Thermal and Photochemical Silicon−Carbon Bond Activation in Donor-Stabilized Platinum(0)−Alkyne Complexes

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Reaction of Pt(COD)$_2$ with Me$_3$SiC≡CPh and a bidentate chelating ligand leads to the formation of the corresponding donor-stabilized Pt-η^2-alkyne complexes (PN)Pt(η^2-Me$_3$SiC≡CPh) (**1**) and (dcpe)Pt(η^2-Me$_3$SiC≡CPh) (**3**) (PN = (diisopropylphosphinodimethylamino)ethane; dcpe = bis(dicyclohexylphosphino)ethane). The nitrogen donor ligand in **1** facilitates the cleavage of the Si−C(sp) bond, and the Pt(II) complex (PN)Pt(SiMe$_3$)(C≡CPh) (**2**) is formed at room temperature. In contrast, the bisphosphino-substituted compound **3** has been isolated as a thermally robust Pt(0) complex. However, the silicon−carbon bond in the latter compound can be photochemically activated, and the oxidative addition product (dcpe)Pt(SiMe$_3$)(C≡CPh) (**4**) is generated. Both Si−C(sp) bonds in Me$_3$Si−C≡C−C≡C−SiMe$_3$ have been thermally activated by a (PN)Pt fragment to afford the dinuclear Pt(II) species (PN)Pt(SiMe$_3$)−C≡C−C≡C−Pt(SiMe$_3$)(PN) (**6**).

Introduction

The scission of silicon−carbon bonds by transition metal complexes has recently attracted much interest due to its potential application in functionalization and transformation reactions of organosilanes.[1] Furthermore, detailed studies on the interaction of organosilanes with transition metal centers provide better insight into important processes, such as the hydrosilylation of alkenes,[1a,2] the dehydrogenative coupling of primary and secondary silanes,[3] or the dehydrogenative silylation of olefins.[4]

While the oxidative addition of Si−C(sp^3) bonds to transition metal centers is still quite rare,[5] Si−C(sp^2) bond cleavage has been studied much more frequently.[6] Several examples of Si−C(sp) bond activation reactions in L$_n$M(η^2-Me$_3$SiC≡CR) complexes have also been documented in the literature so far. However, migration of the silyl group to the metal center is generally not observed in these systems. Instead, 1,2-silyl migration occurrs to form vinylidene complexes under thermal or photochemical conditions.[7] Cleavage of Si−C bonds in alkynylsilanes with coordination of both the SiR$_3$ and the alkynyl fragment is much less common and has been reported only in some isolated cases.[8]

We report here on the synthesis of 1-phenyl-2-trimethylsilylacetylene and 1,4-bis(trimethylsilyl)-1,3-butadiyne complexes of Pt(0) in which the Pt(η^2-Me$_3$SiC≡CR) fragment is stabilized by the chelating donor (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$ (PN)[9] or (Cy)$_2$PCH$_2$CH$_2$P(Cy)$_2$ (bis(dicyclohexylphosphino)ethane, dcpe). The PN-substituted compounds show remarkable differences in Si−C(sp) bond activation and reductive elimination reactions compared to the bisphosphino-substituted complexes.

Results and Discussion

We recently reported on the synthesis of the zerovalent platinum complexes (PN)Pt(η^2-PhC≡CPh) and (PP)Pt(η^2-PhC≡CPh) (PP = dcpe; bis(diisopropylphosphino)ethane, dippe).[10] These compounds undergo oxidative addition of the C(sp)−C(sp^2) bond in diphenylacetylene to the metal center under photochemical conditions. However, a thermal reaction with diphenylacetylene to form a platinacyclopentadiene complex was only observed for (PN)Pt(η^2-PhC≡CPh).[11] This indicates an enhanced reactivity of the platinum atom due to the hemilabile character of the bidentate P,N hybrid ligand.[12]

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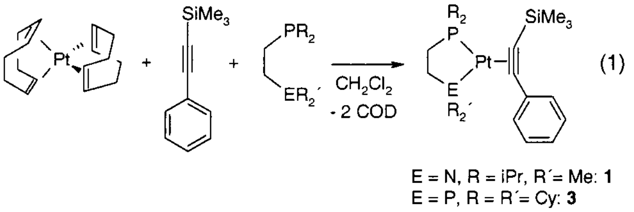
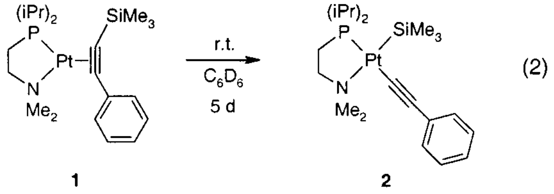
We were further interested in the reactivity of donor-stabilized Pt(0) fragments toward $SiMe_3$-substituted alkynes, such as 1-phenyl-2-trimethylsilylacetylene[13] and 1,4-bis(trimethylsilyl)-1,3-butadiyne[13b,e,14] complexes. Reaction of $Pt(COD)_2$ with 1 equiv of $Me_3SiC{\equiv}CPh$ and 1 equiv of $(^iPr)_2CH_2CH_2NMe_2$ in C_6D_6 led to the formation of the η^2-alkyne complex $(PN)Pt(\eta^2\text{-}Me_3SiC{\equiv}CPh)$ (**1**) (eq 1). A singlet with platinum satellites at $\delta = 66.4$ ppm ($^1J_{Pt-P} = 3952$ Hz) was observed for **1** in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum displayed the characteristic *ortho*-, *meta*-, and *para*-protons of $Me_3SiC{\equiv}CPh$ in the ratio of 2:2:1. However, the η^2-alkyne complex **1** quantitatively rearranged to a new compound (**2**) within approximately 5 days at room temperature (24 h at $T = 70$ °C). **2** was obtained as a colorless solid after recrystallization from C_6D_6/pentane. The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6) of **2** showed a singlet with platinum satellites at $\delta = 59.3$ ppm ($^1J_{Pt-P} = 2760$ Hz). The comparatively smaller platinum–phosphorus coupling constant is indicative for a Pt(II) species with substitutents σ-bonded to the metal center. Furthermore, a $SiMe_3$ group with platinum satellites was observed for **2** in the ^1H NMR spectrum, suggesting that the $SiMe_3$ group is attached to the platinum center. The NMR spectroscopic data are consistent with an oxidative addition of the silicon–carbon bond in $Me_3SiC{\equiv}CPh$ to the donor-stabilized platinum fragment at ambient temperature (eq 2). A crystal of **2** suitable for X-ray diffraction was obtained by recrystallization from C_6D_6/pentane. The molecular structure of **2** is illustrated in Figure 1; selected bond lengths and distances are summarized in Table 1. The structural analysis confirmed that **2** is the Si–C(sp) cleavage product $(PN)Pt(SiMe_3)(C{\equiv}CPh)$. Interestingly, the insertion of the metal center into the Si–C bond is selective. Only one isomer with the alkynyl group *trans* to the phosphorus atom and the $SiMe_3$ group *trans* to the nitrogen atom was generated.





