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Experimental and Theoretical Studies on the Platinum-Mediated Selective C(sp)−Si Bond Cleavage of Alkynylsilanes

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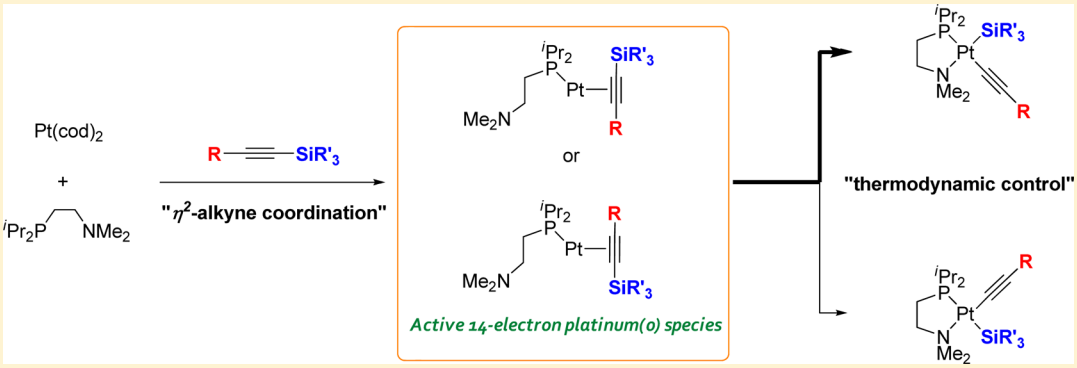
Supporting Information



ABSTRACT: A series of *cis*-alkynyl(silyl)platinum(II) complexes was prepared via the chemoselective C(sp)−Si bond cleavage of alkynylsilanes by a platinum(0) complex ligated with the P−N hemilabile bidentate ligand. The coordination of the triple bond to the platinum center triggers selective C(sp)−Si bond cleavage. Hammett plots of the $^{31}P\{^{1}H\}$ NMR spectroscopic properties (δ and J values) reflect an electronic effect on platinum(II) complexes; trans substituents of arylethynyl groups are influenced, but cis-positioned silyl groups are not affected, as evidenced by $^{29}Si\{^{1}H\}$ NMR. In comparison, Hammett plots show that C(sp)−Si bond cleavage rates are accelerated by electron-rich alkynylsilanes, which is opposite to the ordinary oxidative addition of aryl halides to transition metals often observed in catalytic cross-coupling reactions. A DFT calculation reveals that intermediates and transition states are stabilized by electron-rich alkynylsilanes and that the five-membered hemilabile P−N ligand is essential, in which a reactive electron-deficient 14-electron platinum(0) species is produced via the dissociation of nitrogen, giving rise to a monodentate phosphine coordination. Electron-rich alkynylsilanes allow decreased π back-donation from the platinum center to the ligand, accelerating the dissociation of the more labile nitrogen. Steric congestion between diisopropylphosphino and silyl groups thermodynamically disfavors C(sp)−Si bond cleavage.

INTRODUCTION

Organosilicon compounds have attracted considerable attention, owing to their low toxicity, high stability, low cost, and the ready availability of silicon, the second most abundant element.[1] In respect to the utilization of organosilicon compounds, for example, Hiyama coupling has served as a practical tool in the preparation of a series of complex natural products, pharmaceuticals, and agrochemicals.[2] Since Hiyama coupling requires the selective and effective activation of a strong C−Si bond (BDE ≈ 290 kJ/mol),[3] achieving this bond activation has been regarded as an extremely important research topic. Initially, the activation of C−Si bonds was achieved by using fluoride or alkoxide ions.[4] Another C−Si bond cleavage, the transition-metal-mediated activation of C−Si bonds, has recently received a great deal of attention as a superior method.[5] Also, transmetalation between C−Si bonds and M−X bonds (M = transition metals, X = halides or alkoxy groups),[6,7] intramolecular transformation,[8] electrophilic metalation/desilylation,[9] radical reactions,[10] silyl migration,[11] and other reactions[12] have been reported. Although the inert C(sp^3)−Si bond can also be cleaved in a wide variety of ways, to selectively cleave the target bond requires the use of transition metals. In general, C(sp^2)−Si bonds have been activated through an aromatic electrophilic substitution/desilylation sequence, and C(sp)−Si bonds can be cleaved via transmetalation or oxidative addition.

For practical purposes, the most straightforward method to cleave C−Si bonds is thought to be transition-metal-mediated oxidative addition. However, conventional transition-metal-mediated C−Si bond activation often takes place in an

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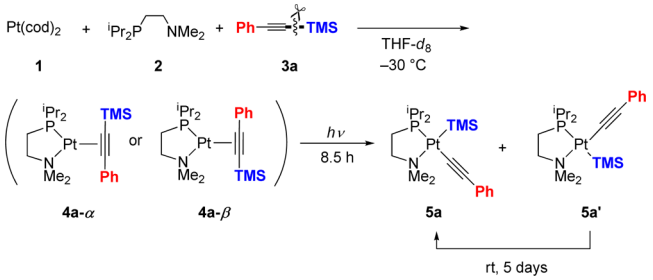
intramolecular manner, where only C−Si bonds in the auxiliary ligand are activated.[13] Despite recent advances in these fields, a mechanistic understanding of transition-metal-mediated C−Si bond cleavage remains elusive.

Jones and co-workers have reported the oxidative addition of the C(sp)−Si bond of alkynylsilane **3a** to a platinum(0) complex derived from $Pt(cod)_2$ (**1**) and the P−N bidentate ligand **2** (Scheme 1).[14] This bond activation proceeded under

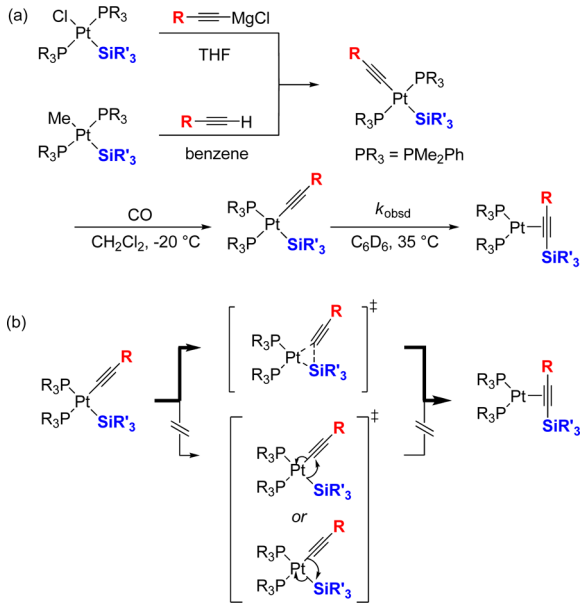
Scheme 1. C(sp)−Si Bond Activation of an Alkynylsilane under Thermal and Photochemical Conditions



both thermal (room temperature, 5 days) and photochemical (UV, −30 °C) conditions. However, under photochemical conditions the two conformational isomers **5a** and **5a′** were generated, while under thermal conditions only the thermodynamically stable isomer **5a** was formed, due to isomerization.

On the other hand, a notable study on Pt-mediated C(sp)−Si bond-forming reactions has been reported by Ozawa and co-workers (Scheme 2a).[15] They primarily prepared

Scheme 2. (a) Preparation of *cis*-Alkynyl(silyl)platinum(II) and Kinetic Study of C(sp)−Si Bond-Forming Reductive Elimination and (b) Proposed Mechanism for C(sp)−Si Bond-Forming Reductive Elimination



cis-alkynyl(silyl)platinum(II) complexes and examined the electronic effect of silyl and alkynyl ligands on reductive elimination rates using NMR. It was shown that the rates of reductive eliminations that formed C(sp)−Si bonds were affected by electron-withdrawing substituents in both silyl and alkynyl ligands. From this observation, they concluded that C(sp)−Si bond-forming reductive elimination involves a concerted three-center mechanism rather than a nucleophilic attack of one ligand on the other (Scheme 2b).

Herein, we report the details of the C(sp)−Si bond cleavage of a series of alkynylsilanes **3** by P−N ligated Pt(0) complexes. The reaction proceeded chemo- and regioselectively under thermal conditions, and the intermediates, η^2-alkyne-coordinating complexes and their regioisomers, were characterized by NMR spectroscopy. Additionally, we elucidated the effects of the substituents of the silyl and aryl groups in alkynylsilanes on chemical shifts and coupling constants in the $^{31}P\{^1H\}$ NMR spectra and on reaction rates of the C(sp)−Si bond cleavage. Theoretical calculations were performed to disclose the details of the oxidative addition of the C(sp)−Si bond on the Pt(0) complex assisted by the hemilabile P−N ligand **2**.

RESULTS AND DISCUSSION

Synthesis of *cis*-Alkynyl(silyl)platinum(II) Complexes by Oxidative Addition of Alkynylsilanes. We prepared platinum(II) complexes via C(sp)−Si bond cleavage with various alkynylsilanes **3** using the Jones method.[14] We found that the reactions proceeded smoothly at 70 °C and the C(sp)−Si bond cleavage was completed within 1 h, except for **3c**. The yields and representative chemical shifts and coupling constants are summarized in Table 1. On the basis of the H−Pt coupling constants (ca. 30 Hz) assigned to the Si−Me bond in the ^1H NMR spectra, as well as the reported $^{31}P\{^1H\}$ NMR data (δ 59.3, $^1J_{P-Pt}$ = 2760 Hz), in most cases *cis*-alkynyl(silyl)platinum(II) complexes **5-*α*** were exclusively formed in 19−72% yields, where silyl and arylethynyl groups were directly bonded to a platinum center. In particular, the Si−P coupling constants ($^2J_{Si-P}$) strongly support the mutual cis configuration of silyl and phosphine groups, as observed in a previous report.[14]

In the case of alkynylsilane **3c** (Table 1, entry 3), the corresponding alkynyl(silyl)platinum(II) complex was not formed. Judging from the reported coupling constants of $^1J_{P-Pt}$ = 3952 Hz for **4a-*α*** and **4a-*β*** in the $^{31}P\{^1H\}$ NMR spectrum,[14] we concluded that the η^2-alkyne-coordinating complex was mainly formed (**4c-*α*** and **4c-*β***: δ 65.6, $^1J_{P-Pt}$ = 4006 Hz) without subsequent C(sp)−Si bond cleavage, presumably owing to the sterically hindered triisopropylsilyl group. As shown in entries 1−3, the steric hindrance of the silyl groups caused drastic thermodynamic destabilization against C(sp)−Si bond cleavage. The destabilization of complex **5c-*α*** is attributed to the steric repulsion between diisopropylphosphino and silyl groups, evidenced by X-ray crystal structure analyses of the related complexes shown below. It is noteworthy that bond cleavage proceeded exclusively at the C(sp)−Si bond, even though alkynylsilanes bear aromatic and heteroaromatic groups that possess three types of C−Si bonds: C(sp)−Si, C(sp^2)−Si, and C(sp^3)−Si (entries 4 and 6). The aliphatic alkynylsilane 1-trimethylsilyl-1-propyne (**3g**) is susceptible to the present reaction (entry 7). The present reactions showed a wide range of functional group compatibility; both electron-deficient and electron-rich alkynylsilanes could be subjected to C(sp)−Si bond cleavage (entries 8−13).

X-ray crystal structure analyses were examined for the four platinum(II) complexes **5e-*α***, **5f-*α***, **5g-*α***, and **5l-*α***. ORTEP drawings are shown in Figure 1, and selected bond distances and bond angles are summarized in Table 2.

