

Reactivity Differences of Pt⁰ Phosphine Complexes in C–C Bond Activation of Asymmetric Acetylenes

Ahmet Gunay, Christian Müller, Rene J. Lachicotte, William W. Brennessel, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

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Carbon–carbon bond activation reactions of asymmetric acetylene derivatives of the type L₂Pt(PhC≡CR) were studied with 1,2-bis(diisopropylphosphino)ethane (dippe), 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe), and 1-diisopropylphosphino-2-dimethylaminoethane (dippdmae) chelates. (dippe)Pt(η²-PhC≡CCH₃) (**1a**), (dippe)Pt(η²-PhC≡CCF₃) (**1b**), and (dippe)Pt(η²-PhC≡CC(CH₃)₃) (**1c**) showed no thermal reactivity at 160 °C, but **1b** showed evidence for C–C cleavage to form (dippe)Pt(Ph)(C≡CCF₃) upon irradiation with UV light (> 300 nm). In comparison, dtbpe analogues of these metal complexes, (dtbpe)Pt(η²-PhC≡CCH₃) (**2a**), (dtbpe)Pt(η²-PhC≡CCF₃) (**2b**), and (dtbpe)Pt(η²-PhC≡CC(CH₃)₃) (**2c**), showed either C–H or C–C activation products upon photolysis. **2b** produced (dtbpe)Pt(Ph)(C≡CCF₃), but **2a** or **2c** showed the formation of (dtbpe)Pt(D)(C₆D₅) (**2D**) by activation of the C₆D₆ solvent. Compounds **2a–c** showed no thermal reactivity at 160 °C. Two complexes with the hemilabile chelate dippdmae were synthesized and fully characterized, (dippdmae)Pt(η²-PhC≡CCF₃) (**3b**) and (dippdmae)Pt(η²-PhC≡CC(CH₃)₃) (**3c**). C–C cleavage products of the type (L₂)Pt(Ph)(C≡CCF₃) were observed only upon photolysis of compounds **1b**, **2b**, and **3b**.

Introduction

Carbon–carbon bond activation with the aid of transition metal complexes remains one of the most challenging fields in organometallic chemistry.^{1–4} While C–H bond activations have found many successful applications in organic synthesis and industrial chemistry, mild C–C bond activation is currently far from practical use.⁵ New routes for the efficient cleavage of C–C bonds will help convert naturally abundant traditionally unreactive molecules into useful raw materials¹ and could offer potential applications in organic synthesis and petroleum research.

To further develop this field, factors influencing C–C bond cleavage need to be understood, and new examples of metal insertions need to be elucidated.² Our group recently reported a new method⁶ for C–C bond activation that does

not take advantage of the known strategies of relief of ring strain,^{7–13} attainment of aromaticity,^{14,15} or forcing the targeted bond into close proximity to the transition metal center.^{1,2,16,17} The new examples involve alkynes containing sp–sp² (i.e., C≡C–aryl) bonds. Here we report attempts to activate the sp–sp³ C–C bonds by photolysis of mixed aryl–alkyl acetylene complexes. Also, a comparison is made between the effects of dippe, dtbpe, and dippmae ligands on the activation reaction.

Results and Discussion

Synthesis and Characterization of L₂Pt(alkyne) Complexes. To examine the possibility of sp–sp³ C–C bond activation, several aryl–alkyl acetylene complexes of the type (chelate)Pt(η²-PhC≡CR) containing the phosphine ligands dippe (Prⁱ₂PCH₂CH₂PPrⁱ₂), dtbpe (Bu^t₂PCH₂CH₂PBu^t₂), or dippdmae (Prⁱ₂PCH₂CH₂NMe₂) were prepared as shown in eq 1. The syntheses all involve reaction of a 1:1:1 mixture of

*Corresponding author. E-mail: jones@chem.rochester.edu.

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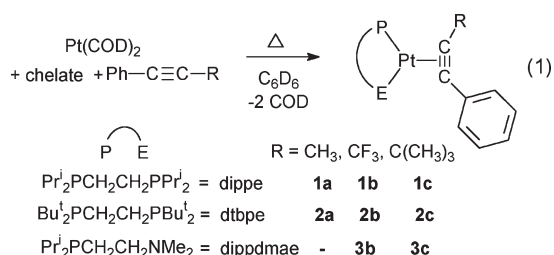
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chelate, $\text{Pt}(\text{COD})_2$, and $\text{PhC}\equiv\text{CR}$ in C_6D_6 , and heating at 55–100 °C for several hours is necessary. The *tert*-butyl acetylene derivatives (**c**) were more difficult to form. Formation of **1c** required heating at 100 °C for 20 h to obtain 100% conversion. Formation of **2c** required heating to 100 °C in the presence of 20 equiv of alkyne. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds **1a–c** and **2a–c** typically show two doublets with platinum satellites ($J_{\text{P-P}} \approx 50$ Hz; $J_{\text{P-Pt}} \approx 3000$ Hz). The “b” series of compounds containing a CF_3 -substituted acetylene showed one of the phosphorus resonances as a doublet of quartets due to the additional P–F coupling ($J_{\text{P-F}} = 10$ –16 Hz).



Complexes **3b–c** have the potential to form two regioisomers. Heating a 1:1:1 ratio of dippdmae, $\text{Pt}(\text{COD})_2$, and $\text{PhC}\equiv\text{CCF}_3$ at 70 °C overnight produced **3b** in 51% yield. The product was obtained as a mixture of two isomers (90% isomer with the CF_3 group *trans* to P, 10% isomer with the CF_3 group *cis* to P). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the major isomer of **3b** shows a quartet at δ 64.7 ($J_{\text{P-Pt}} = 3844$ Hz, $J_{\text{P-F}} = 16$ Hz), and the minor isomer appears as a singlet at δ 66.6 ($J_{\text{P-Pt}} = 3633$ Hz).

The single-crystal structures of **1b–3c** have been determined and are shown Figure 1. Table 1 lists similar bond distances and angles for the compounds. While $\text{d}^{10} \text{Pt}^0$ complexes might be expected to have a tetrahedral geometry, the structural analysis revealed a distorted trigonal geometry at the metal center with the alkyne ligand in the P–Pt–P plane. One can notice asymmetrical binding of the trifluoromethylphenylacetylene derivatives, in that the Pt–C(2) bond is noticeably shorter in **1b** and **2b**, but not in **3b**. The C≡C–C bending of the alkyne substituents ranges from 135° to 145°, indicative of strong π -back-bonding.^{18,19} The presence of an elongated C–C triple bond compared to free

diphenylacetylene is also indicative of back-bonding.²⁰ Rosenthal has characterized a large number of related L_2Ni -(alkyne) complexes,²¹ and some Pd and Pt derivatives are known.²²