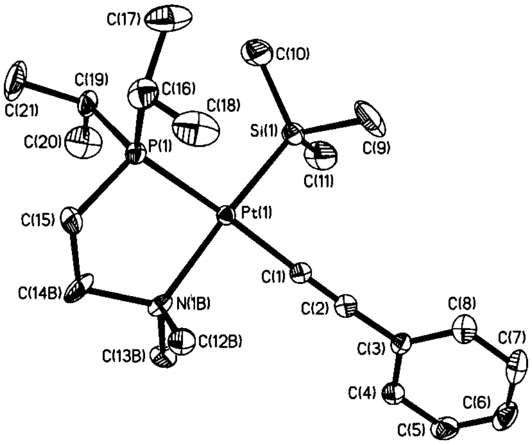


Figure 1. Molecular structure of $(PN)Pt(SiMe_3)(C{\equiv}CPh)$ (**2**) (ORTEP diagram; 30% probability ellipsoids). The $-CH_2NMe_2$ portion of the P,N ligand showed some disorder. Only one contributor is shown.

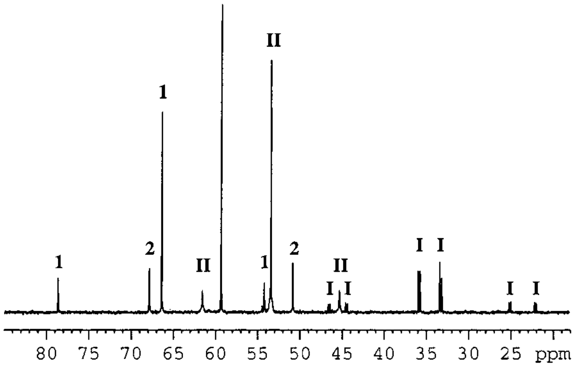


Figure 2. ^{31}P NMR spectrum (162 MHz) of the thermal Si–C bond activation reaction in **1** at $t = 48$ h ($T =$ rt).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

	Bond Lengths		
Pt(1)–N(1B)	2.25(4)	Pt(1)–C(1)	1.998(8)
Pt(1)–P(1)	2.262(2)	C(1)–C(2)	1.199(11)
Pt(1)–Si(1)	2.313(2)	C(2)–C(3)	1.440(11)
	Bond Angles		
Si(1)–Pt(1)–C(1)	82.9(2)	N(1B)–Pt(1)–P(1)	84.0(9)
Si(1)–Pt(1)–P(1)	101.63(8)	Pt(1)–C(1)–C(2)	176.4(7)
C(1)–Pt(1)–N(1B)	91.8(9)	C(1)–C(2)–C(3)	176.3(9)

Although **1** is quantitatively converted to **2** within ~5 days at room temperature, two transient intermediates (**I** and **II**) were observed during the course of the reaction. Figure 2 displays a $^{31}P\{^1H\}$ NMR spectrum (C_6D_6) of the reaction mixture, recorded after $t = 48$ h. Two doublets with platinum satellites at $\delta = 33.2$ ppm ($^1J_{Pt-P} = 3626$ Hz, $^2J_{P-P} = 37.3$ Hz) and $\delta = 35.8$ ppm ($^1J_{Pt-P} = 3468$ Hz, $^2J_{P-P} = 37.3$ Hz) were detected for intermediate **I**. The ^1H NMR spectrum of the reaction mixture, however, revealed a ratio of complexed alkyne to P,N ligand of 1:2 for compound **I**, as well as 1 equiv of free alkyne. The spectroscopic data are consistent with an asymmetric $Pt(\eta^2\text{-}Me_3SiC{\equiv}CPh)$ complex, containing two monodentate P,N ligands which coordinate

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(12) For the concept of hemilability see for example: (a) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658. (b) Okuda, J. *Comments Inorg. Chem.* **1994**, *16*, 185. (c) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233. (d) Müller, C.; Vos, D.; Jutzi, P. *J. Organomet. Chem.* **2000**, *600*, 127. (e) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680.

(13) For zerovalent group-10-(η^2-$Me_3SiC{\equiv}CPh$) complexes see: (a) Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170. (b) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *210*, 403. (c) Hoffman, D. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1982**, 1471. (d) Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11*, 1235. (e) Rosenthal, U.; Nauck, C.; Arndt, P.; Pulst, S.; Baumann, W.; Burlakov, V. V.; Görls, H. *J. Organomet. Chem.* **1994**, *484*, 81. (f) Rosenthal, U.; Pulst, S.; Kempe, R.; Pörschke, K.-R.; Goddard, R.; Proft, B. *Tetrahedron* **1998**, *54*, 1277.

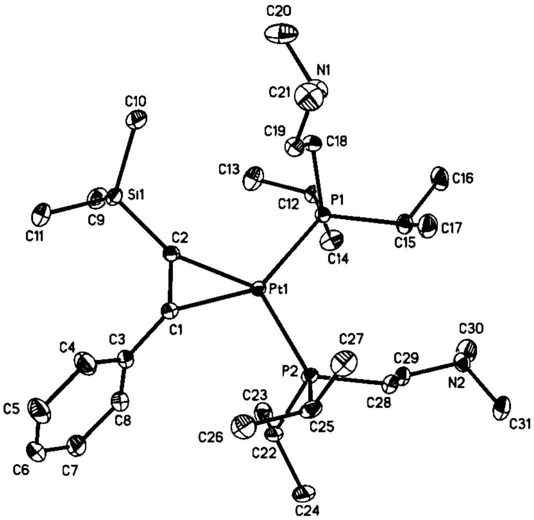
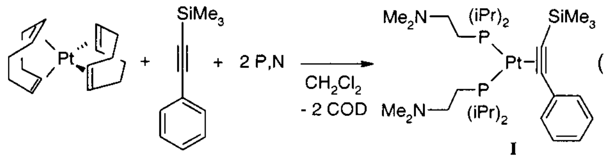