As shown in Table 2, the Pt−N bonds in complexes **5** (2.25(4)−2.309(4) Å) are longer than those in ordinary P−N

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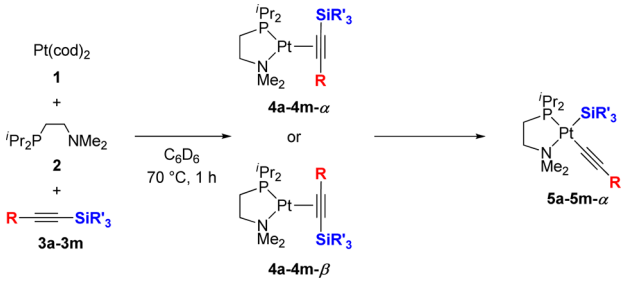
Table 1. Preparation of Alkynyl(silyl)platinum(II) Complexes Produced via C(sp)−Si Bond Cleavage of Alkynylsilanes 3[a]



	alkynylsilanes **3**				^{1}H NMR		^{29}Si{^{1}H} NMR		^{31}P{^{1}H} NMR	
entry	R	SiR′$_3$	complex	yield/%	δ(Si−Me)/ppm	$^{3}J_{H-Pt}$/Hz	δ/ppm	$^{2}J_{Si-P}$/Hz	δ/ppm	$^{1}J_{P-Pt}$/Hz
1	Ph	TMS	**5a-α**	60	0.89	31	−20.8	8	59.3	2757
2	Ph	TES	**5b-α**	61			−1.7	8	58.2	2765
3	Ph	TIPS	**4c-α** (or **4c-β**)						65.6	4006
4	Ph	$SiMe_2Ph$	**5d-α**	72	1.10	32	−22.4	8	57.8	2734
5	Ph	$SiMe_2Bn$	**5e-α**	48	0.70	*b*	−14.7	8	59.2	2748
6	Ph	$SiMe_2Th$	**5f-α**	69	1.13	32	−29.2	8	58.2	2728
7	Me	TMS	**5g-α**	42	0.85	31	−21.0	8	59.3	2740
8	4-$O_2NC_6H_4$	TMS	**5h-α**	58	0.78	30	−20.0	8	59.1	2772
9	4-$CF_3C_6H_4$	TMS	**5i-α**	22	0.83	30	−19.9	8	59.2	2770
10	4-ClC_6H_4	TMS	**5j-α**	22	0.84	31	−20.1	8	59.3	2766
11	4-MeC_6H_4	TMS	**5k-α**	49	0.86	30	−20.4	8	59.4	2754
12	4-$MeOC_6H_4$	TMS	**5l-α**	19	0.89	29	−20.4	8	59.4	2751
13	4-$Me_2NC_6H_4$	TMS	**5m-α**	56	0.88	30	−20.7	8	59.5	2745

[a]Abbreviations: TMS = trimethylsilyl, TES = triethylsilyl, TIPS = triisopropylsilyl, Bn = benzyl, Th = 2-thienyl. [b]A *J* value was not determined due to overlap with other signals.

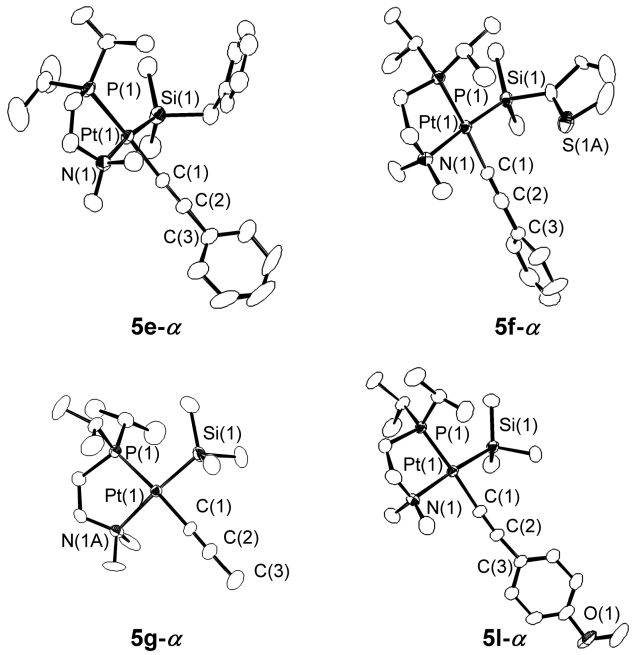


Figure 1. ORTEP drawings of *cis*-alkynyl(silyl)platinum(II) complexes **5e-α**, **5f-α**, **5g-α**, and **5l-α** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Since the 2-thienyl group in **5f-α** and the $-CH_2NMe_2$ portion of the P−N ligand in **5g-α** showed disorder, only one contributor is shown.

ligated platinum(II) complexes (2.09−2.20 Å)[16] but are similar to those in P−N ligated platinum(II) complexes possessing a silyl or methyl group trans to the Pt−N bond (~2.3 Å).[17] These results strongly suggest a significant trans influence from the silyl group. In addition, N−Pt−P angles are found to be only 83.5(2)−84.0(9)° and the P−Pt−Si angles are larger than the other bond angles around platinum, indicating steric repulsion between diisopropylphosphino and silyl groups.

Substituent Effect of Aryl Groups on the ^{31}P{^{1}H} NMR Properties. We next systematically examined the substituent effect of the aryl group in alkynylsilanes **3** on the ^{31}P{^{1}H} NMR properties of the produced platinum(II) complexes **5-α**. Ozawa and co-workers have reported a correlation between electronic factors and NMR properties for Hammett substituent constants at the para position (σ_p) in similar alkynyl(silyl)platinum(II) complexes (Scheme 2).[15] Plotting σ_p and the ^{31}P{^{1}H} NMR values (δ or *J*) of platinum(II) complexes **5a-α** and **5h-5m-α** showed a good correlation with the electronic properties of the aryl substituents. Figure 2 shows that the electronic effect (the trans influence) is transferred from the para substituents of aryl groups even beyond the ethynyl moieties.[18]

We also plotted Hammett substituent constants against the values of the ^{29}Si{^{1}H} NMR spectra, but no correlation with the electronic effect of para substituents on aryl groups was observed (see the Supporting Information). Hence, we concluded that the steric effect of the cis-positioned silyl groups and an electronic effect of the trans-positioned arylethynyl groups influence the thermodynamic stability of platinum(II) complexes **5-α** and their ^{31}P{^{1}H} NMR properties, respectively.

Kinetic Studies. Next, we examined the kinetics of oxidative addition, using ^{31}P{^{1}H} NMR spectroscopy. Although there are some equilibria, as previously reported by Jones,[14] the formation of η^2-alkyne-coordinating intermediates **4a-α**−**4m-α** (and **4a-β**−**4m-β**) is found to be quantitative and reasonably fast. We thus calculated kinetic constants (k_{obsd}) for the conversion of intermediates **4a-α**−**4m-α** (and **4a-β**−**4m-β**) into alkynyl(silyl)platinum complexes **5a-α**−**5m-α**. On the basis of

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in *cis*-Alkynyl(silyl)platinum(II) Complexes 5a-*α*,[14] 5e-*α*, 5f-*α*, 5g-*α*, and 5l-*α*

	5a-*α*	5e-*α*	5f-*α*	5g-*α*	5l-*α*
			Bond Lengths		
Pt(1)−P(1)	2.262(2)	2.2702(15)	2.274(2)	2.2534(10)	2.2658(10)
Pt(1)−N(1)	2.25(4)	2.298(3)	2.283(8)	2.309(4)	2.303(3)
Pt(1)−Si(1)	2.313(2)	2.3144(14)	2.310(2)	2.3026(15)	2.3139(11)
Pt(1)−C(1)	1.998(8)	2.010(5)	1.983(9)	2.004(4)	2.005(4)
C(1)−C(2)	1.199(11)	1.194(7)	1.201(14)	1.180(7)	1.191(6)
C(2)−C(3)	1.440(11)	1.429(7)	1.445(14)	1.493(9)	1.452(6)
			Bond Angles		
P(1)−Pt(1)−Si(1)	101.63(8)	103.12(5)	101.13(8)	100.46(4)	100.71(3)
Si(1)−Pt(1)−C(1)	82.9(2)	84.63(14)	84.2(2)	83.59(13)	83.06(13)
C(1)−Pt(1)−N(1)	91.8(9)	88.51(17)	91.2(3)	92.04(16)	92.71(15)
N(1)−Pt(1)−P(1)	84.0(9)	83.58(10)	83.5(2)	83.93(11)	83.65(8)
Pt(1)−C(1)−C(2)	176.4(7)	172.6(4)	178.7(9)	178.6(4)	175.0(4)
C(1)−C(2)−C(3)	176.3(9)	176.9(5)	178.0(11)	178.5(7)	174.4(4)

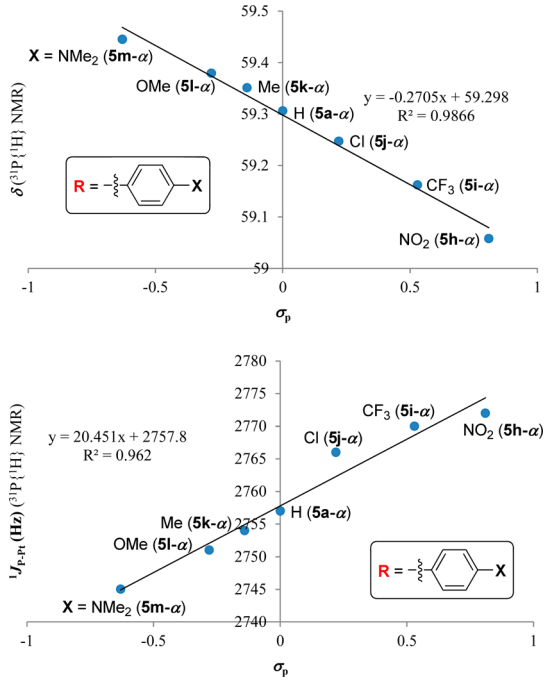
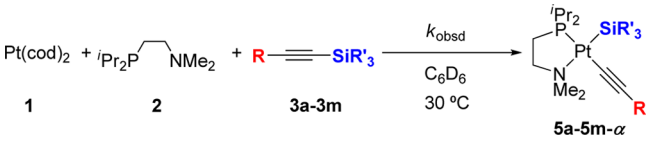


Figure 2. Dependence of the $^{31}P\{^1H\}$ NMR properties (δ and $^1J_{P-Pt}$) on the σ_p values of para substituents on the aryl groups (SiR′$_3$ = TMS).

