Interaction of (triphenylphosphine)$_2$PtC$_2$H$_4$ with Alkynyl(phenyl)iodonium Triflates. Formation of η^3-Propargyl/Allenyl–Pt and σ-Acetylide–Pt Complexes. Molecular Structure of [(Ph$_3$P)$_2$Pt(η^3–CHCH$_3$CCBu-*t*)]OSO$_2$CF$_3$[†,‡]

Peter J. Stang,* Charles M. Crittell, and Atta M. Arif

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

Received August 10, 1993[●]

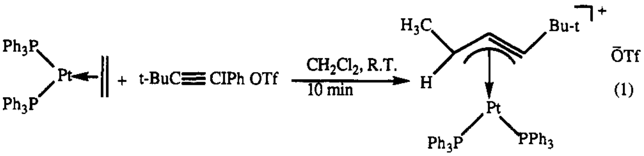
Reaction of RC≡CI$^+$Ph$^-$OTf (R = Me, η-Bu, *t*-Bu, Me$_3$Si) with (Ph$_3$P)$_2$PtC$_2$H$_4$ in CH$_2$Cl$_2$ at room temperature results in the formation of either the [*trans*-(Ph$_3$P)$_2$Pt(CCR-σ)]OSO$_2$CF$_3$ complexes or the novel η^3-propargyl/allenyl [(Ph$_3$P)$_2$Pt(η^3-CHCH$_3$CCR)]OSO$_2$CF$_3$ complexes depending upon R and the exact reaction conditions. A single crystal study of **3** (PtC$_{45}$H$_{43}$P$_2$SO$_3$F$_3$·$^1/_2$(OC$_4$H$_{10}$ + CH$_2$Cl$_2$)) at 20 °C reveals a triclinic crystal system belonging to the space group $P1$ with $Z = 2$ with $R(F) = 0.0254$, $R_w(F) = 0.0289$, and $d_{calc} = 1.541$ g/cm^3. The unit cell parameters are $a = 12.502(1)$ Å, $b = 16.833(1)$ Å, $c = 11.619(1)$ Å, $\alpha = 90.39(1)°$, $\beta = 103.81(1)°$, and $\gamma = 93.46(1)°$.

Propargyl and allenyl transition metal complexes are of considerable current interest, for reasons of both unusual structural features and novel reactivity and chemistry. The great majority of such complexes are of the η^1-propargyl and η^1-allenyl type.[1,2] η^3-Propargyl/allenyl complexes are of much more recent vintage and considerably less common.[3–9] For similar reasons, the related σ-acetylide and σ-alkynyl transition metal complexes are also the subject of current research activities.[10,11]

Recently, we reported[12] the use of alkynyl(phenyl)iodonium salts, RC≡CIPhOTf, in the ready preparation of alkynyl complexes of Ir and Rh. In this paper, we wish to report the formation and characterization of both η^3-propargyl/allenyl–Pt complexes and σ-alkynyl–Pt complexes via the interaction of alkynyl(phenyl)iodonium triflates with (Ph$_3$P)$_2$PtC$_2$H$_4$.

Results and Discussion

Interaction of (Ph$_3$P)$_2$PtC$_2$H$_4$, **1**, with (*tert*-butylethynyl)(phenyl)iodonium triflate, **2**, in degassed dry CH$_2$Cl$_2$ for 10 min gave the η^3-complex **3** in 84% isolated yield (eq 1). Monitoring the reaction by ^{31}P NMR indicated that formation of **3** was essentially quantitative with no other product(s) being observed.



1 **2** **3**

Compound **3** was characterized by spectral means and its structure firmly established by a single crystal X-ray determination. Specifically, the ^{31}P NMR of **3** shows two signals at 12.87 and 15.16 ppm, respectively, with appropriate P–P coupling and Pt satellites. The ^{1}H NMR spectrum, besides the expected resonances of the *tert*-butyl group and the aromatic signals, displays a multiplet centered at 3.2 ppm for the methine hydrogen and a multiplet centered at 1.1 ppm due to the CH$_3$ group. Especially characteristic are the signals of the three "allenyl" carbons in the ^{13}C NMR. In particular, all three signals show both P and Pt coupling (see Experimental Section for details) with the central carbon at 100.7 ppm and the two termini at 117.56 and 67.22 ppm, respectively.

In contrast, reaction of **1** with propynyl(phenyl)iodonium triflate, **4**, in degassed toluene gave the trans σ-propynyl–Pt complex, **5**, exclusively in 91% isolated yield

---

[†] Dedicated to the memory of Dr. Kenneth G. Hancock.

[‡] Abstracted in part from the Ph.D. dissertation of C. M. Crittell, University of Utah, 1993.

[●] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

(1) Reviews: Welker, M. E. *Chem. Rev.* **1992**, *92*, 97. Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35. Wojcicki, A. In *Fundamental Research in Organometallic Chemistry*; Tsutsui, M., Ishii, Y., Huang, Y., Eds.; Van Nostrand-Reinhold: New York, 1982; pp 569–597.

(2) Inter alia: Breckenridge, S. M.; Taylor, N. J.; Carty, A. J. *Organometallics* **1991**, *10*, 837. Shuchart, C. E.; Young, G-H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Ibid.* **1990**, *9*, 2417. Young, G-H.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Bresciani-Pahor, N. *J. Am. Chem. Soc.* **1987**, *111*, 6890. Curtis, M. D. *Polyhedron* **1987**, *6*, 759. Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716. Pasto, D. J.; Huang, N. Z. *Ibid.* **1985**, *4*, 1386.

(3) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993.

(4) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994.

(5) Huang, T. M.; Chen, J. T.; Lee, G-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170.

(6) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597.

(7) Krivykh, V. V.; Taits, E. S.; Petrovski, P. V.; Struchkov, Yu. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991**, 103.

(8) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453.

(9) McMullen, A. K.; Seleque, J. P.; Wang, J. G. *Organometallics* **1991**, *10*, 3421.