Reactivity of $\text{L}_2\text{Pt}(\text{alkyne})$ Complexes. Complexes **1a–2c** were all found to be thermally very stable. Heating to 160 °C for 1–3 days in C_6D_6 showed no evidence of reaction for **1a**, **2a**, **1b**, **2b**, **1c**, or **2c**. However, **3b** and **3c** proved to be more thermally sensitive. Upon heating (dippdmae) $\text{Pt}(\eta^2\text{-PhC}\equiv\text{CCF}_3)$ (**3b**) either alone or with 5 equiv of $\text{PhC}\equiv\text{CCF}_3$ at 75 °C, another complex was seen to grow in. This species shows two resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a multiplet at δ 30.7 ($J_{\text{P-Pt}} = 3565$ Hz) and a doublet ($J_{\text{P-P}} = 18$ Hz) at δ 32.7 ($J_{\text{P-Pt}} = 3304$ Hz). In earlier studies of the diphenylacetylene complex (dippdmae) $\text{Pt}(\eta^2\text{-PhC}\equiv\text{CPh})$, it was established that the bis-monodentate complex (dippdmae) $_2\text{Pt}(\eta^2\text{-PhC}\equiv\text{CPh})$ can form if an extra equivalent of dippdmae is present.²³ By analogy to the chemical shift and the Pt–P coupling constants of (dippdmae) $_2\text{Pt}(\eta^2\text{-PhC}\equiv\text{CPh})$ (δ 32.2, $J_{\text{P-Pt}} = 3336$ Hz), the new resonances seen in the ^{31}P NMR spectrum were assigned to (dippdmae) $_2\text{Pt}(\eta^2\text{-PhC}\equiv\text{CCF}_3)$ (Scheme 1). The high value of the Pt–P coupling constant and the fact that one of the phosphorus resonances was a multiplet while the other was a doublet support this assignment. The fate of the residual Pt^0 was not determined, and heating **3b** at 100 °C for 1 day caused decomposition.

Similarly, (dippdmae) $\text{Pt}(\eta^2\text{-PhC}\equiv\text{CC}(\text{CH}_3)_3)$ (**3c**) also proved to be thermally sensitive. Upon heating **3c** at 55 °C for 2 days, similar to the case for **3b**, a new complex appears with a doublet at δ 27.8 ($J_{\text{P-P}} = 28$ Hz; $J_{\text{P-Pt}} = 3208$ Hz) and another doublet at δ 34.1 ($J_{\text{P-P}} = 28$ Hz; $J_{\text{P-Pt}} = 3483$ Hz). Comparison to the literature data for (dippdmae) $_2\text{Pt}(\eta^2\text{-PhC}\equiv\text{CPh})$ ²³ suggests that the new complex was (dippdmae) $_2\text{Pt}(\eta^2\text{-PhC}\equiv\text{CC}(\text{CH}_3)_3)$ (Scheme 1). Heating **3c** at 75 °C for 1 day caused decomposition.

Our previous studies showed that aryl–alkyne C–C bonds undergo oxidative addition upon photolysis.⁶ Therefore, compound **1a** was irradiated with UV light ($\lambda > 300$ nm) in C_6D_6 solution. After irradiation overnight, no evidence for activation product was seen, and only **1a** remained. Similar irradiation of **1c** also showed no evidence for C–C cleavage. Irradiation of **1b** for 10 days, however, showed the formation of a new product (60%) whose ^{31}P NMR spectrum showed multiplets at δ 63.95 ($J_{\text{Pt-P}} = 2251$ Hz) and 71.90 ($J_{\text{Pt-P}} = 1566$ Hz). These chemical shifts and coupling constants are consistent with the formation of the C–C insertion product (dippe) $\text{Pt}(\text{Ph})(\text{C}\equiv\text{CCF}_3)$, **4b**.⁶ As further evidence for aryl–alkyne C–C cleavage, the ^1H NMR spectrum showed a change in the ortho C–H resonance of the alkyne phenyl group from δ 8.10 (d, $J = 7$ Hz) in **1b** to δ 7.75 (t, $J = 7$ Hz) with platinum satellites ($J_{\text{Pt-H}} = 27$ Hz) in **4b** (see Supporting Information for spectra). Irradiation for 18 days showed ~80% conversion to **4b**, but the product could not be isolated cleanly. No evidence for sp-sp^3 bond cleavage was seen.

In contrast to **1a**, irradiation of **2a** in C_6D_6 with UV light ($\lambda > 300$ nm) for 20 h led to the complete conversion to a Pt^{II} product, as observed by ^{31}P NMR spectroscopy. The product that appeared displayed a 1:1:1 triplet ($J = 30$ Hz) at δ 83.8 with platinum satellites ($J_{\text{P-Pt}} = 1721$ Hz) and a singlet

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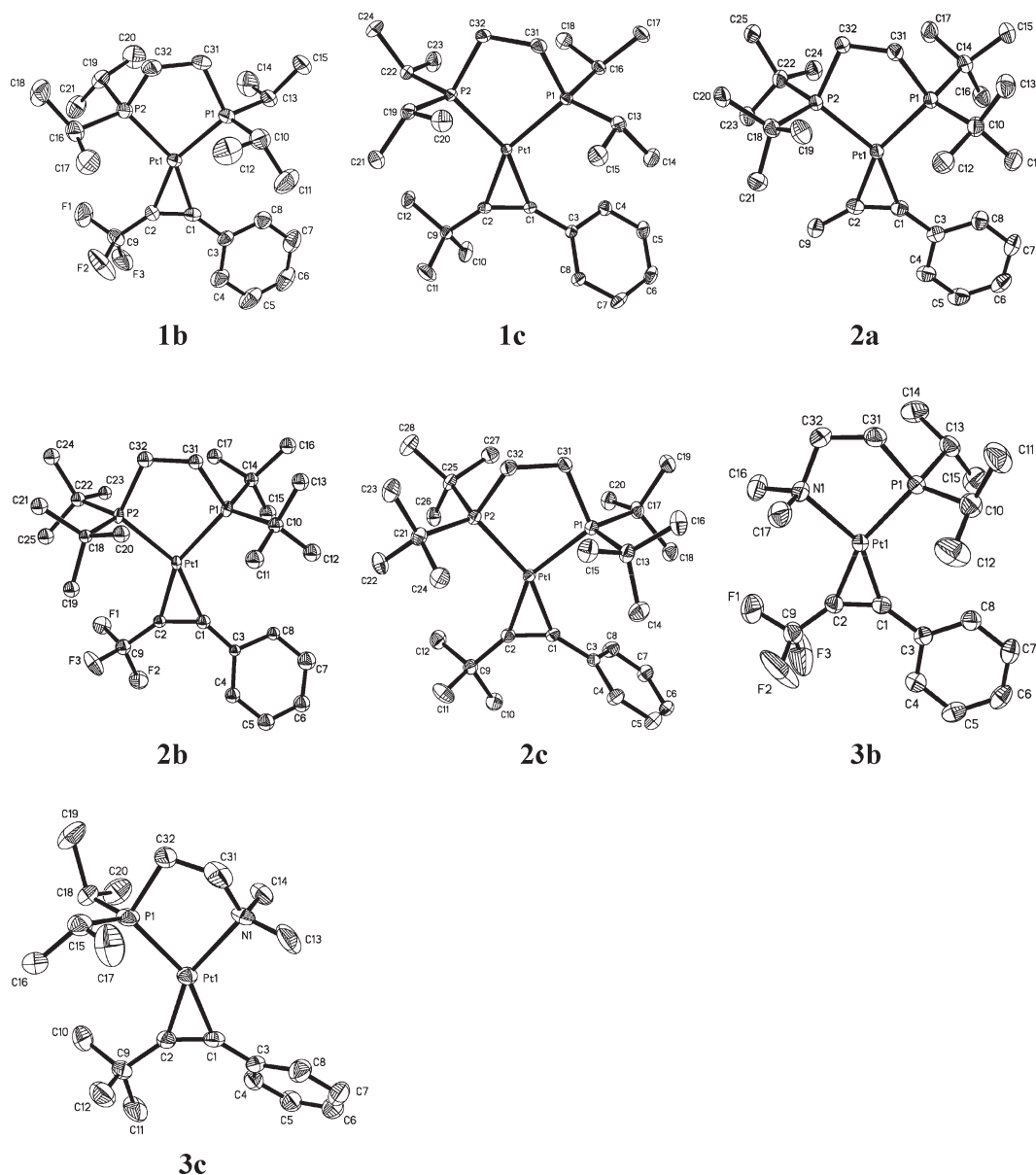