Table 3. First-Order Rate Constants in C(sp)−Si Bond Cleavage Monitored by the $^{31}P\{^1H\}$ NMR Spectra[a]



1 2 3a-3m 5a-5m-*α*

	alkynylsilane 3				
entry		R	SiR′$_3$	$10^{-4}k_{obsd}/s^{-1}$	σ_p[19]
1	**3a**	Ph	TMS	1.057	0.00
2	**3b**	Ph	TES	2.397[b]	
3	**3c**	Ph	TIPS	∞	
4	**3d**	Ph	$SiMe_2Ph$	0.293	
5	**3e**	Ph	$SiMe_2Bn$	0.521	
6	**3f**	Ph	$SiMe_2Th$	0.252	
7	**3g**	Me	TMS	2.102[b]	
8	**3h**	4-$O_2NC_6H_4$	TMS	0.222	0.81
9	**3i**	4-$CF_3C_6H_4$	TMS	0.402	0.53
10	**3j**	4-ClC_6H_4	TMS	0.837	0.22
11	**3k**	4-MeC_6H_4	TMS	1.855	−0.14
12	**3l**	4-$MeOC_6H_4$	TMS	2.583[b]	−0.28
13	**3m**	4-$Me_2NC_6H_4$	TMS	6.462[c]	−0.63

[a]Abbreviations: TMS = trimethylsilyl, TES = triethylsilyl, TIPS = triisopropylsilyl, Bn = benzyl, Th = 2-thienyl. [b]0−3 h. [c]0−1 h.

this method, we monitored the reactions by following the $^{31}P\{^1H\}$ NMR over 6 h, and the calculated rate constants are given in Table 3. With regard to silyl groups, alkynylsilane **3b** with a triethylsilyl group reacted twice as fast as alkynylsilane **3a** with a trimethylsilyl group, but no C(sp)−Si bond activation occurred with alkynylsilane **3c** with a triisopropylsilyl group (vide supra) (entries 1−3). This peculiar trend indicates that the electronic and steric effects of the silyl groups may compete with as well as complement each other; a sterically hindered silyl group destabilizes the approach to a platinum center, whereas electron-rich silyl groups can accelerate oxidative addition. When one methyl group was replaced with a phenyl or 2-thienyl and benzyl groups in alkynylsilanes, kinetic constants diminished to a fourth of that for **3a** (entry 1 vs entries 4 and 6) and to half of that for **3a** (entry 1 vs entry 5), respectively. These results imply that substituents more sterically bulky and less electron donating than a methyl group suppress C(sp)−Si bond activation. We also examined the electronic effect of an R group. A methyl group accelerated rates twice as much a phenyl group (entry 1 vs entry 7). Accordingly, the reaction rates were calculated with alkynylsilanes **3** having para substituents on the benzene ring (entries 1 and 8−13). The Hammett plot shown in Figure 3 indicates that electron-rich alkynylsilanes accelerate the C(sp)−Si cleavage reaction. This tendency is completely opposite to the general order found in the oxidative addition of organic halides to low-valent transition metals.[20]

C(sp)−Si Bond Activation Mechanism. To explore C(sp)−Si bond activation in more detail, we investigated the possibility of a radical reaction. We confirmed the stability of alkynyl(silyl)platinum(II) complex **5a-*α*** when it was treated with TEMPO, finding that no decomposition took place. We then carried out the reactions of **1**, **2**, and **3a** in the presence of equimolar TEMPO, as shown in eq 1. After 1 h, the desired complex **5a-*α*** was formed in 58% yield, indicating that C(sp)−Si bond activation was not retarded by a radical scavenger.

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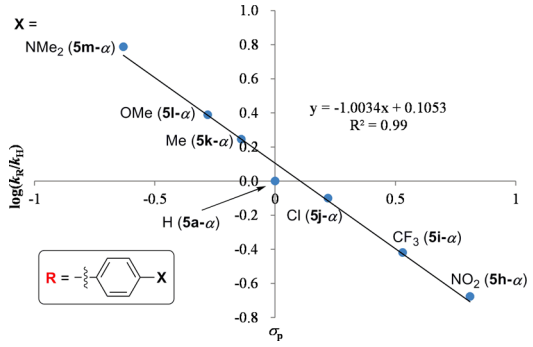
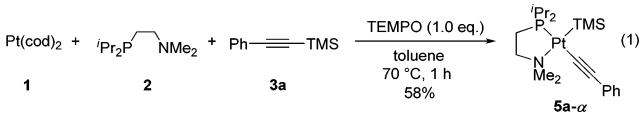


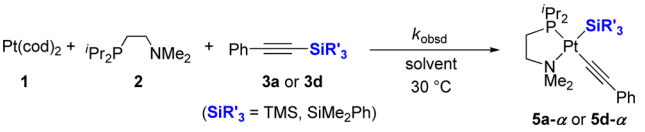
Figure 3. Hammett plot of rate constants (k_{obsd}) for oxidative addition of alkynylsilanes **3** versus σ_p values, corresponding to Table 3, entries 1 and 8−13.



Thus, we concluded that a radical pathway can be ruled out in the present platinum-mediated C(sp)−Si bond activation.

Next, we measured the reaction rate for C(sp)−Si bond cleavage in different solvents. If oxidative addition proceeds via polarized or ionized intermediates, the reaction might be accelerated in polar solvents. As shown in Table 4, in all cases

Table 4. Solvent and Silyl Substituent Effects on Kinetic Constants

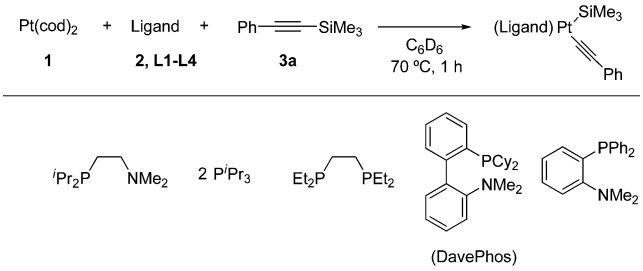


entry	SiR'_3	solvent	$10^{-4}k_{obsd}/s^{-1}$
1	TMS	C_6D_6	1.057
2	TMS	CD_3CN	0.320
3	TMS	DMF-d_7	0.248
4	$SiMe_2Ph$	C_6D_6	0.293
5	$SiMe_2Ph$	CD_3CN	0.168
6	$SiMe_2Ph$	DMF-d_7	0.120

the generation of the η^2-alkyne-coordinating complex is fast and quantitative. However, C(sp)−Si bond cleavage was somewhat retarded in polar solvents such as CD_3CN and DMF-d_7. From these results, the following two conclusions can be drawn. (1) Polarization in the C(sp)−Si bond cleavage step does not affect reaction rates at all. (2) The coordination of polar solvents to the vacant coordination site on platinum stabilizes the complexes. In particular, the latter factor indicates that hemilabile P−N ligand properties play a key role during the reaction. The transient platinum complex becomes an unsaturated species by the dissociation of nitrogen in the ligand, which could be more reactive for C(sp)−Si bond cleavage. We next screened various ligands in order to gain more insight into the mechanism of oxidative addition of alkynylsilanes **3**.

Ligand Effect. We examined the series of ligands **2** and **L1**−**L4** for C(sp)−Si bond activation of **3a** by measuring the ^1H and $^{29}Si\{^1H\}$ NMR spectra, because a characteristic singlet with platinum satellites ($^3J_{H-Pt}$) and a doublet with Si−P coupling ($^2J_{Si-P}$) are observed, respectively. The results are summarized

Table 5. Ligand Effect in C(sp)−Si Bond Activation

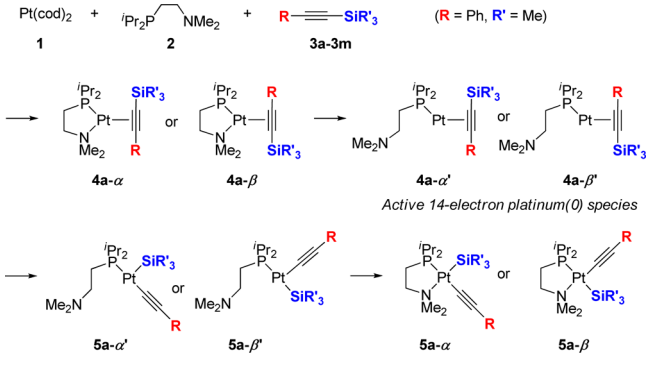


Ligand	**2**	**L1**	**L2**	**L3**	**L4**
Yield(%)	60	0	0	0	<1

in Table 5. However, no reaction occurred, except for **2**. Only a trace of a doublet (δ −15.9, $^2J_{Si-P}$ = 7.1 Hz) assigned to the desired Pt complex was detected in the $^{29}Si\{^1H\}$ NMR spectrum when **L4** was employed. These results undoubtedly indicate that an inherent property of ligand **2** controls some important functions in C(sp)−Si bond activation. Specifically, the following requirements must be considered for activation of the C(sp)−Si bond by the Pt(0) complex: the ligand must (1) be bidentate (vs **L1**), (2) have a P−N chelate system (vs **L2**), (3) consist of a five-membered chelation (vs **L3**), and (4) enable free rotation around a P−N coordination mode (vs **L4**). We assumed that these requirements must be implicated in the hemilabile property of the ligand employed. Thus, after the generation of η^2-alkyne-coordinating intermediates, a key 14-electron platinum(0) complex would be generated through the dissociation of nitrogen from the platinum center. Consequently, we hypothesized that the active species in C(sp)−Si bond activation is the 14-electron platinum(0) species possessing a monodentate phosphine ligand. Additionally, we supposed that electron-rich alkynylsilanes would be able to stabilize this inherently electron deficient 14-electron active species. To elucidate the reaction mechanism, we next explored theoretical calculations.

Theoretical Studies on the Reaction Mechanism of C(sp)−Si Bond Activation and Configuration of Complexes 5-α. To study the detailed mechanism of oxidative addition of alkynylsilanes **3** to Pt(0), we performed density functional theory (DFT) calculations for the proposed mechanism, as shown in Scheme 3. As the ideal structure, we

Scheme 3. Possible Mechanism of C(sp)−Si Bond Cleavage



tried to examine a 16-electron transition state in oxidative addition without the dissociation of nitrogen in the P−N ligand. However, we could not optimize the structure of such a species and observed that the nitrogen atom, a harder base than

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Table 6. Selected Distances (Å) in Each Optimized Structure in the Reaction of Pt(0)/P−N Ligand with Alkynylsilane 3a at the B3LYP (PCM, Solvent = Toluene)/SDD(Pt)-6-311G(d) Level[a]

	4a-α	TS1a-α	4a-α'	TS2a-α	5a-α'	TS3a-α	5a-α	4a-β	TS1a-β	4a-β'	TS2a-β	5a-β'	TS3a-β	5a-β
Pt−P	2.326	2.322	2.312	2.303	2.374	2.375	2.343	2.315	2.326	2.312	2.303	2.368	2.488	2.444
Pt−N	2.392	3.421	5.007	4.535	4.889	3.788	2.451	2.410	3.800	5.022	5.116	5.111	3.388	2.279
Pt−Si	3.683	3.590	3.566	2.694	2.352	2.349	2.367	3.757	3.585	3.575	2.712	2.354	2.385	2.429
Pt−C(α)	2.058	2.107	2.136	2.010	1.979	1.978	1.996	2.112	2.120	2.133	2.007	1.979	1.916	1.948
Pt−C(β)	2.070	2.099	2.114	3.135	3.201	3.199	3.219	2.016	2.102	2.110	3.134	3.202	3.136	3.169
C(α)−C(β)	1.298	1.271	1.263	1.235	1.225	1.225	1.224	1.300	1.267	1.264	1.236	1.225	1.224	1.223

[a] C(α) and C(β) denote the α and β carbons of the SiR'_3 group in **3a**, respectively.

phosphorus, tends to dissociate from the platinum center. We thus determined a 14-electron species to be the key part of the transition state in C(sp)−Si bond cleavage. Selected bond distances in each optimized structure are summarized in Table 6.