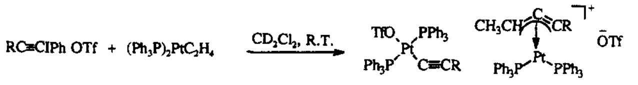
(10) Early reviews: Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. Rauthby, P. R.; Rosales, M. *J. Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. Nas, R. *Coord. Chem. Rev.* **1982**, *47*, 89. Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

(11) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276. Bianchini, C.; Laschi, F.; Masi, D.; Ottaviani, F. M.; Pastor, A.; Peruzzini, M.; Zanello, P.; Sanobini, F. *J. Am. Chem. Soc.* **1993**, *115*, 2723. Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735. Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 5890 and references therein.

(12) Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191. Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411.

0276-7333/93/2312-4799$04.00/0

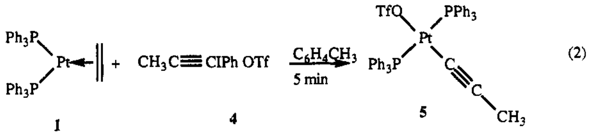
Scheme I[a]



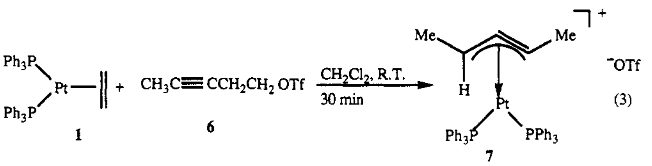
Entry	R	RXN Cond.	σ-complex	η^3-complex
1	t-Bu	a[1]	0	100 (3)
2	t-Bu	b[2]	25	75
3	Me_3Si	c[3]	0	100 (8)
4	Me_3Si	a	17	83
5	Me_3Si	b	41	59
6	n-Bu	c	50	50
7	n-Bu	a	31	69
8	n-Bu	b	~100 (9)	trace
9	Me	c	78	22 (7)
10	Me	a	100 (5)	0

[a] Legend: (1) no added gas; (2) Ar bubbling; (3) ethylene bubbling.

(eq 2). ${}^{31}P$ NMR analysis of the reaction indicated only traces (<1%) of the η^3-complex, analogous to **3**. Complex **5** was characterized by spectral and analytical means: the ${}^{31}P$ NMR shows a singlet at 23.2 ppm (${}^{3}J_{Pt-P} = 2699$ Hz), the ${}^{1}H$ NMR (besides aromatic resonances) only a P-coupled triplet at 1.17 ppm (${}^{5}J_{P-H} = 2$ Hz), and the ${}^{13}C$ NMR, P-coupled triplets at 45 ppm (${}^{2}J_{P-C} = 16$ Hz) and 100 ppm (${}^{3}J_{P-C} = 3.2$ Hz), respectively, for the α- and β-alkynyl carbons. Further details can be found in the Experimental Section.



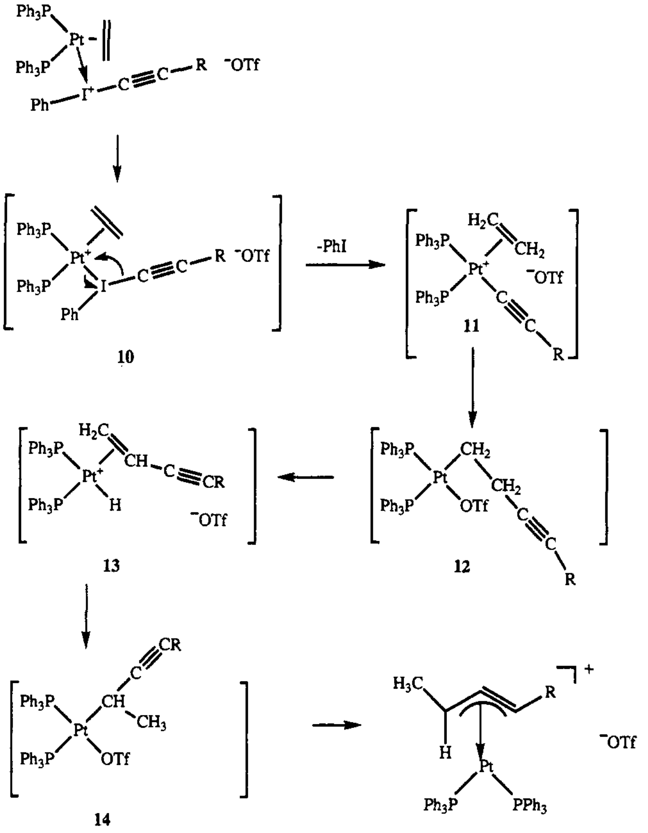
η^3-Complex **7** was alternatively prepared by the reaction of **1** with 3-pentynyl triflate, **6** (eq 3). This allenyl complex was also fully characterized by spectral and analytical means, as detailed in the Experimental Section.



To gain further insight into these divergent reactions, the behavior of two additional alkynyliodonium species were investigated along with different reaction conditions. Specifically, reactions were carried out between the appropriate alkynyliodonium salt and **1** in degassed CD_2Cl_2 under three different conditions: (a) alone; (b) while continuously bubbling argon through the solution; (c) while continuously bubbling ethylene through the solution. Our intention in these experiments was to enhance the formation of the σ-alkynyl complex under condition b and the formation of the η^3-allenyl complexes under condition c. The reactions were monitored by ${}^{31}P$ NMR and the ratios of products determined by integration of the respective ${}^{31}P$ signals due to the σ- and η^3-complexes. The results are summarized in Scheme I.

Control experiments established that once formed, the respective σ- and η^3-complexes were stable to the reaction conditions. Specifically, heating the solutions of the η^3-complexes did not give σ-complexes. More interestingly, bubbling ethylene through the σ-complexes did not afford any η^3-complexes.