Figure 3. Molecular structure of $(NP)_2Pt(\eta^2\text{-}Me_3SiC{\equiv}CPh)$ (**I**) (ORTEP diagram; 30% probability ellipsoids).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for I

	Bond Lengths		
Pt(1)−P(1)	2.2955(10)	C(1)−C(2)	1.304(6)
Pt(1)−P(2)	2.2820(11)	Si(1)−C(2)	1.848(5)
Pt(1)−C(1)	2.047(4)	C(1)−C(3)	1.460(6)
Pt(1)−C(2)	2.100(4)		
	Bond Angles		
C(1)−Pt(1)−C(2)	36.63(17)	C(2)−Pt(1)−P(1)	108.44(12)
P(2)−Pt(1)−P(1)	110.08(4)	Si(1)−C(2)−C(1)	134.3(4)
C(1)−Pt(1)−P(2)	104.87(13)	C(2)−C(1)−C(3)	140.1(4)

to the metal center via the diisopropylphosphino group. Intermediate **I** was independently synthesized by reaction of $Pt(COD)_2$ with 1 equiv of $Me_3SiC{\equiv}CPh$ and 2 equiv of $(^iPr)_2PCH_2CH_2NMe_2$ in C_6D_6 according to eq 3. This compound was isolated as an air- and moisture-sensitive, colorless solid. Crystals of **I** suitable for X-ray diffraction were obtained after recrystallization from petroleum ether at $T = -30$ °C. The molecular structure of **I** is illustrated in Figure 3; selected bond lengths and distances are listed in Table 2. The structural analysis revealed that intermediate **I** is indeed the $Pt(\eta^2\text{-}Me_3SiC{\equiv}CPh)$ complex with two P,N ligands coordinated to the platinum atom in a monodentate fashion. Compound **I** adopts the expected distorted square-planar geometry at the metal center with the alkyne ligand in the P(1)−Pt−P(2) plane. The bending of the C≡C−C(Si) angles reflects a major contribution of Pt→π^* back-donation.[15] The P(1)−Pt(1)−P(2) angle of 110.1° is similar to the one reported for $(Ph_3P)_2Pt(\eta^2\text{-}PhC{\equiv}CPh)$ (102.0°),[16] but about 24° larger compared to $Pt(\eta^2\text{-alkyne})$ complexes bearing chelating $R_2PCH_2CH_2PR_2$ ligands.[17]



(3)

For intermediate **II**, however, a singlet with broad platinum satellites at $\delta = 53.5$ ppm ($^1J_{Pt-P} = 2631$ Hz) was observed in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum showed a singlet with platinum satellites for a $SiMe_3$ group. The resonances of the trimethylsilyl group, the P,N ligand, and the phenylalkynyl group were detected in a ratio of 1:1:1. Again, these data are consistent with a silicon−carbon bond activation product. We were able to isolate intermediate **II** from the reaction mixture by fractional crystallization. The compound was obtained as a pale yellow solid. Unfortunately, any attempt to grow crystals of **II** suitable for X-ray diffraction failed. However, heating a solution of pure **II** in C_6D_6 for 48 h at $T = 100$ °C resulted in the quantitative formation of $(PN)Pt(SiMe_3)(C{\equiv}CPh)$ (**2**). Interestingly, the color of the solution changed from yellow to dark gray upon heating, suggesting the generation of colloidal platinum. Furthermore, an elemental analysis as well as an electrospray-MS of compound **II** is consistent with the formula $C_{42}H_{76}N_2P_2Pt_3Si_2$ and the mass 1312.2 g/mol, respectively. We propose that **II** is the platinum-bridged dimer shown in Figure 4. The additional platinum atom in **II** balances the stoichiometry for the formation of **I** and free alkyne from two molecules of the starting material **1** (vide supra). Similar triplatinum compounds with the schematic structure **A** are known and have been reported by Stone et al. before (Figure 4).[18]

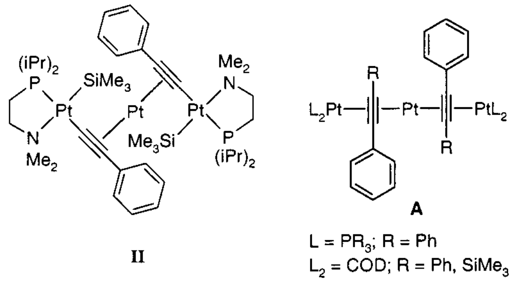


Figure 4. Schematic structures of intermediate **II** and the triplatinum compound **A**.

We assume that the initial step in the silicon−carbon bond cleavage reaction in **1** is migration of the metal fragment with subsequent oxidative addition of the Si−C(sp) bond to the platinum(0) center. Additionally, an equilibrium between **1** and intermediate **I**, which contains two P,N ligands, must also exist according to the

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(14) For zerovalent group-10-$(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$ complexes see: (a) Klein, H.-F.; Beck-Hemetsberger, H.; Reitzel, L.; Rodenhäuser, B.; Cordier, G. *Chem. Ber.* **1989**, *122*, 43. (b) Rosenthal, U.; Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R. *Z. Naturforsch.* **1995**, *50b*, 368. (c) Rosenthal, U.; Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R. *Z. Naturforsch.* **1995**, *50b*, 377. (d) Rosenthal, U. Pulst, S.; Arndt, P.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Bulakov, V. V. *Organometallics* **1995**, *14*, 2961. (e) Tillack, A.; Pulst, S.; Baumann, W.; Baudisch, H.; Kortus, K.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *532*, 117. (f) Bruce, M. I.; Low, P. J.; Werth, A.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 1551.

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(16) Glanville, J. O.; Stewart, J. M.; Grim, S. O. *J. Organomet. Chem.* **1967**, *7*, P9.

(17) The P−Pt−P angles in $(dippe)Pt(\eta^2\text{-}PhC{\equiv}CPh)$ and $(dippe)Pt(\eta^2\text{-}tBuC{\equiv}CPh)$ are 86.84(3)° and 87.20(3)°, respectively: ref 11 and unpublished results.