Figure 1. Molecular structures of (chelate)Pt(η^2 -PhC \equiv CR) (**1b**, **1c**, **2a**, **2b**, **2c**, **3b**, and **3c**) where chelate = dippe (**1**), dtbpe (**2**), or dippdmae (**3**) and R = CH₃ (**a**), CF₃ (**b**), or *t*-Bu (**c**) (50% probability ellipsoids).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **1a–3c**

	Bond Lengths						
	1b	1c	2a	2b	2c	3b	3c
Pt(1)–P(1)	2.2527(10)	2.2603(5)	2.2862(8)	2.276(4)	2.2798(10)	2.2502(9)	2.249(3)
Pt(1)–P(2)/N(1) ^a	2.2638(10)	2.2589(5)	2.2783(8)	2.299(4)	2.2788(9)	2.221(3) ^a	2.242(6) ^a
Pt(1)–C(1)	2.040(4)	2.0411(17)	2.060(3)	2.098(16)	2.043(3)	1.998(4)	2.067(7)
Pt(1)–C(2)	2.006(4)	2.0497(17)	2.023(3)	2.027(15)	2.060(3)	2.022(4)	1.995(7)
C(1)–C(2)	1.299(5)	1.303(2)	1.310(4)	1.342(18)	1.285(5)	1.301(5)	1.302(9)
C(1)–C(3)	1.463(5)	1.458(2)	1.456(4)	1.37(2)	1.459(5)	1.465(5)	1.449(9)
C(2)–C(9)	1.471(5)	1.503(2)	1.463(4)	1.50(2)	1.528(5)	1.457(5)	1.497(9)
	Bond Angles						
	1b	1c	2a	2b	2c	3b	3c
P(1)–Pt(1)–P(2)/N(1) ^a	87.12(4)	87.244(18)	88.51(3)	88.32(12)	88.34(4)	84.21(9) ^a	83.7(4) ^a
C(1)–Pt(1)–C(2)	37.44(15)	37.14(7)	37.41(13)	37.9(5)	36.51(13)	37.76(14)	37.3(3)
C(3)–C(1)–C(2)	142.1(4)	145.31(17)	140.0(3)	135.3(17)	142.6(4)	143.2(4)	144.8(7)
C(9)–C(2)–C(1)	140.5(4)	140.34(16)	143.9(3)	141.9(16)	138.1(3)	140.4(4)	144.2(7)

^a Replace P(2) with N(1) in these compounds.

Scheme 1. Reactivity of Alkyne Complexes

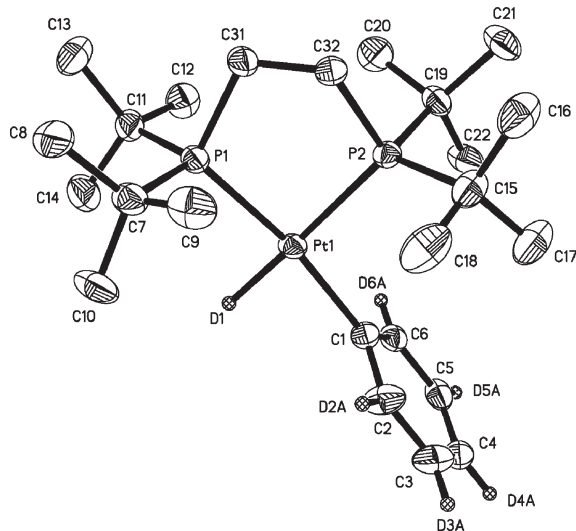
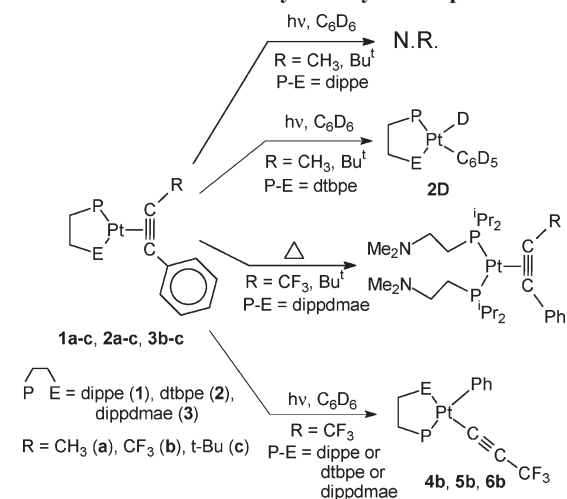


Figure 2. Product (dippe)Pt(D)(C₆D₅) (**2D**) arising from irradiation of **2a** in C₆D₆ (50% probability ellipsoids).

at δ 102.0 ($J_{\text{P-Pt}} = 1794$ Hz). This sample was crystallized, and the X-ray structure of the product was determined (Figure 2, Table 2), indicating that the product was (dtbpe)Pt(D)(C₆D₅) (**2D**), arising from reaction with the solvent (C₆D₆) rather than the C–C activation of 1-phenyl-1-propyne (Scheme 1). Irradiation of **2c** gives a similar result, producing **2D**. A related result was reported earlier describing the formation of C₆H₆-activated product (dtbpe)Pt(H)(C₆H₅) upon photolysis of (dtbpe)PtH₂ in benzene.²⁴