Scheme II. Likely Mechanism for the Formation of η^3-Propargyl/Allenyl Pt Complexes



Perusal of the data in Scheme I indicates that the formation of σ-alkynyl or η^3-allenyl complexes depends both upon the size of R in the alkynyliodonium salts as well as upon reaction conditions. Specifically, as R increases from Me to *n*-Bu to Me_3Si to *t*-Bu, the amount of the η^3-complex increases from 0 to 69 to 83 to 100%. Addition of external ethylene before and during the reaction increases the formation of the η^3-allenyl complex from 0 to 22% for R = Me and from 83 to 100% for R = Me_3Si but seems to decrease it from 69 to 50% when R = *n*-Bu. In contrast, bubbling of argon through the reaction mixture before and during the reaction increases the formation of the σ-alkynyl complex from 0 to 25% when R = *t*-Bu, from 17 to 41% when R = Me_3Si, and from 31 to 100% when R = *n*-Bu.

The effect of the added gas (Ar and C_2H_4) is likely due to its impact upon the equilibrium with the $(Ph_3P)_2Pt$ fragment being the likely reactive species. Interaction of $(Ph_3P)_2Pt$ with RC≡CIPhOTf and loss of iodobenzene results in the observed σ-alkynyl–Pt complexes.

$$(Ph_3P)_2PtC_2H_4 \rightleftarrows (Ph_3Pt)_2 + C_2H_4$$

Formation of the η^3-complexes is more complicated. A likely mechanism is outlined in Scheme II. Interaction of **1** with the alkynyliodonium species first gives the hypervalent I–Pt complex **10**, that upon loss of PhI by reductive elimination, collapses to the cationic π-ethylene–σ-alkynyl complex **11**. Migratory insertion of the ethylene into the Pt–alkynyl bond in **11** results in the neutral homopropargyl complex **12**. Complex **12** rearranges to the enyne hydride complex **13** via an overall 1,2-H shift. Complex **13** rearranges to propargyl triflate complex **14** that in turn results in the final product, the η^3-complex. Although this is an elaborate mechanism, each step is precedented.

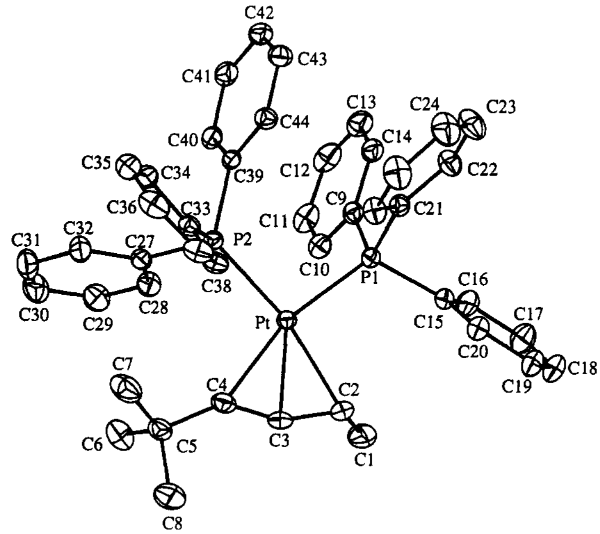
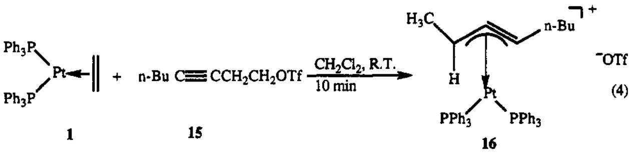


Figure 1. ORTEP diagram of the cation of 3.

Specifically, interaction of nucleophiles with the iodine of iodonium species is known.[13,14] and the 1,2-hydrogen shift (via β-hydride elimination) is well established.[15]

In an attempt to observe possible intermediates, the reaction was monitored by ^{31}P NMR at low temperatures. However, even at −20 °C the reaction proceeded too rapidly to observe any intermediates; only starting materials (1 and 2) and clean, rapid formation of final product 3 were observed.

To partially test this mechanism, the homopropargyl systems 6 (eq 3) and 15 (eq 4) were reacted with 1. The respective η^3-propargyl/allenyl complexes 7 and 16 cleanly formed in high isolated yields. Reaction of the homopropargyl triflates 6 and 15 presumably proceeds via initial formation of 12 and subsequent rearrangement to the η^3-complexes, as outlined in Scheme II.



(4)

X-ray Structure Determination of Complex 3. A single crystal of 3 was obtained by recrystallization from CH_2Cl_2 and diethyl ether as described in the Experimental Section. The ORTEP diagram of the cation 3 is presented in Figure 1, and a summary of crystallographic data and selected bond lengths and angles are reported in Tables I and II (positional parameters are reported in Table III). A comparison of the key structural features of 3 and the related η^3-complex $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)]SO_2CF_3$, 17,[3] is given in Figure 2. The structural data clearly indicate the unique η^3-allenyl/propargyl nature of complex 3. Particularly significant are the C2–C3 bond distance of 1.390 Å and the C3–C4 distance of 1.266 Å. The former is between the length of a C–C single bond of 1.52 Å and a C–C double bond of 1.34 Å; the latter is between a C–C double bond of 1.34 Å and a C–C triple bond of 1.21 Å. Hence these bond distances for C2–C3 and C3–C4 correspond to a bond order of approximately 1.5 and 2.5, respectively, in accord with the allenyl/propargyl nature of the ligand. Likewise, the C–C–C bond angle of 154° is consistent with this mode of complexation. Moreover complex 3 is essentially planar around the Pt center with P1, P2, C2, and C4 deviating less than 0.010 Å from planarity and C3 and only 0.5 Å out of plane.