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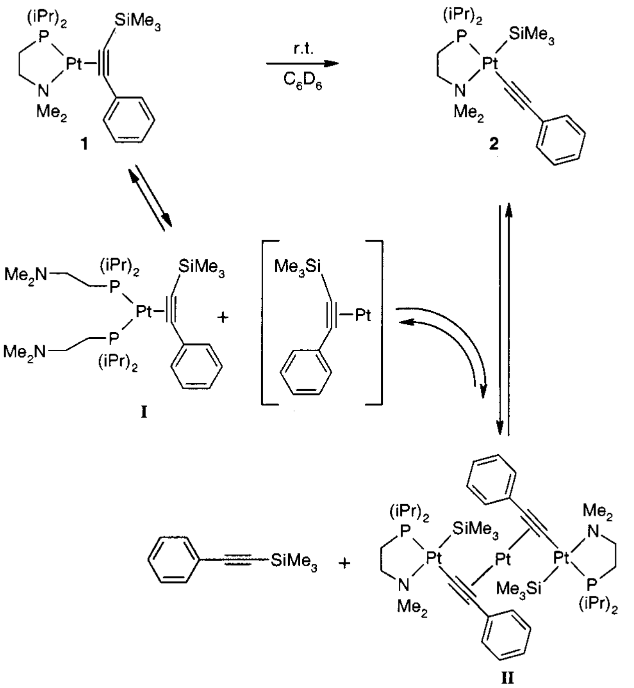
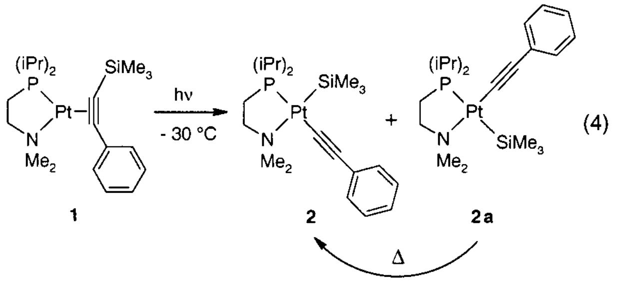
Scheme 1



data recorded by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 2). The remaining fragment “$Pt(\eta^2\text{-}Me_3SiC\equiv CPh)$” would react with the Si−C bond activation product **2** to form the second intermediate **II** together with free alkyne (Scheme 1). The temporary presence of free $Me_3SiC\equiv CPh$ during the course of the reaction was indeed verified by ^1H NMR spectroscopy. The latter reaction is also reversible, leading again to a decrease of **II** as well as of **I** to form the final product **2** quantitatively after ∼5 days at room temperature.

The reactivity of the metal fragment toward Si−C bond activation is most likely due to the differences in σ-donor and π-acceptor capabilities of the donor functionalities in $(^iPr)_2PCH_2CH_2NMe_2$. While the PR_2 group is a good σ-donor and π-acceptor, the NR_2 group lacks in π-acceptor character. The increased electron density at the metal center might facilitate the oxidative addition reaction. This assumption is based on the fact that intermediate **I**, in which two monodentate P,N ligands coordinate to the $Pt(\eta^2\text{-}Me_3SiC\equiv CPh)$ fragment via the diisopropylphosphino group, does not show any thermal Si−C bond activation at all. Another possibility for the increased reactivity of **1** is that a coordinatively unsaturated Pt species is required for the oxidative addition process. The $-NMe_2$ group as a “hard” Lewis-basic functionality offers this lability.

We were further interested in the reactivity of (PN)-$Pt(\eta^2\text{-}Me_3SiC\equiv CPh)$ under *photochemical* conditions. A solution of **1** in THF-d_8 was irradiated with UV light at $T = -30$ °C to prevent thermal rearrangement of **1** to compound **2**. Within 8.5 h of photolysis, the starting material was quantitatively converted to an approximately 1:1 mixture of the products **2** and **2a**. The $^{31}P\{^1H\}$ NMR spectrum of **2a** displayed a singlet with platinum satellites at $\delta = 66.0$ ppm ($^1J_{Pt-P} = 1126$ Hz) as well as coupling to silicon ($^2J_{P-Si} = 191$ Hz). We assume that **2a** is an isomer of **2** with the SiR_3 group *trans* to phosphorus and the alkynyl group *trans* to nitrogen. However, on warming the mixture of isomers to room temperature, only the silicon−carbon bond cleavage product **2** could be detected by NMR spectroscopy. This suggests that rearrangement of **2a** to **2** had occurred, which is the thermodynamically favored product (eq 4). In the photochemical Si−C(sp) bond scission,

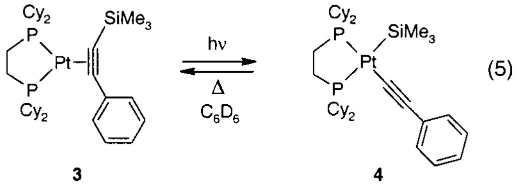


(4)

only small amounts (<5%) of the intermediates **I** and **II** were recorded by $^{31}P\{^1H\}$ NMR spectroscopy. The formation of **I** and **II** in this reaction is most likely due to a thermal conversion of **1** to compound **2** (vide supra).

We extended our investigations on thermal and photochemical silicon−carbon bond activation to $Pt(\eta^2\text{-}Me_3SiC\equiv CPh)$ species, which are stabilized by a chelating bisphosphino ligand. Reaction of $Pt(COD)_2$ with 1 equiv of $Me_3SiC\equiv CPh$ and 1 equiv of bis(dicyclohexylphosphino)ethane (dcpe) in C_6D_6 led to the quantitative formation of the η^2-alkyne complex $(dcpe)Pt(\eta^2\text{-}Me_3SiC\equiv CPh)$ (**3**) (eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **3** showed two doublets with platinum satellites at $\delta = 67.7$ ppm ($^1J_{Pt-P} = 3274$ Hz, $^2J_{P-P} = 53.9$ Hz) and $\delta = 69.1$ ppm ($^1J_{Pt-P} = 3116$ Hz, $^2J_{P-P} = 53.9$ Hz). In contrast to **1**, compound **3** was isolated as a yellow solid after recrystallization from pentane/dichloromethane at $T = -30$ °C. A solution of **3** in C_6D_6 showed no thermal Si−C(sp) bond activation at room temperature. Even prolonged heating for 8 days at $T = 100$ °C resulted in no significant change in the ^{31}P NMR spectrum. These observations support the assumption that the enhanced reactivity of the (PN)Pt(0) fragment toward *thermal* bond scission is mainly due to the NR_2 donor functionality.