In comparison with representative atomic distances, the root-mean-square deviation of 0.102 Å shows that the DFT-optimized structures of the heavy atoms (not hydrogen) in **5a-*α*** are in good agreement with its X-ray crystal structure. The bond distance between platinum and the η^2-coordinating alkyne (Pt−C(α) and Pt−C(β)) becomes larger and the bond between C(α) and C(β) atoms becomes shorter in the nitrogen dissociation step (**4a-*α*** to **4a-*α*′**or **4a-*β*** to **4a-*β*′**). These changes indicate that π donation from the alkyne and/or π back-donation from platinum become weaker during the course of the nitrogen dissociation step. We discuss the latter issue in more detail below. In addition, the Pt−Si bond distance also becomes smaller in the same step, which implies that the approach of the C(sp)−Si bond onto platinum had already occurred.

As shown in Figure 4, the thermodynamic difference between coordination modes (α and β manner) in η^2-alkyne-coordinating intermediates **4a-*α*** and **4a-*β*** is extremely small.

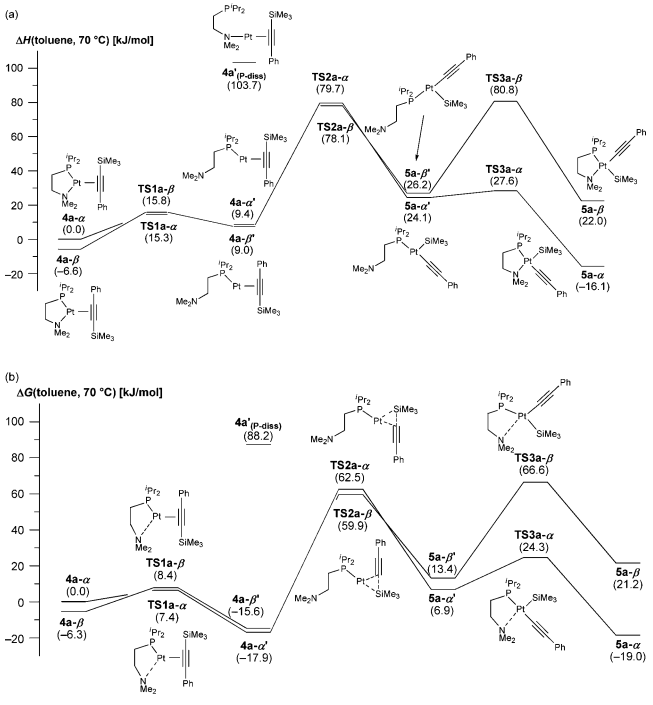

Figure 4. Thermodynamic plots for C(sp)−Si bond cleavage of alkynylsilane **3a** relative to **1** + **2** + **3a** (70 °C, in units of kJ/mol): (a) enthalpies; (b) Gibbs energies.

We also found that the activation barrier to the dissociation of nitrogen (**4a-*α*** to **TS1a-*α***; **4a-*β*** to **TS1a-*β***) is comparatively low ($\Delta\Delta G^{\ddagger}$: 7.4 kJ/mol for α selectivity; 14.7 kJ/mol for β selectivity) and that the generation of the 14-electron species **4a-*α*′** or **4a-*β*′** is not favored by ΔH, but is favorable in terms of ΔG. These features indicate that the dissociation of nitrogen is an endothermic process, and thus spontaneous; therefore, it readily takes place in situ.

Consequently, the subsequent C(sp)−Si bond activation step requires a moderate (70−80 kJ/mol) activation energy. After the C(sp)−Si bond is cleaved, the intermediates **5a-*α*′** and **5a-*β*′** show similar thermodynamic stabilities. However, the consequent recoordination of nitrogen generates a large energy difference; **TS3a-*β*** is presumed to be a destabilized state because the recoordination and rearrangement of the coordination site of the monodentate phosphine ligand occur in concert. In comparison with **5a-*α***, the generated **5a-*β*** is also destabilized due to the P−Pt−Si trans geometry caused by the thermodynamic nature of transition metals, widely known as the trans effect.[21] The silyl group possessing the stronger trans effect tends to locate at the trans position of the weakly coordinating platinum−nitrogen bond.

We also examined the possibility of the dissociation of the phosphine moiety, and the optimized structure (**4a′$_{P\text{-}diss}$**) shows a linear alkyne−Pt−N coordination geometry with a Pt−P interaction (Figure 5). The relative energy of **4a′$_{P\text{-}diss}$** is much

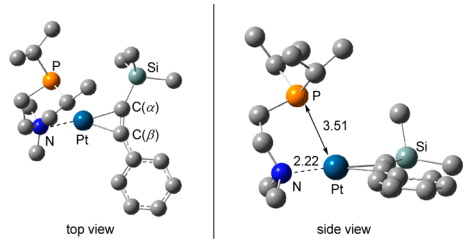

Figure 5. Two views of the optimized structure of **4a′$_{P\text{-}diss}$**. Atomic distances are shown in angstroms. Hydrogen atoms are omitted for clarity.

higher than that of either **4a-*α*′** and **4a-*β*′**. We thus concluded that the dissociation of the nitrogen moiety is the sole driver that generates the active 14-electron platinum complex.

To determine the origin of the thermodynamically unstable configuration of complex **5a-*β***, we compared the relative energies along each pathway. The results are shown in Figure 6. The subsequent transition state **TS3a-*β*** involves not only a coordinating nitrogen atom but also a rearrangement of the coordination site of phosphorus from the trans position of an alkynyl group to that of a silyl group. This rearrangement could be observed in IRC analyses from **TS3a-*β***. From these

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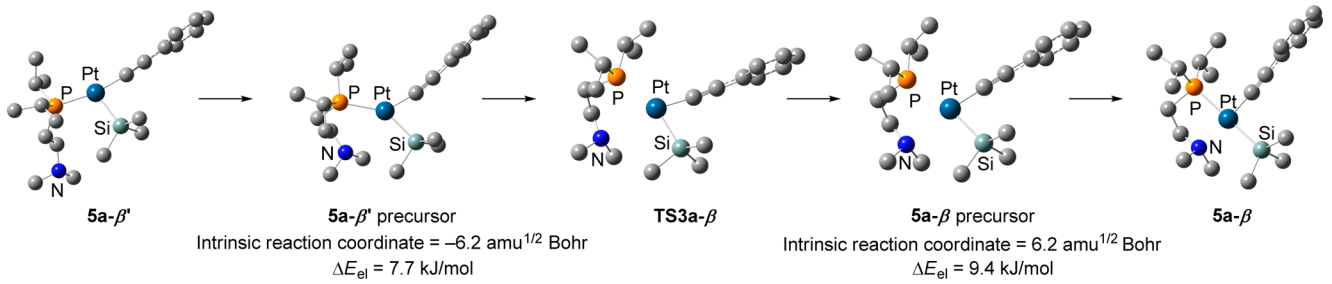

Figure 6. IRC processes from **TS3a-*β*** and the presumed transformation into **5a-*β*′**. Hydrogen atoms are omitted for clarity. IRC analyzed values relative to **TS3a-*β*** are shown.

investigations, after the C(sp)−Si bond activation, the regioisomer of oxidative adduct **5a-*β*** is disfavored because the silyl group is situated in the position trans to the coordinating phosphine.

Theoretical Studies on the Substituent Effect. In experiments, we observed that sterically hindered silyl groups retarded the C(sp)−Si bond cleavage and electron-rich alkynylsilane accelerated oxidative addition on C(sp)−Si bonds. To explain this specific trend, we carried out theoretical investigations of various alkynylsilanes **3**. With regard to the substituent effect of silicon on the reactivity, as shown in Figure 7,

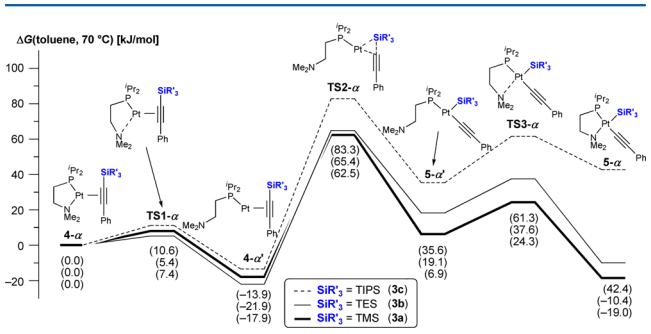

Figure 7. Computed Gibbs free energies (kJ/mol) for the C(sp)−Si bond cleavage of alkynylsilanes bearing various silyl groups (R = Ph).

a triisopropylsilyl group caused remarkable thermodynamic destabilization, in comparison to less bulky substituents such as methyl and ethyl groups. These results unambiguously support experimental observations showing no occurrence of C(sp)−Si bond cleavage in the reaction with **3c**. From the viewpoint of the steric factor, the interaction between TIPS and diisopropylphosphino groups would primarily affect the thermodynamic stability. This trend is also observed in the reaction with **3b** (SiR'_3 = TES); the transformation from **5-*α*′** to **5-*α*** is found to be destabilized, in comparison to that with **3a** (SiR'_3 = TMS). Accordingly, the activation barriers ($\Delta\Delta G^{\ddagger}$) are 80.4 kJ/mol for **3a** (SiR'_3 = TMS) and 87.3 kJ/mol for **3b** (SiR'_3 = TES), respectively. However, our kinetic observation indicates that the reaction with **3b** is twice as fast as that with **3a**, which is opposite to this energetic analysis. These results may be ascribed to the extra isomerization pathway to **5-*α***. Actually, for **3b** (SiR'_3 = TES), the relatively smaller activation barrier ($\Delta\Delta G^{\ddagger}$) from **4-*β*′** to **TS2-*β*** is found to be 76.3 kJ/mol. Otherwise, an electron-rich platinum(0) complex suppresses solvent coordination to the vacant site and renders the generation of the resting state more difficult. Obviously, the latter reason must be supported by the results of the solvent effect, as shown in Table 4.

We also examined the substituent effect of the aryl groups to explain how electron-rich alkynylsilanes accelerate the C(sp)−Si bond cleavage. Starting from **4a-*α***, **4h-*α***, and **4m-*α***, the DFT results are shown in Figure 8. This thermodynamic plot

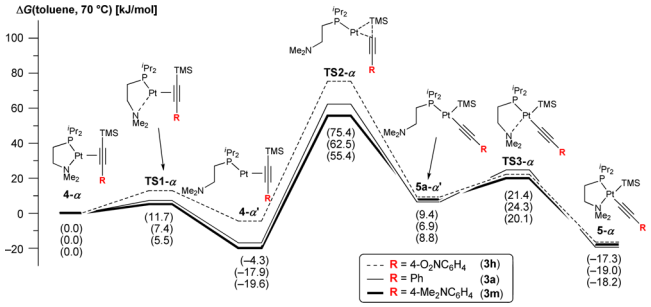

Figure 8. Computed Gibbs free energies (kJ/mol) for C(sp)−Si bond cleavage of alkynylsilanes bearing various arylethynyl groups (SiR'_3 = TMS).

clearly shows that electron-rich alkynylsilanes stabilize both the 14-electron platinum(0) species **4-*α*′** and the transition states in the C(sp)−Si bond cleavage through the transformation from **TS1-*α*** to **TS2-*α***. This can also be demonstrated by comparing the activation energies for C(sp)−Si bond cleavage ($\Delta\Delta G^{\ddagger}$: 79.7 kJ/mol for **3h** (R = 4-$O_2NC_6H_4$) vs 75.0 kJ/mol for **3m** (R = 4-$Me_2NC_6H_4$)).