Table I. Crystallographic Data for 3

molecular formula	$C_{46}H_{45}PtP_2ISO_3F_3{\cdot}0.5Et_2O{\cdot}0.5CH_2Cl_2$
mol wt	1099.9
cryst color	off white
cryst syst	triclinic
space group	$P1$
cell dimens	
a (Å)	12.502(1)
b (Å)	16.833(1)
c (Å)	11.619(1)
α (deg)	90.39(1)
β (deg)	103.81(1)
γ (deg)	93.46(1)
cell vol (Å^3)	2369.72
d_{calc} (g/cm^3)	1.541
cryst dimens (mm)	0.28 × 0.23 × 0.11
radiation, λ (Å)	Mo, 0.710 73
abs coeff (cm^{-1})	32.639
no. of reflns measd	6747
scan technique	$\theta/2\theta$
2θ range (deg)	2.0–48
scan speed (deg/min)	3.0
scan range	$K = 1.0$ to $K + 1.0$
total bkgd time/scan time	0.0
decay corr	anisotropic
no. reflns between std	98
min abs corr	79.6000
max abs corr	99.9900
ignorance factor	$P = 0.05$
no. of observns	5934
no. of variables	543
data to param ratio	10.928
shift to error ratio	0.012
$R(F)$	0.0289
$R_w(F)$	0.0289

Table II. Selected Bond Distances (Å) and Angles (deg) for 3[a]

Pt–P1	2.2792(7)	C1–C2	1.505(6)
Pt–P2	2.2995(7)	C2–C3	1.390(5)
Pt–C2	2.243(3)	C3–C4	1.266(5)
Pt–C3	2.140(3)	C4–C5	1.483(4)
Pt–C4	2.265(3)		
P1–Pt–P2	97.33(3)	Pt–C2–C1	118.2(3)
P1–Pt–C2	94.30(9)	Pt–C2–C3	67.5(2)
P2–Pt–C4	98.28(9)	C1–C2–C3	119.7(4)
C2–Pt–C3	36.9(1)	C2–C3–C4	154.1(3)
C2–Pt–C4	70.1(1)	Pt–C4–C3	67.9(2)
C3–Pt–C4	33.2(1)	Pt–C4–C5	150.6(2)
		C3–C4–C5	141.4(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

In summary, interaction of $(Ph_3P)_2PtC_2H_4$ with $R\text{-}C{\equiv}CI^+Ph^-OTf$ results in either novel η^3-propargyl/allenyl—Pt complexes or σ-alkynyl—Pt complexes depending upon R and the reaction conditions. Bulky R groups such as t-Bu and Me_3Si favor η^3-complexation whereas smaller R groups such as Me and n-Bu favor σ-alkynyl complex formation. The course of the reaction may be influenced by addition of external ethylene favoring η^3-complexation, or argon gas favoring σ-alkynyl complex formation. η^3-Propargyl/allenyl-Pt complexes can also be formed by interaction of $(Ph_3P)_2PtC_2H_4$ with homopropargyl triflates $RC{\equiv}CCH_2CH_2OTf$.

Experimental Section

General Data. All melting points were measured on a Mel-

---

[13] Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274.

[14] Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315.

[15] Liebeskind, L. *Advances in Metal-Organic Chemistry*; Wiley: New York, 1991.

Table III. Positional Parameters for 3

atom	*x*	*y*	*z*	B^a (Å^2)
Pt	0.31173(1)	0.29678(1)	0.08446(2)	2.895(3)
Cl1	0.6795(3)	0.4080(2)	0.2914(4)	15.7(1)
Cl2	0.9036(3)	0.4574(3)	0.3430(4)	20.5(1)
S	0.1376(2)	0.7545(1)	0.3408(2)	7.50(5)
P1	0.37467(9)	0.18067(7)	0.0328(1)	3.00(2)
P2	0.24676(9)	0.24927(7)	0.2417(1)	2.86(2)
F1	0.9265(5)	0.7628(5)	0.2895(7)	18.8(3)
F2	0.9821(5)	0.6692(5)	0.3921(6)	20.9(2)
F3	0.9794(8)	0.6695(5)	0.2160(9)	23.7(4)
O1	0.1379(6)	0.8025(5)	0.2427(6)	14.7(2)
O2	0.1450(8)	0.7959(6)	0.4467(7)	17.6(3)
O3	0.2001(6)	0.6909(4)	0.3554(9)	18.0(3)
C1	0.4841(6)	0.3847(4)	–0.0492(6)	7.7(2)
C2	0.3627(5)	0.3666(3)	–0.0595(5)	5.5(1)
C3	0.3077(5)	0.4115(3)	0.0060(5)	4.9(1)
C4	0.2641(4)	0.4241(3)	0.0917(5)	4.3(1)
C5	0.2204(4)	0.4887(3)	0.1509(5)	4.3(1)
C6	0.3097(6)	0.5187(4)	0.2608(6)	6.7(2)
C7	0.1163(5)	0.4618(4)	0.1875(7)	7.3(2)
C8	0.1973(6)	0.5568(4)	0.0648(7)	7.7(2)
C9	0.4765(4)	0.1423(3)	0.1549(4)	3.4(1)
C10	0.5528(4)	0.1994(3)	0.2227(4)	4.0(1)
C11	0.6382(4)	0.1771(4)	0.3143(5)	4.9(1)
C12	0.6499(5)	0.0976(4)	0.3373(5)	5.7(1)
C13	0.5749(5)	0.0409(4)	0.2728(5)	5.6(1)
C14	0.4873(4)	0.0621(3)	0.1823(4)	4.3(1)
C15	0.4467(4)	0.1859(3)	–0.0865(4)	3.5(1)
C16	0.5604(4)	0.1793(4)	–0.0682(5)	4.8(1)
C17	0.6111(5)	0.1872(4)	–0.1632(5)	6.2(2)
C18	0.5485(5)	0.2025(4)	–0.2748(5)	6.3(2)
C19	0.4369(5)	0.2076(4)	–0.2941(5)	5.6(1)
C20	0.3853(4)	0.1987(3)	–0.2014(4)	4.4(1)
C21	0.2653(4)	0.1049(3)	–0.0284(4)	3.5(1)
C22	0.2901(4)	0.0297(3)	–0.0621(5)	4.7(1)
C23	0.2058(5)	–0.0265(4)	–0.1103(6)	6.4(2)
C24	0.0987(5)	–0.0079(4)	–0.1280(6)	7.1(2)
C25	0.0723(5)	0.0673(4)	–0.0996(6)	6.3(2)
C26	0.1566(4)	0.1236(3)	–0.0501(5)	4.4(1)
C27	0.3026(4)	0.3121(3)	0.3745(4)	3.5(1)
C28	0.4136(4)	0.3367(3)	0.3987(5)	4.5(1)
C29	0.4626(5)	0.3823(4)	0.5003(5)	5.5(1)
C30	0.4003(6)	0.4051(4)	0.5757(5)	6.3(2)
C31	0.2904(5)	0.3821(4)	0.5515(5)	6.1(2)
C32	0.2403(4)	0.3350(3)	0.4516(5)	4.7(1)
C33	0.0965(4)	0.2446(3)	0.2128(4)	3.3(1)
C34	0.0432(4)	0.2132(3)	0.2970(4)	4.0(1)
C35	–0.0713(4)	0.2113(3)	0.2748(5)	5.1(1)
C36	–0.1316(4)	0.2380(3)	0.1682(6)	5.6(1)
C37	–0.0808(4)	0.2650(3)	0.0825(6)	5.0(1)
C38	0.0344(4)	0.2702(3)	0.1052(5)	4.1(1)
C39	0.2762(3)	0.1493(3)	0.2962(4)	2.90(9)
C40	0.3631(4)	0.1372(3)	0.3936(4)	3.7(1)
C41	0.3825(4)	0.0603(3)	0.4337(4)	4.5(1)
C42	0.3171(5)	–0.0039(3)	0.3761(5)	4.7(1)
C43	0.2325(4)	0.0074(3)	0.2797(5)	4.4(1)
C44	0.2115(4)	0.0836(3)	0.2393(4)	3.7(1)
C45	–0.0025(8)	0.7157(6)	0.3130(8)	10.3(3)
C46	0.8088(9)	0.4065(6)	0.389(1)	12.6(4)
C47	0.8473(6)	0.9168(4)	0.4222(6)	7.0(2)*
C48	0.1119(9)	0.0458(7)	0.5482(9)	8.2(3)*
C48′	0.941(2)	–1.025(1)	0.508(2)	10.6(5)*
O4	1.00(1)	0.955(1)	0.450(2)	12.2(5)*
O4′	0.947(1)	–0.989(1)	0.441(2)	12.2(5)*