Silicon−carbon bond activation in **3**, however, was achieved under *photochemical* conditions. A solution of **3** in C_6D_6 was irradiated with UV light, and the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 1 h of photolysis the formation of a new species was observed. Within 6 h, **3** was quantitatively converted into the product (**4**), which was obtained as a pale yellow solid after recrystallization. The $^{31}P\{^1H\}$ NMR spectrum of **4** displayed two doublets with platinum satellites at $\delta = 67.2$ ppm ($^1J_{Pt-P} = 2593$ Hz, $^2J_{P-P} = 5.2$ Hz) and $\delta = 71.3$ ppm ($^1J_{Pt-P} = 1113$ Hz, $^2J_{P-P} = 5.2$ Hz). Additionally, a $SiMe_3$ group with platinum satellites was recorded in the ^1H NMR spectrum of **4**. The spectroscopic data are again consistent with the formation of an asymmetric Pt(II) species with a $SiMe_3$ and alkynyl group σ-bonded to the platinum center (eq 5).



(5)

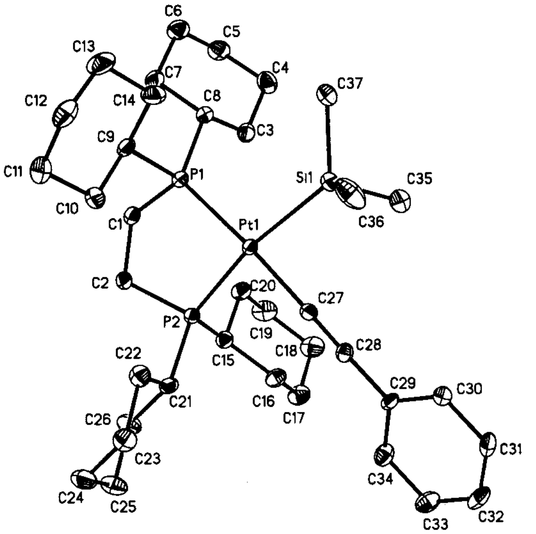


Figure 5. Molecular structure of (dcpe)Pt(SiMe$_3$)(C≡CPh) (**4**) (ORTEP diagram; 30% probability ellipsoids).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

	Bond Lengths		
Pt(1)−P(1)	2.2711(15)	Pt(1)−C(27)	2.007(6)
Pt(1)−P(2)	2.3302(15)	C(27)−C(28)	1.200(8)
Pt(1)−Si(1)	2.3910(17)	C(28)−C(29)	1.445(8)
	Bond Angles		
Si(1)−Pt(1)−C(27)	81.64(17)	C(27)−Pt(1)−P(2)	90.68(17)
P(1)−Pt(1)−P(2)	86.50(5)	Pt(1)−C(27)−C(28)	176.3(5)
Si(1)−Pt(1)−P(1)	101.55(6)	C(27)−C(28)−C(29)	177.2(6)

Crystals of **4** suitable for X-ray diffraction were obtained after recrystallization from C$_6$D$_6$/pentane. The molecular structure of **4** is depicted in Figure 5; selected bond lengths and distances are summarized in Table 3. The structural analysis confirmed the oxidative addition of the Si−C(sp) bond in Me$_3$SiC≡CPh to the metal center under photochemical conditions. However, the bond cleavage reaction turned out to be a reversible process. On thermal activation reductive elimination occurred and the Pt-η^2-alkyne complex **3** was regenerated (eq 5). *The thermal accessibility of this reverse reaction indicates that the oxidative addition of the Si−C(sp) bond in **3** is uphill thermodynamically, whereas it is downhill in complex **1**! This conclusion also argues against chelate lability as being responsible for the thermal reactivity of **1**.*

Using 1,4-bis(trimethylsilyl)-1,3-butadiyne instead of 1-phenyl-2-trimethylsilylacetylene, both silicon−carbon bonds were activated by a (PN)Pt fragment. Reaction of (CODPt)$_2$(η^2;η^2-Me$_3$Si−C≡C−C≡CSiMe$_3$) (**5**) with 2 equiv of (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$ in C$_6$D$_6$ and subsequent heating to T = 70 °C for 16 h led to the formation of a yellow precipitate (**6**), which was isolated and characterized by NMR spectroscopy. A SiMe$_3$ group with platinum satellites and coupling to phosphorus at δ = 0.98 ppm was observed for compound **6** in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} NMR spectrum showed a singlet with platinum satellites at δ = 58.6 ppm ($^1J_{\mathrm{Pt-P}}$ = 2734 Hz), while a silicon resonance with silicon−phosphorus coupling ($^2J_{\mathrm{Si-P}}$ = 8.0 Hz) was observed at δ = −16.6 ppm in the ^{29}Si NMR spectrum. The spectroscopic data indicate that oxidative addition of both silicon−carbon bonds to the platinum center occurred, with the SiMe$_3$ group in a *cis* position to phosphorus (Scheme 2). The Si−C bond cleavage was confirmed by single-crystal X-ray diffraction. Although we were not able to obtain satisfying structural analysis data (R$_1$ = 9.70%), the activation of both silicon−carbon bonds in 1,4-bis(trimethylsilyl)-1,3-butadiyne by the (PN)Pt fragments was obvious. The molecular structure of **6** is illustrated in Figure 6. Bond activation reactions in Me$_3$Si−C≡C−C≡C−SiMe$_3$ with early transition metal fragments have been reported by Rosenthal et al. before. Interestingly, the cleavage of the central C(sp)−C(sp) single bond instead of the Si−C(sp) bond was observed with in situ-generated “Cp$_2$M” species (M = Ti, Zr).[19]

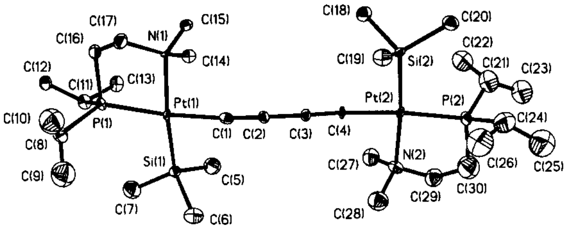
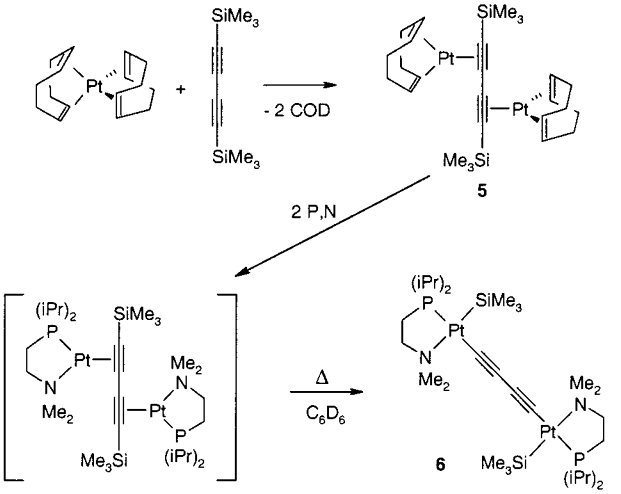


Figure 6. Molecular structure of (PN)Pt(SiMe$_3$)−C≡C−C≡C−Pt(SiMe$_3$)(PN) (**6**) (ORTEP diagram).