Irradiation of **2b** in C₆D₆ also led to the formation of a new Pt^{II} product, **5b**. In this case, however, the ³¹P NMR spectrum showed two distinct singlets, each with platinum satellites (Figure 3, δ 71.1, $J_{\text{P-Pt}} = 2564$ Hz; 80.0, $J_{\text{P-Pt}} = 1547$ Hz). Complete conversion to **5b** was not observed even after 8 days of irradiation by UV light, the highest conversion reaching 60%, suggesting attainment of a photostationary state. These chemical shifts and coupling constants are consistent with the formation of the C–C insertion product (dtbpe)Pt(Ph)(C \equiv CCF₃), **5b**.⁶

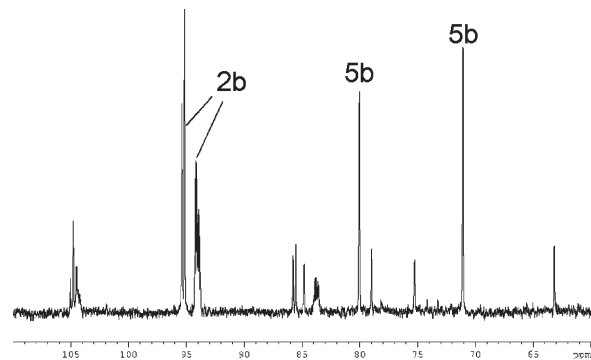


Figure 3. ³¹P NMR spectrum upon irradiation of **2b** in C₆D₆ for 4 days.

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

Bond Lengths			
Pt(1)–P(1)	2.2880(10)	Pt(1)–C(1)	2.084(4)
Pt(1)–P(2)	2.3317(10)	Pt(1)–D(1)	1.5854
Bond Angles			
D(1)–Pt(1)–P(1)	90.2	D(1)–Pt(1)–C(1)	82.1
P(2)–Pt(1)–P(1)	87.74(4)	Pt(1)–P(1)–C(31)	108.47(13)
C(1)–Pt(1)–P(2)	99.90(11)	Pt(1)–P(2)–C(32)	106.61(13)

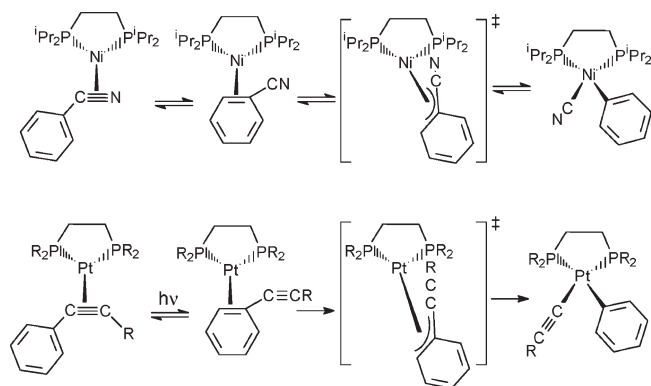
Likewise, photolysis of **3b** with UV light for 9 h showed evidence for the slow formation of a new product (60%) with $J_{\text{Pt-P}} = 2802$ Hz. This product is assigned to the C–C cleavage product (dippdmae)Pt(Ph)(C \equiv CCF₃) (**6b**). As with **5b**, the ¹H NMR spectrum showed a change in the ortho C–H resonance of the alkyne phenyl group from δ 7.96 (d, $J = 7$ Hz) in **3b** to δ 7.64 (d, $J = 7$ Hz) with platinum satellites ($J_{\text{Pt-H}} = 66$ Hz) in **6b** (see Supporting Information for spectra). Longer irradiation led to decomposition, which prevented isolation of **6b**.

The lack of C–C cleavage in **1a**, **2a**, **1c**, and **2c** was unexpected on the basis of prior reactivity seen in other L₂Pt(acetylene) complexes.⁶ Evidently, 1-phenyl-1-propyne and *tert*-butylphenylacetylene do not coordinate sufficiently strongly so that upon irradiation dissociation occurs prior to C–C cleavage. The vacant coordination site can then be occupied by C₆D₆, which is then activated. As these alkynes have an electron-donating alkyl group on the acetylene, this electron donation may cause poor back acceptance by the acetylene, and hence a weaker coordination. Therefore, a similar substrate with an electron-withdrawing substituent may show a better coordination to the platinum and facilitate C–C activation, as seen with trifluoromethylphenylacetylene.

While the detailed mechanism of the photoinduced C–C cleavage is not known, a pathway involving orthometalation can be ruled out, as para-substituents on the aryl ring remain para in the Pt-aryl product.^{6b} We propose that the mechanism of cleavage is the same as seen in the isoelectronic C–CN cleavage of benzonitrile by [Ni(dippe)], which was established by experiment and DFT theory.²⁵ In this mechanism, coordination to the triple bond is not important for C–C cleavage. The molecule must first rearrange to the η^2 -arene complex, which then undergoes C–C oxidative cleavage, as

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Scheme 2. Mechanism of C–C Cleavage in Benzonitrile and Proposed Mechanism for Phenylacetylenes

shown in Scheme 2. Perhaps the role of photolysis is to destabilize the metal–alkyne interaction and promote the migration to the phenyl ring. This pathway would also account for the lack of $sp-sp^3$ C–C cleavage. Since only the CF_3 -containing phenylalkynes undergo C–C activation, perhaps the stronger binding of this alkyne leads to the η^2 -arene complex upon photolysis rather than dissociation, as seen with the Me- and *t*-Bu-substituted alkynes. Additionally, the initial coordination of the $[L_2Pt]$ fragment to the alkyne triple bond is apparently faster than the rate of coordination to the arene π -system, since no C–C cleavage is seen thermally when the η^2 -alkyne complexes were synthesized.

Conclusions

Pt^0 complexes of η^2 -coordinated asymmetric acetylene derivatives 1-phenyl-1-propyne, trifluoromethylphenylacetylene, and *tert*-butylphenylacetylene have been synthesized and characterized. Only the Pt^0 complexes with the electron-deficient trifluoromethylphenylacetylene ligand showed evidence for C–C cleavage. The strong donor chelate dtbpe on platinum showed evidence for C–H activation of benzene solvent following alkyne loss. In no case was evidence for $sp-sp^3$ C–C cleavage observed.

Experimental Section

General Considerations. All experiments were carried out under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox, unless otherwise stated. The solvents were available commercially and distilled from dark purple solutions of benzophenone ketyl. 1H , $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance-400, Bruker AMX-400, and Bruker Avance-500 spectrometers. All 1H chemical shifts were referenced to residual proton resonances or to TMS in the deuterated solvents. An external standard of 85% H_3PO_4 was used to reference the $^{31}P\{^1H\}$ NMR data. All crystal structures were determined by using a Siemens-SMART 3-circle CCD diffractometer. All photolysis experiments were performed in sealed NMR tubes with an Oriel arc source using a 200 W Hg(Xe) bulb. Elemental analyses were obtained from Desert Analytics. 1-Phenyl-1-propyne was obtained from commercial sources, and $Pt(COD)_2$,^{26,27} trifluoromethylphenyl-

acetylene,²⁸ 1,2-bis(diisopropylphosphino)ethane (dippe),²⁹ 1-diisopropylphosphino-2-dimethylaminoethane (dippdme),³⁰ 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe),³¹ and *tert*-butylphenylacetylene³² were synthesized according to the reported procedures.