^{a} Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Temp capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Mattson-Polaris FT-IR spectrometer. The ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a Varian XL-300 spectrometer in $CDCl_3$ solvent. The chemical shifts were referenced to residual protons in the deuterated NMR solvent ($CDCl_3$: 7.24 ppm) or the solvent ^{13}C resonance (77.00 ppm). The ^{31}P NMR spectra were referenced to external 85% H_3PO_4 at 0.0 ppm and the ^{19}F NMR spectra were referenced to $CFCl_3$ at 0.0 ppm.

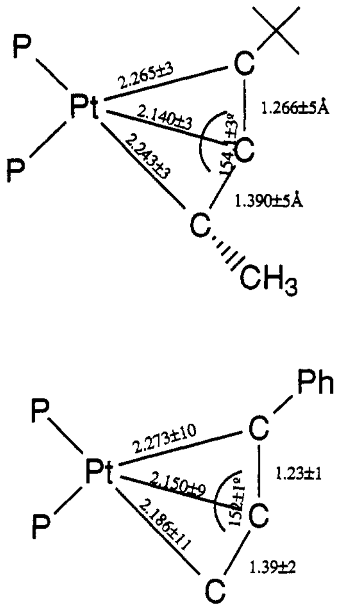


Figure 2. Key structural features of 3 (top) and 17 (bottom).

Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Mass spectra were recorded on either a Finnigan MAT 90 mass spectrometer with Finnigan MAT ICIS II operating system or on a VG Micromass 7050E double focusing high resolution mass spectrometer.

Potassium tetrachloroplatinate was received on loan from Johnson Matthey and used without purification. All reactions were carried out in an atmosphere of nitrogen using Schlenk techniques but were worked up in the air unless otherwise noted. Solvents were purified according to standard literature procedures,[16] and in the case of reactions involving transition metals, they were first acid washed, neutralized, dried, distilled, and then degassed (freeze–thaw method, three times) prior to use.

[$(PPh_3)_2Pt(\eta^3\text{-}CH_3CHCC{\equiv}CC\text{-}t\text{-}C_4H_9)$]OTf (3). Method A. Bis(triphenylphosphine)platinum ethylene complex, 1[17] (74.7 mg, 0.100 mmol), was dissolved in 8 mL of dry degassed methylene chloride, and a suspension of (3,3-dimethylbutynyl)(phenyl)iodonium triflate,[18] **2** (43.4 mg, 0.100 mmol), in 5 mL of methylene chloride was added. The reaction was complete within 10 min, as monitored by ^{31}P NMR. Dry degassed hexanes (20 mL) was then added to the solution, resulting in the precipitation of the product. The white powder was filtered and washed with additional hexanes and the product dried overnight in vacuo to give 82 mg (84% yield) of **3**: mp 152–154 °C dec; IR (thin film CCl_4) 3056, 2970, 2950, 2929, 2905, 1481, 1437, 1365, 1269 (OTf), 1222 (OTf), 1185 (OTf), 1146, 1097, 1030, 999, 919, 844, 835, 745, 699, 636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.16 (m), 3.30–3.15 (m, 1 H), 1.11 (CH_3, t, $^2J_{PH}$ = 2 Hz; d, $^3J_{HH}$ = 5 Hz), 0.80 ($C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.57 (*ortho*, d, $^2J_{PC}$ = 12 Hz, $^2J_{PtC}$ = 23 Hz), 133.22 (*ortho*, d, $^2J_{PC}$ = 12 Hz, $^2J_{PtC}$ = 25 Hz), 131.62 (*para*), 131.61 (*para*), 128.83 (*meta*, d, $^3J_{PC}$ = 11 Hz), 128.42 (*meta*, d, $^3J_{PC}$ = 11 Hz), 130.94 (*ipso*, d, $^1J_{PC}$ = 57 Hz, $^2J_{PtC}$ = 36 Hz), 129.52 (*ipso*, d, $^1J_{PC}$ = 60 Hz, $^2J_{PtC}$ = 39 Hz), 121.02 (OTf, q, $^1J_{CF}$ = 321 Hz), 117.56 (*C*—$C(CH_3)_3$, dd, $^2J_{PC}$ = 3 Hz, $^2J_{PC}$ = 56 Hz, $^1J_{PtC}$ = 160 Hz), 100.70 (C*C*C, dd, $^2J_{PC}$ = 4 Hz, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 54 Hz), 67.22 (*C*HMe, dd, $^2J_{PC}$ = 35 Hz, $^2J_{PC}$ = 1 Hz, $^1J_{PtC}$ = 104 Hz, $^1J_{CH}$ = 168 Hz), 33.46 ($C(CH_3)_3$), 32.73 ($C(CH_3)_3$), 16.16 ($^3J_{PC}$ = 4 Hz) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 15.16 ($^1J_{PtP}$ = 3843 Hz, $^2J_{PP}$ = 20 Hz), 12.87 ($^1J_{PtP}$ = 4174 Hz, $^2J_{PP}$ = 20 Hz) ppm; ^{19}F NMR ($CDCl_3$) δ –77.8 ppm; FAB MS *m/z* 1807 (0.6, 2M