Origin of 14-Electron Platinum(0) Species. We have found a novel 14-electron platinum(0) species produced by the dissociation of nitrogen in the P−N ligand **2**. Our observation of this active species prompted additional research to develop other transformations. Using DFT calculations, we examined the charge transfers along the entire pathway of the C(sp)−Si bond cleavage, dividing the complexes into several parts: the platinum center, P−N ligand, silyl group, alkyne moiety, and the phenyl group. As shown in Figure 9, the charge mainly transfers from the alkyne moiety into the platinum center at the dissociation of nitrogen (**4a-*α*** to **4a-*α*′**). As a 14-electron species, the electronically enriched platinum center is noteworthy. From this observation, we found that π back-donation from the platinum center to the alkyne moiety plays a key role in generating the 14-electron platinum(0) species. As speculated from the changes in bond lengths, to fulfill the requirements of this structural arrangement, i.e. stretching the platinum−alkyne bond and shortening the C≡C bond, the electronically enriched platinum center is exclusively derived from the degeneration of π back-donation. Thus, the weakened π back-donation from platinum is required for the generation of this 14-electron species. Meanwhile, an enriched P−N ligand is derived from the bond dissociation. Followed by the C(sp)−Si

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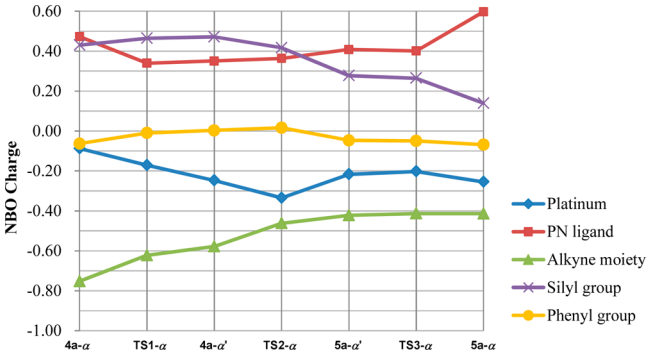
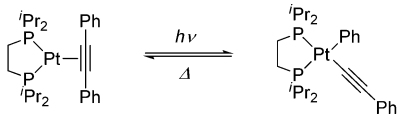


Figure 9. Computed natural atomic charges around the C(sp)−Si bond cleavage with the platinum(0)/PN complex and alkynylsilane **3a**.

bond-cleavage step (i.e., **4a-α′** to **5a-α′**), a charge transfer from the alkyne moiety to the silyl group occurs. This series of charge flows might be based on bond formation. Since the alkynyl group (electronegativity (EN) of carbon: 2.55) has a stronger electron-withdrawing propensity than the silyl group (EN of Si: 1.90),[22] the polarization of the C(sp)−Si bond is canceled during bond cleavage. Finally, recoordination of nitrogen (i.e., **5a-α′** to **5a-α**) and charge transfer from the P−N ligand to the silyl group take place. This is caused by the formation of the platinum−nitrogen bond, and the charge is accepted by the silyl group beyond the platinum center. This trans-electronic effect in the platinum complexes is also supported by our observations on the $^{31}P\{^{1}H\}$ NMR spectra.

MO Interaction between Platinum and Silicon. To bring about C(sp)−Si bond cleavage, platinum migration from the triple bond in alkynylsilanes **3** to a C(sp)−Si bond is essential. We surveyed the origin of this transformation by examining the MO interactions. From the energy diagram shown in Figure 10, the HOMO of **4a-α′** is highly stabilized, and the order of the MOs is inverted. In particular, the orbital coefficient of HOMO-3 in **TS2a-α** was mainly distributed between the inner 3d and 4d orbitals of platinum and the outer 3d orbital of silicon. Such in-phase orbital interactions should cause thermodynamic stabilization of the HOMO of **4a-α′**. Inherently, an η^2-alkyne-coordinating platinum complex possesses a wide overlap between platinum and the coordinating η^2-alkyne in HOMO-13. Thus, complex **4a-α′** naturally possesses a wide MO interaction beyond the alkyne moiety.

Jones et al. have reported photochemically induced platinum-mediated C(sp)−C(aryl) bond cleavage (eq 2).[23] In this report,



(2)

they concluded that C(sp)−C(aryl) bond cleavage is thermodynamically unfavorable and that the inverse reaction of reductive elimination occurs under thermal conditions. Photochemical bond cleavage is thought to proceed by utilizing the LUMO. We also found that the LUMO of **4a-α′** possesses an MO distribution delocalized among platinum, C(sp)−Si, and C(sp)−C(aryl) bonds. Hence, we surmise that platinum migration could occur in both C(sp)−Si and C(sp)−C(aryl) bonds but that C(sp)−Si bond cleavage offers the most favorable thermodynamic stabilization.

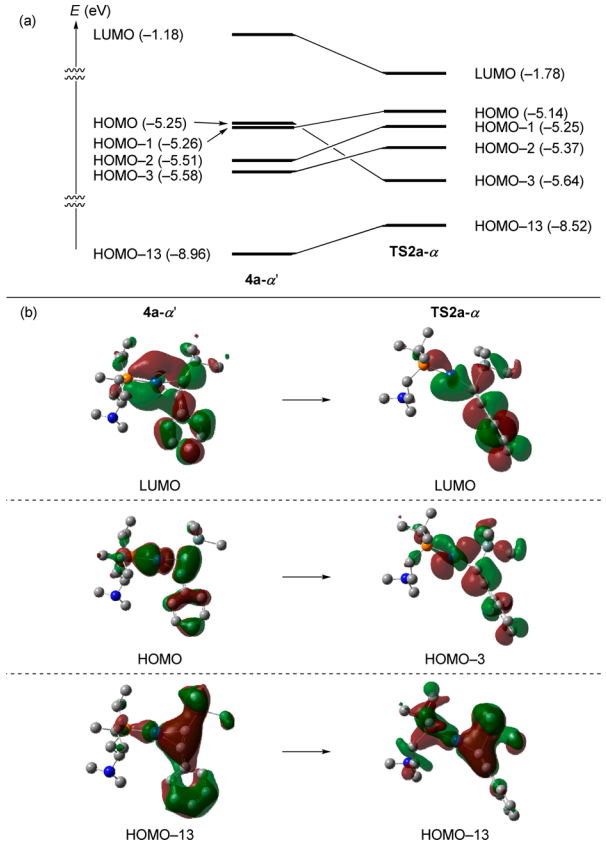


Figure 10. (a) MO energy diagram going from **4a-α′** to **TS2a-α**. Energies of each MO are shown in parentheses in eV. (b) Selected MO drawings.

CONCLUSIONS

In this study, we have synthesized a series of alkynyl(silyl)-platinum(II) complexes through the chemoselective C(sp)−Si bond cleavage of alkynylsilanes. Experimental and theoretical investigations have revealed the detailed reaction mechanisms. The chemoselectivity is determined by the fast and quantitative generation of the η^2-alkyne-coordinating complex and the subsequent thermodynamically favored platinum−silyl MO interaction. The configuration of the Pt complexes is controlled by the thermodynamic stability of the oxidative adducts, and this result can also be understood from the trans effect in platinum(II) complexes. The ligand for the C(sp)−Si bond cleavage must form a hemilabile five-membered chelation. However, the P−N chelation is highly distorted due to steric repulsion between diisopropylphosphino and silyl groups. The dissociation of nitrogen in the P−N ligand on a platinum center gives the inherently electron deficient active 14-electron platinum complex. Electron-rich alkynylsilanes can stabilize 14-electron species, and C(sp)−Si bond cleavage is thereby accelerated. Nonpolar solvents seem to be appropriate for C(sp)−Si bond cleavage, because they are less able to form a strong coordination to vacant coordination sites. Weakened π back-donation and an enriched platinum atom are required for the generation of 14-electron platinum active species on the pathway to C(sp)−Si bond cleavage.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. Dehydrated toluene and deuterated benzene (C_6D_6) were

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purchased from Kanto Chemicals Co. Ltd. and CIL Chemicals Ltd. Nuclear magnetic resonance (^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, ^{31}P{^{1}H} NMR) spectra were measured on a spectrometer operating at 400 MHz (^{1}H NMR), 101 MHz (^{13}C{^{1}H} NMR), 376 MHz (^{19}F{^{1}H} NMR), 161 MHz (^{31}P{^{1}H} NMR), and 119 MHz (^{29}Si{^{1}H} NMR). All ^{1}H NMR chemical shifts were reported in ppm relative to the proton resonance in C_6D_6 at δ 7.16. All ^{13}C{^{1}H} NMR chemical shifts were reported in ppm relative to the carbon resonance in C_6D_6 at δ 128.06. The ^{19}F{^{1}H} NMR chemical shifts were reported in ppm relative to an external reference of trichlorofluoromethane at δ 0.00. The ^{31}P{^{1}H} NMR chemical shifts were reported in ppm relative to an external reference of phosphoric acid at δ 0.00.

Each single crystal of **5e-α**, **5f-α**, **5g-α**, and **5l-α** was glued to the top of a glass fiber with epoxy resin, and X-ray diffraction data were obtained at ambient temperature using a Rigaku SCXmini CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected and processed using the CrystalClear software package[24] for all of the complexes, and numerical absorption corrections were applied.[25] The structures were solved by direct methods (SHELXS97[26]) and refined by a full -matrix least-squares method on F^2 using the SHELXL97 software package.[26] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at idealized positions by using riding models. All calculations were performed with the CrystalStructure crystallographic software package.[27]

Experimental Procedures and Spectroscopic Data. *[(2-Phenyl)ethynyl](trimethylsilyl)[(diisopropylphosphino)-(dimethylamino)ethane]platinum (**5a-α**).* In a 20 mL Schlenk tube, bis(1,5-cyclooctadiene)platinum (**1**; 41 mg, 0.10 mmol) was dissolved in toluene (1 mL). (Diisopropylphosphino)(dimethylamino)ethane (**2**; 21 μL, 0.10 mmol) and 1-phenyl-2-(trimethylsilyl)ethyne (**3a**; 19 μL, 0.10 mmol) were added to this solution, and the mixture was stirred at 70 °C. After 1 h, the solution was warmed to ambient temperature, filtered with toluene (1 × 3 mL) via a cannula, and transferred to another Schlenk tube. The combined brown filtrates were evaporated in vacuo to give a brown solid. The crude product was washed with hexane (1 × 3 mL) and dried under high vacuum, affording the title compound **5a-α** as an off-white powder (34 mg, 0.060 mmol, 60%). ^{1}H NMR (C_6D_6, room temperature, 400 MHz): δ 0.76 (dd, $^3J_{H-P}$ = 12.9 Hz, $^3J_{H-H}$ = 6.9 Hz, 6H, ^{i}Pr (−CH_3)), 0.85 (s, with platinum satellites, $^3J_{H-Pt}$ = 31 Hz, 9H, SiMe$_3$(−CH_3)), 0.98−1.01 (m, 2H, ^{i}Pr (−CH−)), 1.05 (dd, $^3J_{H-P}$ = 17.1 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 1.76−1.84 (m, 4H, PN ligand (−CH_2−)), 2.43 (s, br, with platinum satellites, 6H, N−CH_3), 7.01 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, *p*-Ph), 7.13 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *m*-Ph), 7.73 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, *o*-Ph). ^{13}C{^{1}H} NMR (C_6D_6, room temperature, 101 MHz): δ 7.8 (d, with platinum satellites, $^2J_{C-Pt}$ = 89.4 Hz, $^3J_{C-P(cis)}$ = 2.2 Hz, SiMe$_3$(−CH_3)), 18.1 (d, br, with platinum satellites, $^2J_{C-P}$ = 2.6 Hz, ^{i}Pr (−CH_3)), 20.9 (d, br, $^2J_{C-P}$ = 5.8 Hz, ^{i}Pr (−CH_3)), 22.2 (d, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 24.9 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 83 Hz, ^{i}Pr (−CH−)), 48.9 (s, br, N−CH_3), 61.4 (d, br, $^2J_{C-P}$ = 3.6 Hz, N−CH_2−), 103.8 (d, $^3J_{C-P}$ = 30.0 Hz, C≡C−Pt), 125.1 (s, *m*-Ph), 128.4 (s, *p*-Ph), 130.1 (d, $^4J_{C-P}$ = 3.1 Hz, *ipso*-Ph), 131.5 (d, $^2J_{C-P}$ = 131.8 Hz, C≡C−Pt), 131.7 (d, br, $^5J_{C-P}$ = 1.1 Hz, *o*-Ph). Anal. Calcd for $C_{21}H_{38}$NPSiPt (558.68): C, 45.15; H, 6.86; N, 2.51. Found: C, 44.88; H, 6.50; N, 2.29.