Preparation of (dippe) $Pt(\eta^2$ -PhC \equiv CCH $_3$) (1a). 1-Phenyl-1-propyne (2.82 mg, 0.024 mmol, 3.04 μ L) was dissolved in 0.5 mL of C_6D_6 and transferred onto $Pt(COD)_2$ (10 mg, 0.024 mmol) powder. The color of the solution became dark brown. Then 0.5 mL of C_6D_6 solution of dippe (6.37 mg, 0.024 mmol) was added, and the solution was placed into a resealable NMR tube, which was heated at 70 $^\circ$ C overnight, whereupon the color turned light orange. The solvent and the free COD were removed under vacuum, and the light yellow powder was redissolved in C_6H_6 . Colorless crystals of **1a** were obtained via solvent evaporation at 23 $^\circ$ C. Yield: 7.5 mg, 54%. For **1a**: 1H NMR (C_6D_6): δ 0.83 (dd, J_{H-P} = 13 Hz, J_{H-H} = 7 Hz, 6 H, $CHMe_2$), 0.9 (dd, J_{H-P} = 14 Hz, J_{H-H} = 7 Hz, 6 H, $CHMe_2$), 1.08 (dd, J_{H-P} = 7 Hz, J_{H-H} = 3 Hz, 6 H, $CHMe_2$), 1.12 (dd, J_{H-P} = 7 Hz, J_{H-H} = 3 Hz, 6 H, $CHMe_2$), 1.18 (m, 4 H, CH), 1.65 (s, 3 H, $C\equiv CCH_3$), 1.85 (m, 2 H, CH_2), 2.05 (m, 2 H, CH_2), 7.13 (pseudo t, J_{H-H} = 9 Hz, 1 H, *p*- C_6H_5), 7.39 (t, J_{H-H} = 9 Hz, 2 H, *m*- C_6H_5), 7.95 (d, J_{H-H} = 10 Hz, 2 H, *o*- C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.3 (s, $CHMe_2$), 18.7 (s, $CHMe_2$), 19.0 (s, $C\equiv C-CH_3$), 19.4 (s, $CHMe_2$), 19.8 (s, $CHMe_2$), 24.48 (m, CH_2), 25.7 (d, J_{C-P} = 21 Hz, CH), 26.4 (d, J_{C-P} = 21 Hz, CH), 124.8, 130.5, 131.6 and obscured by C_6D_6 (s, Ph), 135.9 (s, $C\equiv C$), 141.2 (s, $C\equiv C$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 77.5 (d, J_{P-P} = 48 Hz, with platinum satellites J_{P-Pt} = 2944 Hz, P trans to $C-CH_3$), 79.8 (d, J_{P-P} = 48 Hz, with platinum satellites J_{P-Pt} = 3041 Hz, P trans to $C-C_6H_5$).

Preparation of (dtbpe) $Pt(\eta^2$ -PhC \equiv CCH $_3$) (2a). A 0.5 mL portion of a C_6D_6 solution of 1-phenyl-1-propyne (8.5 mg, 0.073 mmol, 9.2 μ L) was added to $Pt(COD)_2$ (30 mg, 0.073 mmol), followed by 0.5 mL of a C_6D_6 solution of dtbpe (23.2 mg, 0.073 mmol). The color of the solution turned brown-red. The sample was heated at 100 $^\circ$ C to obtain the Pt^0 product, whereupon the solution turned red. The volatiles were removed under vacuum, and the red powder was redissolved in C_6H_6 for recrystallization by evaporation. Colorless crystals of **2a** were collected. Yield: 25.7 mg, 56%. For **2a**: 1H NMR (C_6D_6): δ 0.97 (d, J_{H-P} = 14 Hz, 2 H, CH_2), 1.12 (s, 3 H, $C\equiv CCH_3$), 1.16 (d, J_{H-P} = 7 Hz, 18 H, CMe_3), 1.19 (d, J_{H-P} = 7 Hz, 18 H, CMe_3), 1.28 (d, J_{H-P} = 12 Hz, 2 H, CH_2), 7.07 (pseudo t, J_{H-H} = 8 Hz, 1 H, *p*- C_6H_5), 7.33 (t, J_{H-H} = 9 Hz, 2 H, *m*- C_6H_5), 7.80 (d, J_{H-H} = 9 Hz, 2 H, *o*- C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.1 (s, $C\equiv C-CH_3$), 25.8 (m, CH_2), 29.9 (d, J_{C-P} = 12 Hz, $C(CH_3)_3$), 30.1 (d, J_{C-P} = 12 Hz, $C(CH_3)_3$), 34.0 (m, P–Cs), 124.0 (s, ipso-C), 129 (s, C in Ph), the additional resonances obscured by C_6D_6 solvent (aromatic carbons), 141.2 (m, $C\equiv C$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 96.6 (d, J_{P-P} = 55 Hz, with platinum satellites J_{P-Pt} = 3016 Hz, 1 P), 97.5 (d, J_{P-P} = 54 Hz, with platinum satellites J_{P-Pt} = 3155 Hz, 1 P).

Preparation of (dtbpe) $Pt(D)(C_6D_5)$ (2D). A 10 mg (0.016 mmol) portion of **2a** was dissolved in 1 mL of C_6D_6 and placed into a resealable NMR tube with a Teflon stopcock. The sample was irradiated with UV light (λ > 300 nm) for 20 h. A 95% conversion to the solvent activated complex was observed by ^{31}P NMR spectroscopy. Colorless crystals of **2D** were obtained by solvent evaporation. Yield: 7.0 mg, 74%. For **2D**: 1H NMR ($CDCl_3$):

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δ 1.32 (m, 36 H, CMe_3), 1.54 (d, $J_{\text{H-P}} = 13$ Hz, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 30.8 (m, $\text{C}(\text{CH}_3)_3$), 30.3 (m, $\text{C}(\text{CH}_3)_3$), 36.2 (d, $J_{\text{C-P}} = 16$ Hz, CH_2), 36.9 (d, $J_{\text{C-P}} = 27$ Hz, CH_2), 124.0, 127.3, 128.1, and 131.5 (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 83.8 (t, $J_{\text{P-D}} = 30$ Hz, with platinum satellites $J_{\text{P-Pt}} = 1721$ Hz, 1 P, P trans to D), 102.0 (s, with platinum satellites $J_{\text{P-Pt}} = 1794$ Hz, 1 P, P trans to C_6D_5).