---

[16] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1966.

[17] Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* **1968**, *11*, 105.

[18] Bachi, M. D.; Bar-Ner, N.; Crittell, C. M.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1991**, *56*, 3912.

– OTf), 828 (76, M – OTf), 719 (100, Pt(PPh$_3$)$_2$), 641, 455 (30, PtPPh$_3$), 378, 301, 183. Anal. Calcd for $C_{45}H_{43}PtP_2SO_3F_3$: C, 55.27; H, 4.43. Found: C, 55.43; H, 4.48. A solution of 3 in methylene chloride was layered with diethyl ether, and crystals suitable for X-ray crystallographic study were obtained overnight.

***trans*-(PPh$_3$)$_2$Pt(C≡C—CH$_3$)(OTf) (5). Method A.** Bis(triphenylphosphine)platinum ethylene complex, 1 (74.7 mg, 0.100 mmol), was dissolved in 8 mL of dry degassed toluene, and a suspension of propynyl(phenyl)iodonium triflate,[18] 4 (39.2 mg, 0.100 mmol), in 5 mL of toluene was added. The reaction is complete in less than 5 min, as determined by ^{31}P NMR. The solvent was removed in vacuo leaving an off-white solid. The residue was then washed with dry, degassed hexanes, filtered under nigrogen, and dried for 3 h in vacuo (86 mg, 91% yield): IR (thin film CCl$_4$) 3058, 2907, 2115 (C≡C), 1482, 1436, 1323, 1231 (OTf), 1201 (OTf), 1159 (OTf), 1099, 998, 744, 733, 707, 692, 637, 617 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.75–7.65 (m, 12 H), 7.45–7.35 (m, 18 H), 1.17 (t, $^5J_{\mathrm{PH}}$ = 2 Hz) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 134.87 (*ortho*, t, J_{PC} = 6 Hz), 130.58 (*para*), 128.13 (*ipso*, t, J_{PC} = 29 Hz), 127.99 (*meta*, t, J_{PC} = 5 Hz), 118.29 (OTf, q, $^1J_{\mathrm{CF}}$ = 319 Hz), (βC) 99.95 (t, $^3J_{\mathrm{PC}}$ = 3.2 Hz), (αC) 45.02 (t, $^2J_{\mathrm{PC}}$ = 16 Hz), (CH$_3$) 5.63 ppm; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 23.20 ($^1J_{\mathrm{PtP}}$ = 2699 Hz) ppm; ^{19}F NMR (CDCl$_3$): δ –77.7 ppm; FAB MS *m/z* 758 (57, M – OTf), 718 (100, Pt(PPh$_3$)$_2$), 455 (23, PtPPh$_3$), 378, 301, 154; FAB HRMS *m/z* 758.1715 (M – OTf), calcd for $PtP_2C_{39}H_{33}$ *m/z* 758.1705.

Reaction of 1 with (3,3-Dimethylbutynyl)(phenyl)iodonium Triflate (2). Method B. Bis(triphenylphosphine)platinum ethylene complex, 1 (7.5 mg, 0.010 mmol), was placed in a dried NMR tube. The tube was sealed with a rubber septum and evacuated and flushed with argon. Deuteriobenzene (0.5 mL) was added and argon bubbled through the solution for 5 min. A suspension of (3,3-dimethylbutynyl)(phenyl)iodonium triflate, 2 (4.4 mg, 0.010 mmol), in deuteriobenzene (0.5 mL) was added slowly while argon was continuously bubbled through the solution. This reaction resulted in a 25:75 ratio of the desired σ-alkynyl complex to the η^3-allenyl complex, as determined by ^{31}P NMR. Attempts to isolate the (3,3-dimethylbutynyl)platinum triflate complex were unsuccessful and resulted in decomposition.