Scheme 2



Conclusions

In this paper we described the synthesis of novel zerovalent Pt(η^2-Me$_3$SiC≡CR) complexes which are stabilized by a chelating donor molecule. Thermal silicon−carbon bond activation was observed in those compounds which are substituted by a bidentate P,N hybrid ligand to afford the thermodynamically favored Pt(II) species. In contrast, cleavage of the Si−C bond in bisphosphino-stabilized Pt complexes is possible only under photochemical conditions. The latter reaction is uphill thermodynamically and can be reversed thermally. The differences in reactivity of (PN)Pt fragments compared to (PP)Pt systems is attributed to electronic effects.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen atmosphere in a Vacuum Atmospheres

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[19] (a) Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1992**, *439*, C36. (b) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Organometallics* **1994**, *13*, 2903. (c) Rosenthal, U.; Ohff, A.; Tillack, A.; Baumann, W. *J. Organomet. Chem.* **1994**, *468*, C4. (d) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119.

Corporation glovebox unless otherwise stated. The solvents were commercially available and distilled from dark purple solutions of benzophenone ketyl. A Siemens-SMART 3-Circle CCD diffractometer was used for the X-ray crystal structure determinations. All photolysis experiments were conducted with an Oriel arc source using a 200 W Hg(Xe) bulb in NMR tubes. The elemental analyses were obtained from Desert Analytics. ^{1}H, ^{31}P, and ^{29}Si NMR spectra were recorded on a Bruker AMX-400 or Bruker Avance-400 spectrometer, and all ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. The positive electrospray-MS was recorded on a Hewlett-Packard 1100 Series LC/MS (fragmentor set to 70 eV). $Pt(COD)_2$[20] and $(^iPr)_2PCH_2CH_2NMe_2$ (PN)[9] were synthesized according to published procedures. $(Cy)_2PCH_2CH_2P(Cy)_2$ was purchased from STREM Chemicals, and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ was obtained from Aldrich. Both compounds were used without further purification. $Me_3SiC{\equiv}CPh$ was purchased from Aldrich and was degassed prior to use.

In Situ Preparation of (PN)Pt(η^2-$Me_3SiC{\equiv}CPh$) (1). 1-Phenyl-2-trimethylsilylacetylene (7.5 mg, 0.043 mmol) was dissolved in C_6D_6 (0.5 mL) and added to $Pt(COD)_2$ (17.7 mg, 0.043 mmol). A yellow solution was formed, and $(^iPr)_2PCH_2CH_2NMe_2$ (8.1 mg, 9.1 μL, 0.043 mmol) was subsequently added. The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectrum of the orange solution was immediately recorded. ^{1}H NMR (C_6D_6): δ (ppm) 0.50 (s, 9 H, $SiMe_3$), 0.87 (dd, $^3J_{H-H} = 6.9$ Hz, $^2J_{H-P} = 13.0$ Hz, 6 H, ^iPr), 1.08 (dd, $^3J_{H-H} = 7.1$ Hz, $^2J_{H-P} = 16.4$ Hz, 6 H, ^iPr), 1.15 (m, 2 H, $-CH-$), 1.91 (m, 4 H, $-CH_2-$), 2.21 (s, br, 16 H, COD$-CH_2-$), 2.82 (s, with Pt satellites, $^3J_{H-Pt} = 19.4$ Hz, 6 H, $N-CH_3$), 5.58 (s, br, 8 H, COD$-CH-$), 7.11 (t, $^3J_{H-H} = 7.3$ Hz, 1 H, p-C_6H_5), 7.27 (pseudo-t, 2 H, m-C_6H_5), 7.91 (d, $^3J_{H-H} = 7.3$ Hz, 2 H, o-C_6H_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 66.4 (s, with platinum satellites, $^1J_{Pt-P} = 3952$ Hz).

Preparation of (PN)Pt($SiMe_3$)($C{\equiv}CPh$) (2). 1-Phenyl-2-trimethylsilylacetylene (11.1 mg, 0.064 mg) was dissolved in C_6D_6 (0.5 mL) and added to $Pt(COD)_2$ (26.2 mg, 0.064 mmol). Subsequently $(^iPr)_2PCH_2CH_2NMe_2$ (12.1 mg, 13.5 μL, 0.064 mmol) was added, and the orange solution was heated to $T = 70$ °C. The reaction was monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy, and **2** was obtained in 97% spectroscopic yield within 24 h. **2** was obtained as a white solid after recrystallization from C_6D_6/pentane. Yield: 22.2 mg (0.040 mmol, 62%). ^{1}H NMR (C_6D_6): δ (ppm) 0.74 (dd, $^3J_{H-H} = 6.9$ Hz, $^2J_{H-P} = 12.8$ Hz, 6 H, ^iPr), 0.86 (s, with platinum satellites, $^3J_{Pt-H} = 15.2$ Hz, 9 H, $SiMe_3$), 0.99 (m, 2 H, $-CH-$), 1.05 (dd, $^3J_{H-H} = 7.3$ Hz, $^2J_{P-H} = 17.1$ Hz, 6 H, ^iPr), 1.79 (m, 4 H, $-CH_2-$), 2.40 (s, br, with platinum satellites, 6 H, $N-CH_3$), 7.01 (t, $^3J_{H-H} = 7.4$ Hz, 1 H, p-C_6H_5), 7.13 (pseudo-t, 2 H, m-C_6H_5), 7.75 (d, $^3J_{H-H} = 7.0$ Hz, 2 H, o-C_6H_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 59.3 (s, with platinum satellites, $^1J_{Pt-P} = 2760$ Hz). ^{29}Si NMR (C_6D_6): δ (ppm) 0.03 (d, $^2J_{Si-P(cis)} = 8.0$ Hz). Anal. Calcd for $C_{21}H_{38}NPPtSi$ (558.72 g/mol): C, 45.14; H, 6.86; N, 2.51. Found: C, 44.97; H, 6.83; N, 2.39.