Preparation of (dippe)Pt(η^2 -PhC \equiv CCF $_3$) (1b). Trifluoromethylphenylacetylene (13.2 mg, 0.08 mmol) was dissolved in C_6D_6 (0.5 mL) and added to $\text{Pt}(\text{COD})_2$ (32.9 mg, 0.08 mmol). A purple solution was formed, which was transferred to a vial containing dippe (21.0 mg, 0.08 mmol), producing an orange solution. Following evaporation of benzene the compound was dissolved in a 1:4 mixture of petroleum ether and dichloromethane and stored at -20°C , forming yellow crystals. Yield: 25.0 mg, 50%. For **1b**, ^1H NMR (C_6D_6): δ 0.74 (dd, $J_{\text{H-P}} = 14$ Hz, $J_{\text{H-H}} = 8$ Hz, 6 H, CHMe_2), 0.82 (dd, $J_{\text{H-P}} = 16$ Hz, $J_{\text{H-H}} = 12$ Hz, 6 H, CHMe_2), 0.98 (dd, $J_{\text{H-P}} = 17$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2), 1.07 (m, 4 H, P-CH-), 1.12 (dd, $J_{\text{H-P}} = 16$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2), 1.95 (m, 4 H, CH_2), 7.08 (t, $J_{\text{H-H}} = 7$ Hz, 1 H, $p\text{-C}_6\text{H}_5$), 7.27 (pseudo t, $J_{\text{H-H}} = 8$ Hz, 2 H, $m\text{-C}_6\text{H}_5$), 8.02 (d, $J_{\text{H-H}} = 8$ Hz, 2 H, $o\text{-C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 76.8 (dq, $J_{\text{P-P}} = 34$ Hz, $J_{\text{P-F}} = 10$ Hz, $J_{\text{P-Pt}} = 3248$ Hz), 78.9 (d, with platinum satellites, $J_{\text{P-P}} = 34$ Hz, $J_{\text{P-Pt}} = 2999$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6): δ 6.7 (d, with platinum satellites, $J_{\text{F-P}} = 10$ Hz, $J_{\text{F-Pt}} = 57$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 18.5 (s, CHMe_2), 18.7 (s, CHMe_2), 19.4 (s, CHMe_2), 20.0 (s, CHMe_2), 23.5 (dd, $J_{\text{C-P}} = 27$ Hz, $J_{\text{C-P}} = 13$ Hz, CH_2), 24.0 (dd, $J_{\text{C-P}} = 27$ Hz, $J_{\text{C-P}} = 13$ Hz, CH_2), 25.6 (d, $J_{\text{C-P}} = 23$ Hz, CH), 26.7 (d, $J_{\text{C-P}} = 23$ Hz, CH), 125.0, 126.9, 128.0, and 128.3 (s, Ph), 131.4 (m, CF_3), 132.0 (s, $\text{C}\equiv\text{C}$), 134.0 (t, $\text{C}\equiv\text{C}$). Anal. Calcd (found) for $\text{C}_{23}\text{H}_{37}\text{F}_3\text{P}_2\text{Pt}$: C, 44.02 (44.13); H, 5.94 (5.72).

Preparation of (dtbpe)Pt(η^2 -PhC \equiv CCF $_3$) (2b). Trifluoromethylphenylacetylene (4.13 mg, 0.0243 mmol) dissolved in 0.5 mL of C_6D_6 was added to a vial containing $\text{Pt}(\text{COD})_2$ (10 mg, 0.0243 mmol), producing a light pink solution. Then 0.5 mL of a C_6D_6 solution of dtbpe (7.73 mg, 0.0243 mmol) was added, and the sample was heated at 100°C to obtain a light orange solution of **2b** (full conversion by ^{31}P NMR spectroscopy). The volatiles were removed under vacuum, and the sample was recrystallized from C_6H_6 , producing colorless crystals of **2b**. Yield: 12.8 mg, 77%. For **2b**, ^1H NMR (CDCl_3): δ 1.27 (d, $J_{\text{H-P}} = 13$ Hz, 18 H, CMe_3), 1.39 (d, $J_{\text{H-P}} = 13$ Hz, 18 H, CMe_3), 1.85 (m, 4 H, CH_2), 7.21 (t, $J = 7$ Hz, 1 H, $p\text{-H}$), 7.38 (t, $J = 7$ Hz, overlapping with the solvent resonance, 2 H, $m\text{-H}$), 7.45 (d, $J = 7$ Hz, 2 H, $o\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 25.6 (m, C), 30.0 (m, $(\text{CH}_3)_3$), 34.5 (m, CH_2), 125.4, 127.3, 127.5, and 128.6 (s, aromatic C's), 132.2 and 133.7 (m, $\text{C}\equiv\text{C}$), 139.0 (m, CF_3). $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.4 (d, with platinum satellites, $J_{\text{F-P}} = 13$ Hz, $J_{\text{F-Pt}} = 84$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 94.1 (dq, $J_{\text{P-P}} = 39$ Hz, $J_{\text{P-F}} = 12$ Hz, with platinum satellites $J_{\text{P-Pt}} = 3342$ Hz, 1 P, P trans to CF_3), 95.3 (d, $J_{\text{P-P}} = 39$ Hz, with platinum satellites $J_{\text{P-Pt}} = 3116$ Hz, 1 P, P trans to Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 93.7 (m, with platinum satellites $J_{\text{P-Pt}} = 3339$ Hz, 1 P, P trans to CF_3), 94.9 (d, $J_{\text{P-P}} = 58$ Hz, with platinum satellites $J_{\text{P-Pt}} = 3116$ Hz, 1 P, P trans to Ph). Anal. Calcd (found) for $\text{C}_{27}\text{H}_{45}\text{F}_3\text{P}_2\text{Pt}$: 47.43 (48.74) C; 6.63 (6.17) H.

Preparation of (dippe)Pt(η^2 -PhC \equiv CC(CH $_3$) $_3$) (1c). *tert*-Butylphenylacetylene (10.5 mg, 0.0664 mmol) was dissolved in THF-d_8 (0.5 mL) and cooled to -20°C . This solution was transferred onto $\text{Pt}(\text{COD})_2$ (27.3 mg, 0.0664 mmol), forming a dark orange solution, which was added to a vial containing 17.4 mg of dippe (0.0664 mmol). This solution was heated to 100°C for 20 h, whereupon the color changed to bright yellow (complete conversion to the η^2 -alkyne complex was confirmed by ^{31}P NMR spectroscopy). The solvent was evaporated under vacuum and the product recrystallized from pentane/dichloromethane at -20°C . Yield: 31.4 mg, 77%. For **1c**, ^1H NMR (THF-d_8): δ 0.96 (m, 12 H, CHMe_2), 1.06 (dd, $J_{\text{H-P}} = 12$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2), 1.17 (dd, $J_{\text{H-P}} = 15$ Hz, $J_{\text{H-H}} = 7$ Hz,