*[(2-Phenyl)ethynyl](triethylsilyl)[(diisopropylphosphino)-(dimethylamino)ethane]platinum (**5b-α**).* This compound was obtained as a white powder. Yield: 61% (37 mg, 0.061 mmol (0.10 mmol scale)). ^{1}H NMR (C_6D_6, room temperature, 400 MHz): δ 0.76 (dd, $^3J_{H-P}$ = 12.9 Hz, $^3J_{H-H}$ = 6.9 Hz, 6H, ^{i}Pr (−CH_3)), 0.97−1.00 (m, 2H, ^{i}Pr (−CH−)), 1.06 (dd, $^3J_{H-P}$ = 16.9 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 1.29 (q, $^3J_{H-H}$ = 7.7 Hz, 6H, Et (−CH_2−)), 1.48 (t, $^3J_{H-H}$ = 7.7 Hz, 9H, Et (−CH_3)), 1.81 (m, 4H, PN ligand (−CH_2−)), 2.44 (s, br, with platinum satellites, 6H, N−CH_3), 7.01 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *p*-Ph), 7.13 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, *m*-Ph), 7.72 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, *o*-Ph). ^{13}C{^{1}H} NMR (C_6D_6, room temperature, 101 MHz): δ 10.2 (d, with platinum satellites, $^2J_{C-Pt}$ = 78 Hz, $^3J_{C-P(cis)}$ = 2.4 Hz, SiEt$_3$(−CH_2−)), 10.8 (s, with platinum satellites, $^3J_{C-Pt}$ = 33 Hz, SiEt$_3$ (−CH_3)), 18.1 (d, with platinum satellites, $^2J_{C-P}$ = 2.4 Hz, $^3J_{C-Pt}$ = 26 Hz, ^{i}Pr (−CH_3)), 20.8 (d, br, $^2J_{C-P}$ = 5.6 Hz, ^{i}Pr (−CH_3)), 22.4 (d, $^1J_{C-P}$ = 24 Hz, P−CH_2−), 25.2 (d, with platinum satellites, $^1J_{C-P}$ = 27 Hz, $^2J_{C-Pt}$ = 84 Hz, ^{i}Pr (−CH−)), 48.7 (s, br, N−CH_3), 61.4 (d, br, $^2J_{C-P}$ = 3.2 Hz, N−CH_2−), 103.0 (d, $^3J_{C-P}$ = 29.9 Hz, C≡C−Pt), 125.1 (s, *m*-Ph), 128.4 (s, *p*-Ph), 130.1 (d, $^4J_{C-P}$ = 3.4 Hz, *ipso*-Ph), 130.8 (d, $^2J_{C-P}$ = 132.5 Hz, C≡C−Pt), 131.6 (d, br, $^5J_{C-P}$ = 1.1 Hz, *o*-Ph). Anal. Calcd for $C_{24}H_{44}$NPSiPt (600.76): C, 47.98; H, 7.38; N, 2.33. Found: C, 47.61; H, 7.02; N, 2.33.

*[(2-Phenyl)ethynyl](dimethylphenylsilyl)[(diisopropylphosphino)-(dimethylamino)ethane]platinum (**5d-α**).* This compound was obtained as a white powder. Yield: 72% (23 mg, 0.036 mmol (0.05 mmol scale)). ^{1}H NMR (C_6D_6, room temperature, 400 MHz): δ 0.64 (dd, $^3J_{H-P}$ = 12.8 Hz, $^3J_{H-H}$ = 6.8 Hz, 6H, ^{i}Pr (−CH_3)), 0.88−0.93 (m, 2H, ^{i}Pr (−CH−)), 0.97 (dd, $^3J_{H-P}$ = 17.2 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 1.10 (s, with platinum satellites, $^3J_{H-Pt}$ = 32.4 Hz, 6H, SiMe$_2$Ph (−CH_3)), 1.44−1.53 (m, 2H, P−CH_2−), 1.73 (dt, $^3J_{H-P}$ = 18.4 Hz, $^3J_{H-H}$ = 6.6 Hz, 2H, N−CH_2−), 2.43 (s, br, with platinum satellites, 6H, N−CH_3), 7.02 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *p*-Ph or SiMe$_2$Ph), 7.14 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, *m*-Ph or SiMe$_2$Ph), 7.18 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-Ph or SiMe$_2$Ph), 7.30 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, *m*-Ph or SiMe$_2$Ph), 7.72 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, *o*-Ph or SiMe$_2$Ph), 8.06 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, *o*-Ph or SiMe$_2$Ph). ^{13}C{^{1}H} NMR (C_6D_6, room temperature, 101 MHz): δ 6.3 (d, $^3J_{C-P(cis)}$ = 2.0 Hz, SiMe$_2$Ph (−CH_3)), 17.8 (d, with platinum satellites, $^2J_{C-P}$ = 3.1 Hz, ^{i}Pr (−CH_3)), 21.1 (d, $^2J_{C-P}$ = 6.0 Hz, ^{i}Pr (−CH_3)), 21.4 (d, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 24.4 (d, $^1J_{C-P}$ = 28 Hz, ^{i}Pr (−CH−)), 49.0 (s, br, N−CH_3), 61.7 (d, $^2J_{C-P}$ = 3.6 Hz, N−CH_2−), 104.7 (d, $^3J_{C-P}$ = 29.8 Hz, C≡C−Pt), 125.3 (s, *m*- or *p*-Ph or SiMe$_2$Ph), 127.2 (s, *m*- or *p*-Ph or SiMe$_2$Ph), 127.3 (s, *m*- or *p*-Ph or SiMe$_2$Ph), 128.4 (s, *m*- or *p*-Ph or SiMe$_2$Ph), 131.7 (d, br, $^5J_{C-P}$ = 1.4 Hz, *o*-Ph), 129.9 (d, $^4J_{C-P}$ = 3.1 Hz, *ipso*-Ph), 131.6 (d, $^2J_{C-P}$ = 131.4 Hz, C≡C−Pt), 135.1 (s, with platinum satellites, SiMe$_2$Ph (*o*-Ph)), 148.7 (d, $^3J_{C-P(cis)}$ = 2.8 Hz, SiMe$_2$Ph (*ipso*-Ph)). Anal. Calcd for $C_{26}H_{40}$NPSiPt (620.75): C, 50.31; H, 6.49; N, 2.26. Found: C, 50.50; H, 6.53; N, 2.21.

*[(2-Phenyl)ethynyl](benzyldimethylsilyl)[(diisopropylphosphino)-(dimethylamino)ethane]platinum (**5e-α**).* This compound was obtained as a white powder. Yield: 48% (30.5 mg, 0.048 mmol (0.10 mmol scale)). ^{1}H NMR (C_6D_6, room temperature, 400 MHz): δ 0.65 (dd, $^3J_{H-P}$ = 12.9 Hz, $^3J_{H-H}$ = 6.9 Hz, 6H, ^{i}Pr (−CH_3)), 0.70 (s, with platinum satellites, 6H, SiMe$_2$Bn (−CH_3)), 0.78 (dd, $^3J_{H-P}$ = 17.2 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 0.89−0.94 (m, 2H, ^{i}Pr (−CH−)), 1.61−1.69 (m, 2H, P−CH_2−), 1.77 (dt, $^3J_{H-P}$ = 17.9 Hz, $^3J_{H-H}$ = 6.6 Hz, 2H, N−CH_2−), 2.45 (s, br, with platinum satellites, 6H, N−CH_3), 3.06 (s, br, with platinum satellites, 2H, $^3J_{H-Pt}$ = 27.3 Hz, SiMe$_2$Bn(−CH_2−)), 7.02 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *p*-Ph or SiMe$_2$Bn), 7.05 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *p*-Ph or SiMe$_2$Bn), 7.13 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, *m*-Ph or SiMe$_2$Bn), 7.23 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *m*-Ph or SiMe$_2$Bn), 7.64 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, *o*-Ph or SiMe$_2$Bn), 7.74 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-Ph or SiMe$_2$Bn). ^{13}C{^{1}H} NMR (C_6D_6, room temperature, 101 MHz): δ 5.5 (d, $^2J_{C-Pt}$ = 91 Hz, $^3J_{C-P(cis)}$ = 3.0 Hz, SiMe$_2$Bn (−CH_3)), 18.0 (d, with platinum satellites, $^2J_{C-P}$ = 2.4 Hz, $^3J_{C-Pt}$ = 24 Hz, ^{i}Pr (−CH_3)), 20.4 (d, $^2J_{C-P}$ = 5.6 Hz, ^{i}Pr (−CH_3)), 22.2 (d, $^1J_{C-P}$ = 24 Hz, P−CH_2−), 24.8 (d, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 84 Hz, ^{i}Pr (−CH−)), 33.7 (s, with platinum satellites, $^2J_{C-Pt}$ = 69 Hz, Bn (−CH_2−)), 48.9 (s, br, N−CH_3), 61.5 (d, $^2J_{C-P}$ = 3.2 Hz, N−CH_2−), 104.0 (d, $^3J_{C-P}$ = 30.0 Hz, C≡C−Pt), 123.0 (s, *m*- or *p*-Ph or SiMe$_2$Bn), 125.3 (s, *m*- or *p*-Ph or SiMe$_2$Bn), 127.9 (s, *m*- or *p*-Ph or SiMe$_2$Bn), 128.5 (s, *m*- or *p*-Ph or SiMe$_2$Bn), 129.5 (s, SiMe$_2$Bn (*o*-Ph)), 130.0 (d, $^4J_{C-P}$ = 3.1 Hz, *ipso*-Ph), 131.5 (d, $^2J_{C-P}$ = 131.5 Hz, C≡C−Pt), 131.6 (d, br, $^5J_{C-P}$ = 1.1 Hz, *o*-Ph), 145.3 (s, SiMe$_2$Bn (*ipso*-Ph)). Anal. Calcd for $C_{27}H_{42}$NPSiPt (634.78): C, 51.09; H, 6.67; N, 2.21. Found: C, 50.81; H, 6.56; N, 2.15.