Reaction of 1 with [(Trimethylsilyl)butynyl](phenyl)iodonium Triflate. Method A. Bis(triphenylphosphine)platinum ethylene complex, 1 (74.7 mg, 0.100 mmol), was dissolved in 8 mL of dry degassed methylene chloride, and a suspension of [(trimethylsilyl)ethynyl](phenyl)iodonium triflate[18] (45.0 mg, 0.100 mmol) in 5 mL of methylene chloride was added. The reaction was complete within 10 min, as minitored by phosphorus NMR. The ^{31}P NMR also revealed two major products: the η^3-allenyl complex was observed as two doublets at 17.56 and 14.94 ppm, and the σ-alkynyl complex appeared as a singlet at 23.82 ppm with platinum satellites of 2697 Hz. The resonances were integrated at 83% and 17%, respectively. Dry degassed hexanes (20 mL) was then added to the solution, resulting in the precipitation of the product. Several recrystallizations (four times) from methylene chloride followed by the addition of hexane resulted in the isolation of pure η^3-allenyl complex 8. The (σ-alkynyl)platinum triflate complex, however, was unstable, and attempts to purify it by recrystallization were all unsuccessful. The η^3-allenyl complex was then filtered and washed with additional hexanes and the white powder dried overnight in vacuo to give the product (62.4 mg, 63% yield): IR (thin film CCl$_4$) 3054, 3007, 2962, 2958, 1901 (allene), 1481, 1436, 1271 (OTf), 1223 (OTf), 1149 (OTf), 1096, 1031, 845, 753, 694, 636 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.41–7.13 (m, 30H), 3.39–3.24 (m, 1H), 1.03 (d, $^3J_{\mathrm{HH}}$ = 4 Hz; t, $^4J_{\mathrm{PH}}$ = 7 Hz), –0.33 ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 134.61 (*ortho*, d, $^2J_{\mathrm{PC}}$ = 12 Hz, $^2J_{\mathrm{PtC}}$ = 22 Hz), 133.29 (*ortho*, d, $^2J_{\mathrm{PC}}$ = 11 Hz, $^2J_{\mathrm{PtC}}$ = 28 Hz), 131.69 (*para*), 131.66 (*para*), 128.86 (*meta*, d, $^3J_{\mathrm{PC}}$ = 11 Hz), 128.56 (*meta*, d, $^3J_{\mathrm{PC}}$ = 11 Hz), 131.09 (*ipso*, d, $^1J_{\mathrm{PC}}$ = 56 Hz, $^2J_{\mathrm{PtC}}$ = 30 Hz), 129.47 (*ipso*, d, $^1J_{\mathrm{PC}}$ = 62 Hz, $^2J_{\mathrm{PtC}}$ = 35 Hz), 120.97 (OTf, q, $^1J_{\mathrm{CF}}$ = 321 Hz), 118.05 (C*C*C, d, $^2J_{\mathrm{PC}}$ = 5 Hz; d, $^2J_{\mathrm{PC}}$ = 5 Hz, $^1J_{\mathrm{PtC}}$ = 44 Hz), 100.01 (*C*–TMS, d, $^2J_{\mathrm{PC}}$ = 4 Hz; d, $^2J_{\mathrm{PC}}$ = 43 Hz, $^1J_{\mathrm{PtC}}$ = 87 Hz), 64.22 (*C*HMe, d, $^2J_{\mathrm{PC}}$ = 40 Hz, $^1J_{\mathrm{PtC}}$ = 111 Hz), 15.02 (Me, d, $^3J_{\mathrm{PC}}$ = 4 Hz, $^2J_{\mathrm{PtC}}$ = 12 Hz), 2.08 (TMS) ppm; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 17.56 ($^1J_{\mathrm{PtP}}$ = 3692 Hz, $^2J_{\mathrm{PP}}$ = 19 Hz), 14.94 ($^1J_{\mathrm{PtP}}$ = 4429 Hz, $^2J_{\mathrm{PP}}$ = 19 Hz) ppm; ^{19}F NMR (CDCl$_3$) δ –78.2 ppm; FAB MS *m/z* 844 (100, M – OTf), 719 (75, Pt(PPh$_3$)$_2$), 642, 455 (8, PtPPh$_3$), 307, 154, 136. Anal. Calcd for $C_{44}H_{43}SiPtP_2SO_3F_3$: C, 53.17; H, 4.36. Found: C, 53.08; H, 4.34.

Reaction of (1) with [(Trimethylsilyl)butynyl](phenyl)iodonium Triflate. Method B. Bis(triphenylphosphine)platinum ethylene complex, 1 (7.47 mg, 0.010 mmol), was added to a dried NMR tube. The tube was sealed with a rubber septum, evacuated, and flushed with argon. Deuteriobenzene (0.5 mL) was added and argon bubbled through the solution for 5 min. A solution of [(trimethylsilyl)ethynyl](phenyl)iodonium triflate (4.50 mg, 0.010 mmol) in deuteriobenzene (0.5 mL) was added slowly while argon was continuously bubbled through the solution. This reaction resulted in a 41:59 ratio of the desired σ-alkynyl complex to the η^3-allenyl complex, as determined by ^{31}P NMR. Attempts to isolate the alkynylplatinum triflate complex were unsuccessful due to the instability of the product. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 23.82 (σ, $^1J_{\mathrm{PtP}}$ = 2697 Hz), 18.16 (η^3, $^1J_{\mathrm{PtP}}$ = 3764 Hz, $^2J_{\mathrm{PP}}$ = 19 Hz), 13.92 (η^3, $^1J_{\mathrm{PtP}}$ = 4491 Hz, $^2J_{\mathrm{PP}}$ = 19 Hz).

Reaction of 1 with [(trimethylsilyl)butynyl](phenyl)iodonium Triflate. Method C. The synthesis of the η^3 complex was repeated, but ethylene was bubbled through the solution to increase the yield. Bis(triphenylphosphine)platinum ethylene complex, 1 (74.7 mg, 0.100 mmol), was dissolved in 8 mL of dry degassed methylene chloride in a 25-mL round bottom flask, and ethylene was slowly bubbled through the solution for 5 min. To this reaction mixture, a suspension of [(trimethylsilyl)ethynyl](phenyl)iodonium triflate (0.100 mmol, 45.0 mg) in 5 mL of methylene chloride was added while the bubbling of ethylene was continued. After 15 min, the reaction was checked by ^{31}P NMR and only the η^3-allenyl complex was observed. Dry degassed hexanes (20 mL) was then added to the solution, resulting in the precipitation of the product. Compound 8 was recrystallized from methylene chloride and hexanes, filtered out, and washed with additional hexanes, and the white powder was dried overnight in vacuo (91.3 mg, 92% yield). See the previous preparation for the analytical data.