6 H, CHMe_2), 1.31 (s, 9 H, *t*-Bu), 1.58 (m, 4 H, CH), 2.07 (m, 2 H, CH_2), 2.21 (m, 2 H, CH_2), 6.9 (t, $J_{\text{H-H}} = 7$ Hz, 1 H, $p\text{-C}_6\text{H}_5$), 7.13 (pseudo t, $J_{\text{H-H}} = 8$ Hz, 2 H, $m\text{-C}_6\text{H}_5$), 7.25 (d, $J_{\text{H-H}} = 8$ Hz, 2 H, $o\text{-C}_6\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 18.0 (s, CHMe_2), 18.4 (s, CHMe_2), 20.0 (s, CHMe_2), 20.4 (s, $\text{C}\equiv\text{C}-\text{C}-$), 20.6 (s, CHMe_2), 23.1 (dd, $^1J_{\text{C-P}} = 74$ Hz, $^2J_{\text{C-P}} = 47$ Hz, CH_2), 25.0 (dd, $^1J_{\text{C-P}} = 83$ Hz, $^2J_{\text{C-P}} = 57$ Hz, CH_2), 26.2 (d, $J_{\text{C-P}} = 75$ Hz, CH), 32.7 (s, $\text{C}(\text{CH}_3)_3$), 124.2, 128.7, 131.2 and obscured by C_6D_6 (s, Ph), 143.1 and 143.3 (s, $\text{C}\equiv\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-d_8): δ 74.7 (d, with platinum satellites, $J_{\text{P-P}} = 47$ Hz, $J_{\text{P-Pt}} = 3111$ Hz), 75.4 (d, with platinum satellites, $J_{\text{P-P}} = 48$ Hz, $J_{\text{P-Pt}} = 2970$ Hz). Anal. Calcd (found) for $\text{C}_{26}\text{H}_{46}\text{P}_2\text{Pt}$: 50.72 (50.54) C, 7.53 (7.47) H.

Preparation of (dtbpe)Pt(η^2 -PhC \equiv CC(CH $_3$) $_3$) (2c). *tert*-Butylphenylacetylene (3.84 mg, 0.024 mmol) was dissolved in 0.5 mL of C_6D_6 and added to $\text{Pt}(\text{COD})_2$ (10 mg, 0.024 mmol) at room temperature. Then 0.5 mL of a C_6D_6 solution of dtbpe (7.74 mg, 0.024 mmol) was added, and the solution became light yellow. The sample was heated at 100°C overnight to obtain only the η^2 -coordinated Pt^0 complex. However, ^{31}P NMR data showed that only 50% of the products were the target Pt^0 - η^2 complex, **2c**, with $\sim 50\%$ (dtbpe)Pt(COD) still remaining. To obtain only the Pt^0 - η^2 complex, an additional 19 equiv of the alkyne was added to the solution and the sample was heated at 100°C overnight, producing only **2c**. Excess alkyne was required to obtain high conversions. The volatiles were removed under vacuum and the white-yellow powder was recrystallized from C_6H_6 , yielding colorless and air-sensitive crystals of **2c**. Yield: 11.8 mg, 72%. For **2c**, ^1H NMR (C_6D_6): δ 1.02 (d, $J_{\text{H-P}} = 12$ Hz, 18 H, CMe_3), 1.12 (m, 2 H, CH_2), 1.26 (d, $J_{\text{H-P}} = 12$ Hz, 18 H, CMe_3), 1.41 (m, 2 H, CH_2), 1.63 (s, 9 H, $\text{C}\equiv\text{CCMe}_3$), 6.99 (t, 1 H, $p\text{-C}_6\text{H}_5$), 7.25 (t, 2 H, $m\text{-C}_6\text{H}_5$), 7.37 (d, 2 H, $o\text{-C}_6\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 24.9 (m, P-C), 26.9 (m, P-C), 29.7 (d, $J_{\text{C-P}} = 48$ Hz, CMe_3), 29.9 (s, $\text{C}\equiv\text{CC}$), 30.2 (d, $J_{\text{C-P}} = 48$ Hz, CMe_3), 32.8 (s, CCMe_3), 33.7 (dd, $J_{\text{C-P}} = 70$ Hz, $J_{\text{C-P}} = 28$ Hz, CH_2), 34.4 (dd, $J_{\text{C-P}} = 68$ Hz, $J_{\text{C-P}} = 28$ Hz, CH_2), 123.2 (s, ipso-C), resonances overlapping with C_6D_6 (Ph), 144.5 and 146.0 (s, $\text{C}\equiv\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 96.6 (d, $J_{\text{P-P}} = 55$ Hz, with platinum satellites $J_{\text{P-Pt}} = 3016$ Hz, 1 P), 97.5 (d, $J_{\text{P-P}} = 54$ Hz, with platinum satellites $J_{\text{P-Pt}} = 3155$ Hz, 1 P). Anal. Calcd (found) for $\text{C}_{30}\text{H}_{54}\text{P}_2\text{Pt}$: 53.64 (53.20) C, 8.10 (8.40) H.

Preparation of (dippdmac)Pt(η^2 -PhC \equiv CCF $_3$) (3b). $\text{Pt}(\text{COD})_2$ (36.7 mg, 0.089 mmol) was dissolved in a solution of trifluoromethylphenylacetylene (15.2 mg, 0.089 mmol) in C_6D_6 (0.5 mL) to give a purple solution. (*i*-Pr) $_2\text{PCH}_2\text{CH}_2\text{NMe}_2$ (16.9 mg, 0.089 mmol, 18.9 μL) was added, producing a dark orange solution that was heated to 70°C overnight. The volatiles were evaporated under vacuum, and the remaining solid was recrystallized from petroleum ether (0.5 mL) containing a few drops of dichloromethane at -20°C . The product was obtained as orange crystals as a mixture of isomers (90% isomer with the CF_3 group trans to P, 10% isomer with the CF_3 group cis to P). Yield: 25.0 mg, 51%. For **3b**, ^1H NMR (C_6D_6): δ 0.79 (dd, $J_{\text{H-P}} = 13$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2 (major)), 0.86 (dd, $J_{\text{H-P}} = 14$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2 (minor)), 1.02 (dd, $J_{\text{H-P}} = 17$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2 (major)), 1.10 (dd, $J_{\text{H-P}} = 16$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2 (minor)), 1.80 (m, 2×6 H, CH_2 , CH (both)), 2.63 (s, with platinum satellites, $J_{\text{H-Pt}} = 11$ Hz, 6 H, NMe_2 (minor)), 2.70 (s, with platinum satellites, $J_{\text{H-Pt}} = 11$ Hz, 6 H, NMe_2 (major)), 7.06 (t, $J_{\text{H-H}} = 7$ Hz, 1 H, $p\text{-C}_6\text{H}_5$ (major)), 7.08 (t, $J = 7$ Hz, $p\text{-C}_6\text{H}_5$ (minor)), 7.19 (pseudo t, $J_{\text{H-H}} = 7$ Hz, 2 H, $m\text{-C}_6\text{H}_5$ (major)), 7.26 (pseudo t, $J_{\text{H-H}} = 7$ Hz, 2 H, $m\text{-C}_6\text{H}_5$ (minor)), 7.85 (d, $J_{\text{H-H}} = 7$ Hz, 2 H, $o\text{-C}_6\text{H}_5$ (minor)), 7.97 (d, $J_{\text{H-H}} = 7$ Hz, 2 H, $o\text{-C}_6\text{H}_5$ (major)). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 64.7 (q, with platinum satellites, $J_{\text{P-F}} = 16$ Hz, $J_{\text{P-Pt}} = 3844$ Hz (major)), 66.6 (s, with platinum satellites, $J_{\text{P-Pt}} = 3633$ Hz (minor)). Anal. Calcd (found) for $\text{C}_{19}\text{H}_{29}\text{F}_3\text{NPPt}$: 41.15 (41.04) C, 5.27 (5.33) H, 2.53 (2.32) N.