*[(2-Phenyl)ethynyl][dimethyl(2-thienyl)silyl]-[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5f-α**).* This compound was obtained as a white powder. Yield: 69% (43.2 mg, 0.069 mmol (0.10 mmol scale)). ^{1}H NMR (C_6D_6, room temperature, 400 MHz): δ 0.68 (dd, $^3J_{H-P}$ = 12.6 Hz, $^3J_{H-H}$ = 7.0 Hz, 6H, ^{i}Pr (−CH_3)), 0.95−0.97 (m, 2H, ^{i}Pr (−CH−)), 1.02 (dd, $^3J_{H-P}$ = 17.6 Hz, $^3J_{H-H}$ = 7.6 Hz, 6H, ^{i}Pr (−CH_3)), 1.13 (s, with platinum satellites, $^3J_{H-Pt}$ = 31.6 Hz, 6H, SiMe$_2$Th (−CH_3)), 1.54−1.63 (m, 2H, P−CH_2−),

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1.77 (dt, $^3J_{H-P}$ = 18.4 Hz, $^3J_{H-H}$ = 6.7 Hz, 2H, N−CH_2−), 2.44 (s, br, with platinum satellites, 6H, N−CH_3), 7.01 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *p*-Ph), 7.10−7.14 (m, 3H, *m*-Ph and 4-Th), 7.33 (d, $^3J_{H-H}$ = 4.4 Hz, 1H, 3- or 5-Th), 7.66 (d, $^3J_{H-H}$ = 3.2 Hz, 1H, 3- or 5-Th), 7.71 (d, $^3J_{H-H}$ = 6.8 Hz, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz): δ 7.7 (d, with platinum satellites, $^2J_{C-Pt}$ = 88 Hz, $^3J_{C-P(cis)}$ = 2.1 Hz, $SiMe_2Th$ (−CH_3)), 18.0 (d, with platinum satellites, $^2J_{C-P}$ = 3.3 Hz, ^{i}Pr (−CH_3)), 21.3 (d, br, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 21.3 (d, br, $^2J_{C-P}$ = 5.8 Hz, ^{i}Pr (−CH_3)), 24.6 (d, with platinum satellites, $^1J_{C-P}$ = 29 Hz, $^2J_{C-Pt}$ = 81 Hz, ^{i}Pr (−C*H*−)), 49.1 (s, br, N−CH_3), 61.8 (d, br, $^2J_{C-P}$ = 3.2 Hz, N−CH_2−), 104.6 (d, $^3J_{C-P}$ = 29.6 Hz, *C*≡C−Pt), 125.3 (s, *m*-Ph), 127.6 (s, 4-Th or 5-Th), 128.4 (s, *p*-Ph), 128.6 (s, 4-Th or 5-Th), 129.5 (d, $^2J_{C-P}$ = 130.7 Hz, C≡*C*−Pt), 129.9 (d, $^4J_{C-P}$ = 3.2 Hz, *ipso*-Ph), 131.7 (d, br, $^5J_{C-P}$ = 1.1 Hz, *o*-Ph), 133.7 (s, with platinum satellites, 3-Th), 148.5 (s, $^3J_{C-P(cis)}$ = 2.9 Hz, 2-Th). Anal. Calcd for $C_{24}H_{38}NPSSiPt$ (626.78): C, 45.99; H, 6.11; N, 2.23. Found: C, 46.05; H, 6.21; N, 2.21.

(Propynyl)(trimethylsilyl)[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5g-α**). This compound was obtained as an off-white powder. Yield: 42% (41.7 mg, 0.084 mmol (0.2 mmol scale)). ^1H NMR (C_6D_6, room temperature, 400 MHz): δ 0.75 (dd, $^3J_{H-P}$ = 13 Hz, $^3J_{H-H}$ = 6.8 Hz, 6H, ^{i}Pr (−CH_3)), 0.85 (s, with platinum satellites, $^3J_{H-Pt}$ = 31 Hz, 9H, TMS), 0.98 (m, 2H, ^{i}Pr (−C*H*−)), 1.05 (dd, $^3J_{H-P}$ = 17 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 1.75−1.82 (m, 4H, PN ligand (−CH_2−)), 2.10 (d, br, $^5J_{H-P(trans)}$ = 2.0 Hz, 3H, alkynyl Me (−CH_3)), 2.43 (s, br, with platinum satellites, $^3J_{H-Pt}$ = 12 Hz, 6H, N−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz): δ 6.6 (d, $^4J_{C-P(trans)}$ = 3.0 Hz, alkynyl Me(−CH_3)), 7.9 (d, with platinum satellites, $^2J_{C-Pt}$ = 94 Hz, $^3J_{C-P(cis)}$ = 2.4 Hz, $SiMe_3$ (−CH_3)), 18.1 (d, with platinum satellites, $^2J_{C-P}$ = 2.4 Hz, $^3J_{C-Pt}$ = 25 Hz, ^{i}Pr (−CH_3)), 20.9 (d, br, $^2J_{C-P}$ = 5.9 Hz, ^{i}Pr (−CH_3)), 22.2 (d, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 24.8 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 83 Hz, ^{i}Pr (−CH−)), 48.8 (s, with platinum satellites, $^2J_{C-Pt}$ = 13 Hz, N−CH_3), 61.4 (d, with platinum satellites, $^2J_{C-P}$ = 3.5 Hz, N−CH_2−), 96.6 (d, $^3J_{C-P(trans)}$ = 31 Hz, C≡C−Pt), 115.8 (d, $^2J_{C-P(trans)}$ = 133 Hz, C≡*C*−Pt). Anal. Calcd for $C_{16}H_{36}NPSiPt$ (496.61): C, 38.70; H, 7.31; N, 2.82. Found: C, 38.39; H, 7.35; N, 2.75.

[2-(4-Nitrophenyl)ethynyl](trimethylsilyl)[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5h-α**). This compound was obtained as a brown powder. Yield: 58% (70.0 mg, 0.116 mmol (0.2 mmol scale)). ^1H NMR (C_6D_6, room temperature, 400 MHz): δ 0.75 (dd, $^3J_{H-P}$ = 12.6 Hz, $^3J_{H-H}$ = 6.6 Hz, 6H, ^{i}Pr (−CH_3)), 0.78 (s, with platinum satellites, $^3J_{H-Pt}$ = 29.6 Hz, 9H, $SiMe_3$ (−CH_3)), 0.86−0.92 (m, 2H, ^{i}Pr (−C*H*−)), 1.02 (dd, $^3J_{H-P}$ = 17.4 Hz, $^3J_{H-H}$ = 7.4 Hz, 6H, ^{i}Pr (−CH_3)), 1.74−1.84 (m, 4H, PN ligand (−CH_2−)), 2.36 (s, br, 6H, N−CH_3), 7.36 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, 2- or 3-C_6H_4), 7.87 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, 2- or 3-C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz): δ 7.5 (d, with platinum satellites, $^2J_{C-Pt}$ = 87 Hz, $^3J_{C-P(cis)}$ = 2.3 Hz, $SiMe_3$ (−CH_3)), 18.1 (d, br, with platinum satellites, $^2J_{C-P}$ = 2.6 Hz, $^3J_{C-Pt}$ = 19 Hz, ^{i}Pr (−CH_3)), 20.9 (d, br, $^2J_{C-P}$ = 5.5 Hz, ^{i}Pr (−CH_3)), 22.1 (d, $^1J_{C-P}$ = 24 Hz, P−CH_2−), 25.0 (d, with platinum satellites, $^1J_{C-P}$ = 29 Hz, $^2J_{C-Pt}$ = 83 Hz, ^{i}Pr (−CH−)), 48.9 (s, br, N−CH_3), 61.4 (d, br, $^2J_{C-P}$ = 3.0 Hz, N−CH_2−), 103.8 (d, $^3J_{C-P}$ = 29.6 Hz, *C*≡C−Pt), 123.8 (s, 3-nitrophenyl), 131.6 (d, $^5J_{C-P}$ = 1.1 Hz, br, 2-nitrophenyl), 136.7 (d, $^4J_{C-P}$ = 3.1 Hz, 1-nitrophenyl), 142.6 (d, $^2J_{C-P}$ = 130.7 Hz, C≡C−Pt), 144.9 (s, 4-nitrophenyl). Anal. Calcd for $C_{21}H_{37}N_2O_2PSiPt$ (603.68): C, 41.78; H, 6.18; N, 4.64. Found: C, 41.74; H, 5.78; N, 4.39.

[2-(4-(Trifluoromethyl)phenyl)ethynyl](trimethylsilyl)[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5i-α**). This compound was obtained as a white powder. Yield: 22% (27.4 mg, 0.044 mmol (0.2 mmol scale)). ^1H NMR (C_6D_6, room temperature, 400 MHz): δ 0.73 (dd, $^3J_{H-P}$ = 12.8 Hz, $^3J_{H-H}$ = 6.8 Hz, 6H, ^{i}Pr (−CH_3)), 0.83 (s, with platinum satellites, $^3J_{H-Pt}$ = 30.4 Hz, 9*H*, $SiMe_3$ (−CH_3)), 0.94−0.98 (m, 2H, ^{i}Pr (−C*H*−)), 1.03 (dd, $^3J_{H-P}$ = 17.2 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 1.72−1.81 (m, 4H, PN ligand (−CH_2−)), 2.38 (s, br, 6H, N−CH_3), 7.29 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, 2- or 3-C_6H_4), 7.54 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, 2- or 3-C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz): δ 7.6 (d, with platinum satellites, $^2J_{C-Pt}$ = 89 Hz, $^3J_{C-P(cis)}$ = 2.4 Hz, $SiMe_3$ (−CH_3)), 18.0 (d, br, with platinum satellites, $^2J_{C-P}$ = 2.6 Hz, $^3J_{C-Pt}$ = 24 Hz, ^{i}Pr (−CH_3)), 20.9 (d, br, $^2J_{C-P}$ = 5.6 Hz, ^{i}Pr (−CH_3)), 22.1 (d, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 25.0 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 85 Hz, ^{i}Pr (−CH−)), 48.9 (s, br, N−CH_3), 61.4 (d, br, $^2J_{C-P}$ = 3.3 Hz, N−CH_2−), 103.1 (d, $^3J_{C-P}$ = 31.1 Hz, C≡C−Pt), 121.5 (d, $^4J_{C-P}$ = 3.0 Hz, 1-trifluorophenyl), 125.3 (q, $^3J_{C-F}$ = 3.9 Hz, 3-trifluorophenyl), 125.5 (q, $^1J_{C-F}$ = 271.5 Hz, CF_3), 126.5 (q, $^2J_{C-F}$ = 32.1 Hz, 4-trifluorophenyl), 131.6 (d, br, $^5J_{C-P}$ = 1.3 Hz, 2-trifluorophenyl), 136.3 (d, $^2J_{C-P}$ = 131.2 Hz, C≡C−Pt). $^{19}F\{^1H\}$ NMR (C_6D_6, room temperature, 376 MHz): δ −61.9 (s). Anal. Calcd for $C_{22}H_{37}F_3NPSiPt$ (626.68): C, 42.17; H, 5.95; N, 2.24. Found: C, 42.33; H, 5.82; N, 2.36.

