 (d, $^{2}J_{\mathrm{PC}}$ = 51 Hz, C≡*C*Si). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −12.7 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3342 Hz), −13.2 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3552 Hz).

3f. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.28 (d, $^{2}J_{\mathrm{PH}}$ = 7.3 Hz, $^{3}J_{\mathrm{PtH}}$ = 29.3 Hz, 6H, PMe), 1.51 (d, $^{2}J_{\mathrm{PH}}$ = 7.8 Hz, $^{3}J_{\mathrm{PtH}}$ = 29.3 Hz, 6H, PMe), 6.87 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 2H, Ar), 7.18 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, 2H, Ar), 7.20−7.75 (m, 25H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 19.5 (dd, J_{PC} = 27 and 3 Hz, $^{2}J_{\mathrm{PtC}}$ = 40 Hz, PMe), 20.4 (dd, J_{PC} = 27 and 5 Hz, $^{2}J_{\mathrm{PtC}}$ = 43 Hz, PMe), 108.4 (s, Ar), 120.1 (s, CN), 121.7 (dd, $^{2}J_{\mathrm{PC}}$ = 53 and 8 Hz, Ar*C*≡C), 128.1 (s, SiPh), 128.6 (d, $^{3}J_{\mathrm{PC}}$ = 8 Hz, PPh), 128.8 (d, $^{4}J_{\mathrm{PC}}$ = 5 Hz, $^{3}J_{\mathrm{PtC}}$ = 26 Hz, SiPh), 129.7 (s, SiPh and PPh), 131.1 (d, $^{2}J_{\mathrm{PC}}$ = 13 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 131.5 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 131.6 (s, Ar), 136.3 (s, SiPh), 136.9 (s, Ar), 140.7 (dd, J_{PC} = 41 and 3 Hz, PPh), 141.1 (dd, $^{1}J_{\mathrm{PC}}$ = 40 Hz, PPh), 153.9 (dd, $^{2}J_{\mathrm{PC}}$ = 61 and 10 Hz, C≡*C*Si). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −12.6 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3409 Hz), −13.4 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3520 Hz).

3g. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.29 (d, $^{2}J_{\mathrm{PH}}$ = 5.9 Hz, $^{3}J_{\mathrm{PtH}}$ = 27.3 Hz, 6H, PMe), 1.57 (d, $^{2}J_{\mathrm{PH}}$ = 6.3 Hz, $^{3}J_{\mathrm{PtH}}$ = 28.8 Hz, 6H, PMe), 3.78 (s, 9H, OMe), 6.80 (d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 6H, Ar), 6.99 (m, 5H, Ph), 7.32 (m, 6H, Ph), 7.59 (d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 10H, Ar and Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 19.8 (dd, J_{PC} = 25 and 6 Hz, $^{2}J_{\mathrm{PtC}}$ = 43 Hz, PMe), 20.5 (dd, J_{PC} = 23 and 8 Hz, $^{2}J_{\mathrm{PtC}}$ = 43 Hz, PMe), 55.5 (s, OMe), 113.7 (s, SiAr), 117.1 (d, $^{2}J_{\mathrm{PC}}$ = 44 Hz, Ph*C*≡C), 126.0 (s, Ph), 127.9 (s, Ph), 128.5 (d, $^{3}J_{\mathrm{PC}}$ = 8 Hz, PPh), 129.0 (s, PPh), 129.5 (s, Ph), 129.5 (d, $^{4}J_{\mathrm{PC}}$ = 5 Hz, $^{3}J_{\mathrm{PtC}}$ = 26 Hz, SiAr), 131.4 (d, $^{2}J_{\mathrm{PC}}$ = 12 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 131.6 (d, $^{2}J_{\mathrm{PC}}$ = 10 Hz, $^{3}J_{\mathrm{PtC}}$ = 20 Hz, PPh), 137.5 (s, Ph), 137.9 (s, SiAr), 137.5 (s, Ph), 141.5 (dd, J_{PC} = 34 and 6 Hz, PPh), 141.8 (dd, J_{PC} = 33 and 4 Hz, PPh), 153.5 (d, $^{2}J_{\mathrm{PC}}$ = 51 Hz, C≡*C*Si), 161.0 (s, SiAr). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −12.3 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3343 Hz), −12.7 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3553 Hz).

3h. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 1.27 (d, $^{2}J_{\mathrm{PH}}$ = 6.8 Hz, $^{3}J_{\mathrm{PtH}}$ = 28.8 Hz, 6H, PMe), 1.54 (d, $^{2}J_{\mathrm{PH}}$ = 7.3 Hz, $^{3}J_{\mathrm{PtH}}$ = 29.8 Hz, 6H, PMe), 2.33 (s, 9H, Me), 6.98 (m, 5H, Ph), 7.09 (d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 6H, Ar), 7.30 (m, 6H, Ph), 7.57 (d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 10H, Ar and Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ 19.7 (dd, J_{PC} = 23 and 8 Hz, $^{2}J_{\mathrm{PtC}}$ = 43 Hz, PMe), 20.6 (dd, J_{PC} = 22 and 10 Hz, $^{2}J_{\mathrm{PtC}}$ = 46 Hz, PMe), 21.8 (s, Me), 116.6 (d, $^{2}J_{\mathrm{PC}}$ = 41 Hz, Ph*C*≡C), 126.0 (s, Ph), 127.8 (s, Ph), 128.5 (d, $^{3}J_{\mathrm{PC}}$ = 8 Hz, PPh), 128.8 (s, SiAr), 129.5 (s, PPh and Ph), 129.5 (d, $^{4}J_{\mathrm{PC}}$ = 5 Hz, $^{3}J_{\mathrm{PtC}}$ = 26 Hz, SiAr), 131.4 (d, $^{2}J_{\mathrm{PC}}$ = 10 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 131.6 (d, $^{2}J_{\mathrm{PC}}$ = 10 Hz, $^{3}J_{\mathrm{PtC}}$ = 23 Hz, PPh), 134.3 (s, Ph), 136.5 (s, SiAr), 139.3 (s, SiAr), 141.5 (dd, J_{PC} = 33 and 8 Hz, PPh), 141.9 (dd, J_{PC} = 38 and 8 Hz, PPh), 153.7 (dd, $^{2}J_{\mathrm{PC}}$ = 46 and 5 Hz, C≡*C*Si). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 20 °C): δ −12.4 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3343 Hz), −12.8 (d, $^{2}J_{\mathrm{PP}}$ = 38 Hz, $^{1}J_{\mathrm{PtP}}$ = 3558 Hz).

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