Preparation of (dippdmac)Pt(η^2 -PhC \equiv CC(CH $_3$) $_3$) (3c). $\text{Pt}(\text{COD})_2$ (20.1 mg, 0.049 mmol) was suspended in C_6D_6 (0.5 mL), and (*i*-Pr) $_2\text{PCH}_2\text{CH}_2\text{NMe}_2$ (9.3 mg, 0.049 mmol, 10.3 μL) was

added. A yellow solution formed, which was added to *tert*-butylphenylacetylene (7.7 mg, 0.049 mmol). The resultant solution was heated to 55 °C overnight. The volatiles were evaporated under vacuum, and the dark orange oil that remained was dissolved in petroleum ether (0.2 mL) containing a few drops of THF. Recrystallization at -20 °C produced yellow crystals of **3c**. Yield: 12.7 mg, 48%. For **3c**, ^1H NMR (C_6D_6): δ 0.92 (dd, $J_{\text{H-P}} = 13$ Hz, $J_{\text{H-H}} = 7$ Hz, 6 H, CHMe_2), 1.08 (m, 2 H, CH), 1.17 (dd, $J_{\text{H-P}} = 16$ Hz, $J_{\text{H-H}} = 6$ Hz, 6 H, CHMe_2), 1.51 (s, 9 H, *t*-Bu), 1.85 (m, 4 H, CH_2), 2.65 (m, br, 6 H, NMe_2), 7.05 (t, $J_{\text{H-H}} = 7$ Hz, 1 H, *p*- C_6H_5), 7.31 (pseudo t, $J_{\text{H-H}} = 7$ Hz, 2 H, *m*- C_6H_5), 7.62 (d, br, $J_{\text{H-H}} = 6$ Hz, 2 H, *o*- C_6H_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 65.8 (s, with platinum satellites, $J_{\text{P-Pt}} = 3717$ Hz). Anal. Calcd (found) for $\text{C}_{22}\text{H}_{38}\text{NPt}$: 48.70(48.18) C, 7.06(5.88) H, 2.58(1.85) N.

Generation of (dippe)Pt(Ph)(C \equiv CCF $_3$) (4b). A 32 mg (0.052 mmol) amount of **1b** was dissolved in 0.6 mL of C_6D_6 and placed in a resealable NMR tube. The solution was irradiated for 10 days, and NMR spectra were recorded periodically. The Supporting Information shows typical data, showing the conversion of **1b** into a new product assigned as (dippe)Pt(Ph)(C \equiv CCF $_3$) (**4b**, ~60% after 10 days; 80% after 18 days). For **4b**, ^1H NMR (C_6D_6): δ 7.753 (t, $J = 7$ Hz, $J_{\text{Pt-H}} = 27$ Hz, 2 H_{ortho}), 7.285 (t, $J = 7$ Hz, 2 H_{meta}), 7.043 (t, $J = 7$ Hz, 1 H_{para}), 2.17 (m, 2 H, CH_2), 1.87 (m, 2 H, CH_2), 1.24 (dd, $J = 16$, 8 Hz, 6 H, CHMe_2), 0.81 (dd, $J = 16$, 8 Hz, 6 H, CHMe_2), 0.69 (dd, $J = 16$, 8 Hz, 6 H, CHMe_2), 0.67 (dd, $J = 16$, 8 Hz, 6 H, CHMe_2), CHMe_2 obscured. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 63.95 (m, $J_{\text{Pt-P}} = 2551$ Hz), 71.90 (m, $J_{\text{Pt-P}} = 1566$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6): δ 13.62 (s, $J_{\text{Pt-F}} = 28$ Hz).

Generation of (dtbpe)Pt(Ph)(C \equiv CCF $_3$) (5b). A 10 mg (0.015 mmol) amount of **2b** was dissolved in 1 mL of C_6D_6 , and the

sample was placed into a resealable NMR tube. The tube was irradiated with UV light, and a maximum conversion of 60% to the activated complex **5b** was observed by ^{31}P NMR after 8 days of photolysis. Longer photolysis resulted in decomposition. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 71.1 (s, with platinum satellites $J_{\text{P-Pt}} = 2564$ Hz, 1 P, P trans to acetylide), 80.0 (s, with platinum satellites $J_{\text{P-Pt}} = 1547$ Hz, 1 P, P trans to Ph).

Generation of (dippdme)Pt(Ph)(C \equiv CCF $_3$) (6b). A 38 mg (0.068 mmol) sample of **3b** was dissolved in 0.6 mL of C_6D_6 and placed in a resealable NMR tube. The solution was irradiated for 10 days, and NMR spectra were recorded periodically. The Supporting Information shows typical data, showing the conversion of **3b** into a new product assigned as (dippdme)Pt(Ph)(C \equiv CCF $_3$) (**6b**, ~60% after 4 days; ~70% after 10 days). For **6b**, ^1H NMR (C_6D_6): δ 7.643 (d, $J = 7$ Hz, $J_{\text{Pt-H}} = 66$ Hz, 2 H_{ortho}), 7.091 (t, $J = 7$ Hz, 2 H_{meta}), 6.947 (t, $J = 7$ Hz, 1 H_{para}), 3.575 (t, $J = 6$ Hz, 2 H, CH_2), 2.385 (s, $J_{\text{Pt-H}} = 18$ Hz, 6 H, NMe_2), 1.70 (m, 4 H, CH_2 +, CHMe_2), 0.67 (dd, $J = 16$, 8 Hz, 6 H, CHMe_2), 0.63 (dd, $J = 16$, 8 Hz, 6 H, CHMe_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 49.1 (s, $J_{\text{Pt-P}} = 2802$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6): δ 4.356 (s, $J_{\text{Pt-F}} = 155$ Hz).

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Supporting Information Available: ^1H and ^{31}P NMR spectra for the photolyses of **1b**, **2b**, and **3b**. Structural data for **1b**, **1c**, **2a**, **2b**, **2c**, **3b**, **3c**, and **2D** have been deposited with the Cambridge Crystallographic Data Centre, CCDC #732792–732799. This material is available free of charge via the Internet at <http://pubs.acs.org>.