Preparation of $(NP)_2Pt(\eta^2$-$Me_3SiC{\equiv}CPh)$ (I). $Pt(COD)_2$ (26.2 mg, 0.064 mmol) was dissolved in a solution of 1-phenyl-2-trimethylsilylacetylene (11.1 mg, 0.064 mmol) in C_6D_6 (0.5 mL). Subsequently $(^iPr)_2PCH_2CH_2NMe_2$ (24.1 mg, 27.0 μL, 0.127 mmol) was added, and the generation of **I** was confirmed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. The solvent and all volatiles were evaporated in vacuo, and the residue was dissolved in petroleum ether (0.2 mL) and cooled to $T = -30$ °C. **I** was obtained as a colorless, air- and moisture-sensitive solid. Yield: 28.2 mg (0.038 mmol, 59%). ^{1}H NMR (C_6D_6): δ (ppm) 0.37 (s, 9 H, $SiMe_3$), 0.97 (dd, $^3J_{H-H} = 7.0$ Hz, $^2J_{H-P} = 13.0$ Hz, 6 H, ^iPr), 1.07 (dd, $^3J_{H-H} = 7.1$ Hz, $^2J_{H-P} = 15.4$ Hz, 6 H, ^iPr), 1.15 (dd, $^3J_{H-H} = 7.0$ Hz, $^2J_{H-P} = 12.8$ Hz, 6 H, ^iPr), 1.31 (dd, $^3J_{H-H} = 7.1$ Hz, $^2J_{H-P} = 15.3$ Hz, 6 H, ^iPr), 1.90 (m, 2 H, $-CH-$), 2.09 (m, 2 H, $-CH-$), 2.11 (s, 6 H, $N-CH_3$), 2.17 (s, 6 H, $N-CH_3$), 2.21 (m, 4 H, PCH_2-), 2.47 (m, 2 H, NCH_2-), 2.54 (m, 2 H, NCH_2-), 6.98 (t, $^3J_{H-H} = 6.5$ Hz, 1 H, p-C_6H_5), 7.19 (pseudo-t, 2 H, m-C_6H_5), 7.29 (d, $^3J_{H-H} = 7.7$ Hz, 2 H, o-C_6H_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 33.2 (d, with platinum satellites, $^1J_{Pt-P} = 3626$ Hz, $^2J_{P-P} = 37.3$ Hz), 35.8 (d, with platinum satellites, $^1J_{Pt-P} = 3468$ Hz, $^2J_{P-P} = 37.3$ Hz).

Preparation of $[(PN)Pt(SiMe_3)(C{\equiv}CPh)]_2Pt$ (II). 1-Phenyl-2-trimethylsilylacetylene (13.1 mg, 0.075 mmol) was dissolved in 0.3 mL of THF-d_8 and added to $Pt(COD)_2$ (30.9 mg, 0.075 mmol) at $T = -25$ °C. A yellow solution was formed, and $(^iPr)_2PCH_2CH_2NMe_2$ (14.2 mg, 15.9 μL, 0.075 mmol) was added. The initial generation of the η^2-alkyne complex **1** was confirmed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. The orange solution was filled in a vial, and diffusion of pentane into the reaction mixture led to the formation of a white solid within 24 h. The mother liquid was decanted, and the remaining solid was again recrystallized from THF/pentane at $T = -30$ °C. Pure **II** was obtained as a white solid. Yield: 7.2 mg (0.006 mmol, 22%). ^{1}H NMR (C_6D_6): δ (ppm) 0.67 (s, with platinum satellites, $^3J_{H-Pt} = 29.0$ Hz, 18 H, $SiMe_3$), 0.79 (dd, $^3J_{H-H} = 6.8$ Hz, $^2J_{P-H} = 11.8$ Hz, 6 H, ^iPr), 0.92 (dd, $^3J_{H-H} = 6.9$ Hz, $^2J_{H-P} = 13.5$ Hz, 6 H, ^iPr), 1.10 (m, 4 H, $-CH-$), 1.13 (dd, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-P} = 16.2$ Hz, 6 H, ^iPr), 1.18 (dd, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-P} = 17.7$ Hz, 6 H, ^iPr), 1.81−1.99 (2×m, 2×4 H, $-CH_2-$), 2.53, 2.60 (2×s, br, 2×6 H, $N-CH_3$), 7.07 (t, $^3J_{H-H} = 7.5$ Hz, 2 H, p-C_6H_5), 7.23 (pseudo-t, 4 H, m-C_6H_5), 8.16 (d, $^3J_{H-H} = 8.0$ Hz, 4 H, o-C_6H_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 53.5 (s, with platinum satellites, $^1J_{Pt-P} = 2631$ Hz). MS (positive electrospray): m/z (%) 1312.2 (15) (M^+). Anal. Calcd for $C_{42}H_{76}N_2P_2Pt_3Si_2$ (1312.2 g/mol): C, 38.43; H, 5.84; N, 2.13. Found: C, 38.27; H, 5.74; N, 1.97.

Photochemical Si−C Bond Activation in (PN)Pt(η^2-$Me_3SiC{\equiv}CPh$) (1). $Pt(COD)_2$ (29.7 mg, 0.072 mmol) was dissolved in a solution of 1-phenyl-2-trimethylsilylacetylene (12.6 mg, 0.072 mmol) in THF-d_8 (0.5 ml) at $T = -30$ °C. A dark yellow solution was formed, and $(^iPr)_2PCH_2CH_2NMe_2$ (13.7 mg, 15.3 μL, 0.072 mmol) was added. The formation of **1** was confirmed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy (vide supra). The NMR tube was cooled to $T = -30$ °C and irradiated with UV-light. The reaction was monitored by NMR spectroscopy.