[2-(4-Chlorophenyl)ethynyl](trimethylsilyl)[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5j-α**). This compound was obtained as a white powder. Yield: 22% (6.5 mg, 0.011 mmol (0.05 mmol scale)). ^1H NMR (C_6D_6, room temperature, 400 MHz): δ 0.73 (dd, $^3J_{H-P}$ = 12.8 Hz, $^3J_{H-H}$ = 6.9 Hz, 6H, ^{i}Pr (−CH_3)), 0.84 (s, with platinum satellites, $^3J_{H-Pt}$ = 31.0 Hz, 9H, $SiMe_3$ (−CH_3)), 0.94−0.99 (m, 2H, ^{i}Pr (−C*H*−)), 1.04 (dd, $^3J_{H-P}$ = 17.2 Hz, $^3J_{H-H}$ = 7.3 Hz, 6H, ^{i}Pr (−CH_3)), 1.71−1.82 (m, 4H, PN ligand (−CH_2−)), 2.38 (s, br, 6H, N−CH_3), 7.07 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, 2- or 3-C_6H_4), 7.47 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, 2- or 3-C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz): δ 7.7 (d, with platinum satellites, $^2J_{C-Pt}$ = 89.8 Hz, $^3J_{C-P(cis)}$ = 2.1 Hz, CH_3 (−CH_3)), 18.1 (d, br, with platinum satellites, $^2J_{C-P}$ = 2.4 Hz, $^3J_{C-Pt}$ = 27 Hz, ^{i}Pr (−CH_3)), 20.9 (d, br, $^2J_{C-P}$ = 5.8 Hz, ^{i}Pr (−CH_3)), 22.2 (d, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 24.9 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 86 Hz, ^{i}Pr (−CH−)), 48.9 (s, br, N−CH_3), 61.4 (d, br, $^2J_{C-P}$ = 3.4 Hz, N−CH_2−), 102.7 (d, $^3J_{C-P}$ = 29.9 Hz, *C*≡C−Pt), 128.2 (d, $^4J_{C-P}$ = 5.0 Hz, 1-chlorophenyl), 128.6 (s, 3-chlorophenyl), 130.8 (s, 4-chlorophenyl), 132.8 (d, br, $^5J_{C-P}$ = 1.3 Hz, 2-chlorophenyl), 133.0 (d, $^2J_{C-P}$ = 132.0 Hz, C≡*C*−Pt). Anal. Calcd for $C_{21}H_{37}ClNPSiPt$ (593.12): C, 42.53; H, 6.29; N, 2.36. Found: C, 42.42; H, 6.31; N, 2.35.

[2-(4-Methylphenyl)ethynyl](trimethylsilyl)[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5k-α**). This compound was obtained as a white powder. Yield: 49% (56.6 mg, 0.099 mmol (0.2 mmol scale)). ^1H NMR (C_6D_6, room temperature, 400 MHz): δ 0.76 (dd, $^3J_{H-P}$ = 12.8 Hz, $^3J_{H-H}$ = 7.2 Hz, 6H, ^{i}Pr (−CH_3)), 0.86 (s, with platinum satellites, $^3J_{H-Pt}$ = 30.0 Hz, 9H, $SiMe_3$ (−CH_3)), 0.97−1.01 (m, 2H, ^{i}Pr (−C*H*−)), 1.06 (dd, $^3J_{H-P}$ = 17.0 Hz, $^3J_{H-H}$ = 7.4 Hz, 6H, ^{i}Pr (−CH_3)), 1.76−1.84 (m, 4H, PN ligand (−CH_2−)), 2.09 (s, 3H, Me (−CH_3)), 2.44 (s, br, 6H, N−CH_3), 6.96 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, 2- or 3-C_6H_4), 7.68 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, 2- or 3-C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz): δ 7.8 (d, with platinum satellites, $^2J_{C-Pt}$ = 91.1 Hz, $^3J_{C-P(cis)}$ = 2.5 Hz, $SiMe_3$ (−CH_3)), 18.1 (d, br, with platinum satellites, $^2J_{C-P}$ = 2.4 Hz, ^{i}Pr(−CH_3)), 20.9 (d, br, $^2J_{C-P}$ = 6.0 Hz, ^{i}Pr (−CH_3)), 21.4 (s, Me (−CH_3)), 22.2 (d, $^1J_{C-P}$ = 23 Hz, P−CH_2−), 24.9 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 84 Hz, ^{i}Pr (−CH−)), 48.9 (s, br, N−CH_3), 61.4 (d, br, $^2J_{C-P}$ = 3.4 Hz, N−CH_2−), 103.7 (d, $^3J_{C-P}$ = 30.0 Hz, *C*≡C−Pt), 127.2 (d, $^4J_{C-P}$ = 3.2 Hz, 1-methylphenyl), 129.1 (s, 3-methylphenyl), 130.2 (d, $^2J_{C-P}$ = 132.0 Hz, C≡C−Pt), 131.6 (d, br, $^5J_{C-P}$ = 1.1 Hz, 2-methylphenyl), 134.4 (s, 4-methylphenyl). Anal. Calcd for $C_{22}H_{40}NPSiPt$ (572.71): C, 46.14; H, 7.04; N, 2.45. Found: C, 46.16; H, 6.76; N, 2.67.

[2-(4-Methoxylphenyl)ethynyl](trimethylsilyl)[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5l-α**). This compound was obtained as a white powder. Yield: 19% (22.7 mg, 0.039 mmol (0.2 mmol scale)). ^1H NMR (C_6D_6, room temperature, 400 MHz): δ 0.76 (dd, $^3J_{H-P}$ = 12.4 Hz, $^3J_{H-H}$ = 6.8 Hz, 6H, ^{i}Pr (−CH_3)), 0.89 (s, with platinum satellites, $^3J_{H-Pt}$ = 28.8 Hz, 9H, $SiMe_3$ (−CH_3)), 0.97−1.00 (m, 2H, ^{i}Pr (−C*H*−)), 1.06 (dd, $^3J_{H-P}$ = 17.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 6H, ^{i}Pr (−CH_3)), 1.75−1.83 (m, 4H, PN ligand (−CH_2−)), 2.45 (s, br, 6H, N−CH_3), 3.27 (s, 3H, OMe (−OCH_3)), 6.75 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, 2- or 3-C_6H_4), 7.68 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, 2- or 3-C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, room temperature, 101 MHz):

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δ 6.3 (d, $^3J_{C-P(cis)}$ = 2.0 Hz, $SiMe_3$ ($-CH_3$)), 17.8 (d, br, $^2J_{C-P}$ = 3.1 Hz, ^{i}Pr ($-CH_3$)), 21.1 (d, br, $^2J_{C-P}$ = 6.0 Hz, ^{i}Pr ($-CH_3$)), 21.4 (d, $^1J_{C-P}$ = 23 Hz, P$-CH_2-$), 24.4 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, ^{i}Pr ($-CH-$)), 49.0 (s, br, N$-CH_3$), 61.7 (d, br, $^2J_{C-P}$ = 3.6 Hz, N$-CH_2-$), 104.7 (d, $^3J_{C-P}$ = 29.8 Hz, C≡C–Pt), 125.3 (s, 3-methoxyphenyl), 129.9 (d, $^2J_{C-P}$ = 131.6 Hz, C≡C–Pt), 129.9 (d, $^4J_{C-P}$ = 3.1 Hz, 1-methoxyphenyl), 131.7 (d, br, $^5J_{C-P}$ = 1.4 Hz, 2-methoxyphenyl), 135.1 (s, 4-methoxyphenyl). Anal. Calcd for $C_{22}H_{40}NOPSiPt$ (588.71): C, 44.89; H, 6.85; N, 2.38. Found: C, 44.73; H, 6.49; N, 2.18.

*[2-(4-(N,N-Dimethylamino)phenyl)ethynyl](trimethylsilyl)-[(diisopropylphosphino)(dimethylamino)ethane]platinum (**5m-α**).* This compound was obtained as an off-white powder. Yield: 56% (67.9 mg, 0.113 mmol (0.2 mmol scale)). ^{1}H NMR (C_6D_6, room temperature, 400 MHz): δ 0.79 (dd, $^3J_{H-P}$ = 13.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 6H, ^{i}Pr ($-CH_3$)), 0.88 (s, with platinum satellites, $^3J_{H-Pt}$ = 30.4 Hz, 9H, $SiMe_3$ ($-CH_3$)), 1.02–1.03 (m, 2H, ^{i}Pr ($-CH-$)), 1.09 (dd, $^3J_{H-P}$ = 17.0 Hz, $^3J_{H-H}$ = 7.4 Hz, 6H, ^{i}Pr ($-CH_3$)), 1.78–1.88 (m, 4H, PN ligand ($-CH_2-$)), 2.49 (s, br, 6H, N$-CH_3$), 2.50 (s, 6H, NMe_2 ($-CH_3$)), 6.55 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, 2- or 3-C_6H_4), 7.70 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, 2- or 3-C_6H_4). ^{13}C{^{1}H} NMR (C_6D_6, room temperature, 101 MHz): δ 7.9 (d, with platinum satellites, $^2J_{C-Pt}$ = 90.5 Hz, $^3J_{C-P(cis)}$ = 2.4 Hz, $SiMe_3$ ($-CH_3$)), 18.2 (d, br, with platinum satellites, $^2J_{C-P}$ = 2.4 Hz, ^{i}Pr ($-CH_3$)), 20.9 (d, br, $^2J_{C-P}$ = 5.8 Hz, ^{i}Pr ($-CH_3$)), 22.4 (d, $^1J_{C-P}$ = 23 Hz, P$-CH_2-$), 24.9 (d, with platinum satellites, $^1J_{C-P}$ = 28 Hz, $^2J_{C-Pt}$ = 83 Hz, ^{i}Pr ($-CH-$)), 40.4 (s, NMe_2 ($-CH_3$)), 49.0 (s, br, N$-CH_3$), 61.5 (d, br, $^2J_{C-P}$ = 3.5 Hz, N$-CH_2-$), 103.9 (d, $^3J_{C-P}$ = 30.3 Hz, C≡C–Pt), 113.0 (s, 3-(*N*,*N*′-dimethylamino)-phenyl), 118.6 (d, $^4J_{C-P}$ = 3.4 Hz, 1-(*N*,*N*′-dimethylamino)phenyl), 127.5 (d, $^2J_{C-P}$ = 132.4 Hz, C≡C–Pt), 132.5 (d, br, $^5J_{C-P}$ = 1.2 Hz, 2-(*N*,*N*′-dimethylamino)phenyl), 143.6 (s, 4-(*N*,*N*′-dimethylamino)-phenyl). Anal. Calcd for $C_{23}H_{43}N_2PSiPt$ (601.75): C, 45.91; H, 7.20; N, 4.66. Found: C, 45.77; H, 6.83; N, 4.45.

Kinetic Study. To a platinum(0) complex (21 mg, 0.05 mmol) in C_6D_6 (600 μL) in an NMR tube were added P–N ligand (11 μL, 0.05 mmol) and alkynylsilanes **3a–m** (0.05 mmol). The time-dependent transformation at 30 °C was determined by integration of ^{31}P{^{1}H} NMR signals after 1, 2, 3, and 6 h (in the case of alkynylsilane **3m**, data were recorded after 15, 30, 45, and 60 min).

Computational Methodology. All calculations in the present study were performed with the Gaussian 09 program[28] and by using the Becke three-parameter plus Lee–Yang–Parr (B3LYP) density functional theory (DFT) method.[29] For all geometry optimizations and normal-coordinate analyses at stationary points, we used the Stuttgart–Dresden–Cologne (SDD) effective core potential and corresponding basis set for Pt[30] and 6-311G(d) for the others.[31] For the correction of solvation, the polarizable continuum model (PCM)[32,33] with a dielectric constant of 2.3741 (toluene) was also used. Thermal enthalpies and Gibbs free energies were calculated at a temperature of 343.15 K (70 °C) and at a pressure of 1 atm. Intrinsic reaction coordinate (IRC) analyses[34–36] from saddle points (transition states) to minima (reactants, intermediates, and products) were used for confirming the reaction pathways. Natural population analysis was performed to examine atomic charges.[37]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving experimental details, scanned NMR spectra of all new complexes, crystallographic data for complexes **5e-α**, **5f-α**, **5g-α**, and **5l-α**, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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