Preparation of (dcpe)Pt(η^2-$Me_3SiC{\equiv}CPh$) (3). 1-Phenyl-2-trimethylsilylacetylene (18.2 mg, 0.1 mmol) was dissolved in 0.3 mL of C_6D_6 and added to $Pt(COD)_2$ (43.0 mg, 0.1 mmol). A yellow solution was formed. Subsequently a solution of bis(dicyclohexylphosphino)ethane (44.1 mg, 0.1 mmol) in 0.3 mL of C_6D_6 was added, and the formation of **3** was confirmed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. The solvent and all volatiles were evaporated in vacuo, and the remaining yellow solid was dissolved in pentane/CH_2Cl_2. Yellow crystals were formed after recrystallization at $T = -30$ °C. The mother liquor was decanted, and the product was dried in vacuo. **3** was obtained as an air- and moisture-sensitive, yellow solid. Yield: 50.0 mg (0.063 mmol, 61%). ^{1}H NMR (C_6D_6): δ (ppm) 0.56 (s, 9 H, $SiMe_3$), 0.91, 1.18, 1.33, 1.42, 1.56, 1.80, 1.96, 2.11, 2.23 (9×m, 48 H, Cy−H, $-CH_2-CH_2-$), 7.11 (t, $^3J_{H-H} = 7.3$ Hz, 1 H, p-C_6H_5), 7.35 (pseudo-t, 2 H, m-C_6H_5), 7.93 (d, 2 H, $^3J_{H-H} = 7.6$ Hz, o-C_6H_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 67.7 (d, with platinum satellites, $^1J_{Pt-P} = 3274$ Hz, $^2J_{P-P} = 53.9$ Hz), 69.1 (d, with platinum satellites, $^1J_{Pt-P} = 3116$ Hz, $^2J_{P-P} = 53.9$ Hz). Anal. Calcd for $C_{37}H_{62}P_2PtSi$ (792.08 g/mol): C, 56.11; H, 7.89. Found: C, 56.55; H, 8.12.

Preparation of (dcpe)Pt($SiMe_3$)($C{\equiv}CPh$) (4). **3** (21.0 mg, 0.027 mmol) was dissolved in C_6D_6 (0.5 mL) and transferred to a resealable NMR tube. The yellow solution was irradiated with UV-light, and the reaction was monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Pale yellow crystals of **4** were formed during photolysis, and the product was quantitatively formed within 6 h. Recrystallization from C_6D_6/pentane afforded 15.0

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(20) (a) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271. (b) Osborn, J. A.; Wilkinson, G.; Mrowca, J. J. *Inorg. Synth.* **1990**, *28*, 77.

mg (0.019, 70%) of **4**. ^{1}H NMR (C_6D_6): δ (ppm) 0.98 (d, with platinum satellites, $^3J_{H-Pt} = 33.6$ Hz, $^4J_{H-P(trans)} = 2.6$ Hz, 9 H, SiMe$_3$), 1.03−1.30, 1.39−1.75, 2.06, 2.30 (4×m, 48 H, Cy−H, −CH$_2$−), 6.99 (t, $^3J_{H-H} = 7.4$ Hz, 1 H, *p*-C$_6$H$_5$), 7.18 (pseudo-t, 2 H, *m*-C$_6$H$_5$), 7.76 (d, $^3J_{H-H} = 2$ H, *o*-C$_6$H$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 67.2 (d, with platinum satellites, $^1J_{Pt-P} = 2593$ Hz, $^2J_{P-P} = 5.2$ Hz), 71.3 (d, with platinum satellites, $^1J_{Pt-P} = 1113$ Hz, $^2J_{P-Si} = 166$ Hz, $^2J_{P-P} = 5.2$ Hz). ^{29}Si NMR (C_6D_6): δ (ppm) 0.03 (dd, $^2J_{Si-P(trans)} = 161.0$ Hz, $^2J_{Si-P(cis)} = 10.0$ Hz). Anal. Calcd for $C_{37}H_{62}P_2PtSi$ (792.08 g/mol): C, 56.11; H, 7.89. Found: C, 56.20; H, 8.01.

Preparation of [(COD)Pt]$_2$(SiMe$_3$)$_2$C$_4$ (5). Compound **5** was synthesized according to the preparation of (COD)Pt(η^2-diphenylacetylene).[13a] 1,4-Bis(trimethylsilyl)-1,3-butadiyne (50.0 mg, 0.26 mmol) was dissolved in petroleum ether (2.5 mL) and added dropwise to a suspension of Pt(COD)$_2$ (212.0 mg, 0.52 mmol) in petroleum ether (3 mL) at $T = -40$ °C. The color changed to dark brown, and the reaction mixture was allowed to warm to $T = -5$ °C within 45 min. The suspension was concentrated to ∼3 mL, and the brown solution was decanted. The remaining dark orange solid was dried in vacuo at $T = -5$ °C and stored at $T = -30$. **5** was used without further purification. Yield: 64 mg (0.08 mmol, 31%).

Preparation of (PN)Pt(SiMe$_3$)−C≡C−C≡C−Pt(SiMe$_3$)-(PN) (6). A solution of (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$ (13.8 mg, 15.4 μL, 0.073 mmol) in C_6D_6 (0.5 mL) was added to **5** (29.2 mg, 0.037 mmol). The brown solution was transferred to a resealable NMR tube and heated to $T = 70$ °C for 16 h. During the course of the reaction, a yellow precipitate was formed. The suspension was concentrated to ∼0.1 mL and filtered. The yellow solid was washed twice with petroleum ether (0.3 mL) and dried in vacuo. Yield: 20.5 mg (0.021 mmol, 58%). ^{1}H NMR (THF-d_8): δ (ppm) 0.26 (s, with platinum satellites, 18 H, SiMe$_3$, $^3J_{Pt-SiCH} = 13.8$ Hz), 1.20 (dd, $^3J_{H-P} = 7.1$ Hz, $^3J_{H-H} = 3.4$ Hz, 12 H, ^{i}Pr), 1.21 (dd, $^3J_{H-P} = 33.0$ Hz, $^3J_{H-H} = 6.9$, 12 H, ^{i}Pr), 1.87 (m, 4 H, P−CH$_2$−), 2.16 (m, 4 H, −CH−), 2.50 (m, 4 H, N−CH$_2$−), 2.65 (s, br, 12 H, N−CH$_3$). ^{31}P NMR (C_6D_6): δ (ppm) 58.6 (s, with platinum satellites, $^1J_{Pt-P} = 2734$ Hz). ^{29}Si NMR (THF-d_8): δ (ppm) −16.6 (d, $^2J_{Si-P(cis)} = 8.0$ Hz). Anal. Calcd for $C_{30}H_{66}N_2P_2Pt_2Si_2$ (963.23/mol): C, 37.40; H, 6.91; N, 2.91. Found: C, 37.00; H, 6.98; N, 2.65.

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Supporting Information Available: Details of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **2**, **I**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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