Reaction of 1 with Hexynyl(phenyl)iodonium Triflate Method A. Bis(triphenylphosphine)platinum ethylene complex, 1 (7.5 mg, 0.010 mmol), was dissolved in 0.5 mL of dry degassed deuteriobenzene and a solution of hexynyl(phenyl)iodonium triflate (4.5 mg, 0.010 mmol) in 0.5 mL of deuteriobenzene was added. The reaction was complete within 10 min, as monitored by ^{31}P NMR. The ^{31}P NMR also revealed two major products: the η^3-allenyl complex 16 and the σ-alkynyl complex 9. No attempts were made to isolate either product from this reaction mixture. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 23.82 (9, $^1J_{\mathrm{PtP}}$ = 2718 Hz), 19.73 (η^3, $^1J_{\mathrm{PtP}}$ = 3810 Hz), 13.99 (η^3, $^1J_{\mathrm{PtP}}$ = 4325 Hz). The resonances were integrated at 48 and 52%, respectively.

Reaction of 1 with Hexynyl(phenyl)iodonium Triflate. Method B. Bis(triphenylphosphine)platinum ethylene complex, 1 (75 mg, 0.100 mmol), was dissolved in 8 mL of dry degassed methylene chloride in a 25-mL round bottom flask. Argon was then bubbled through the solution for 10 min. Next, a solution of hexynyl(phenyl)iodonium triflate[18] (43.4 mg, 0.100 mmol) in 5 mL of methylene chloride was added while argon was continually bubbled through. After 10 min the reaction was checked by ^{31}P NMR and found to be complete. No signals from the η^3-allenyl complex were observed. The solvent was removed in vacuo leaving an off-white solid 9. The residue was then washed with dry and degassed hexanes, filtered out under nitrogen, and dried in vacuo: IR (thin film CCl$_4$) 3055, 2959, 2927, 2870, 1482, 1435, 1231 (OTf), 1199 (OTf), 1151 (OTf), 1097, 1031, 998, 744, 707, 693, 636 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.72–7.65 (m, 12H), 7.55–7.46 (m, 18H), 1.65–1.61 (m, 2H), 0.83–0.75 (m, 4H), 0.62 (t, $^3J_{\mathrm{HH}}$ = 7 Hz) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 134.54 (*ortho*, t, J_{PC} = 6 Hz), 131.60 (*para*), 128.68 (*meta*, t, J_{PC} = 5 Hz), 128.13 (*ipso*, t, J_{PC} = 30 Hz), 120.86 (OTf, q, $^1J_{\mathrm{CF}}$ = 320 Hz), 105.98 (βC, t, $^3J_{\mathrm{PC}}$ = 4 Hz), 44.02 (αC, t, $^2J_{\mathrm{PC}}$ = 17 Hz), 30.90, 21.34, 20.49, 13.52 ppm; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 23.35 ($^1J_{\mathrm{PtP}}$ = 2720 Hz) ppm; ^{19}F NMR

(CDCl$_3$) δ −77.6 ppm; FAB MS *m/z* 800 (45, M − OTf), 719 (100, Pt(PPh$_3$)$_3$), 455, 378, 302, 183; FAB HRMS *m/z* 800.2160 (M − OTf), calcd for PtP$_2$C$_{42}$H$_{39}$ 800.2175.

Reaction of 1 with Hexynyl(phenyl)iodonium Triflate. Method C. Bis(triphenylphosphine)platinum ethylene complex, 1 (75 mg, 0.100 mmol), was dissolved in 8 mL of dry degassed methylene chloride in a 25-mL round bottom flask. Next, ethylene was bubbled throgh this solution for 5 min. A solution of hexynyl(phenyl)iodonium triflate (43.4 mg, 0.100 mmol) in 5 mL of methylene chloride was added while ethylene was bubbled through the solution. The reaction was complete in less than 5 min, as determined by ^{31}P NMR. Integration of the NMR spectrum indicated the σ-alkynyl and η^3-allenyl complexes in a 31:69 ratio, respectively. The solvent was removed in vacuo leaving an off-white solid. The residue was then dissolved in methylene chloride (3 mL), and hexanes was added dropwise to recrystallize the η^3-allenyl product. This was repeated five times and resulted in **9** as a white powder (33.2 g, 34%): IR (thin film CCl$_4$) 3058, 2907, 2878, 1473, 1440, 1268 (OTf), 1225 (OTf), 1168 (OTf), 1092, 1031, 994, 753, 694 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.32–6.77 (m, 30H), 3.30–3.15 (m, 1H), 1.26–1.12 (m, 5H), 0.91–1.03 (m, 4H), 0.60 (t, 3H) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 133.98 (*ortho*, d, $^2J_{PC}$ = 12 Hz, d, $^2J_{PtC}$ = 21 Hz), 133.27 (*ortho*, d, $^2J_{PC}$ = 12 Hz, $^2J_{PtC}$ = 27 Hz), 131.62 (*para*, d, $^4J_{PC}$ = 3 Hz), 131.48 (*para*, d, $^4J_{PC}$ = 3 Hz), 128.78 (*meta*, d, $^3J_{PC}$ = 11 Hz), 128.69 (*meta*, d, $^3J_{PC}$ = 11 Hz), 129.70 (*ipso*, d, $^1J_{PC}$ = 55 Hz, $^2J_{PtC}$ = 33 Hz), 128.87 (*ipso*, d, $^1J_{PC}$ = 62 Hz, $^2J_{PtC}$ = 35 Hz), 120.96 (OTf, q, $^1J_{CF}$ = 321 Hz), 105.14 (*C*-*n*-Bu, d, $^2J_{PC}$ = 3 Hz, d, $^2J_{PC}$ = 48 Hz, $^1J_{PtC}$ = 132 Hz), 97.92 (C*C*C, d, $^2J_{PC}$ = 4 Hz, d, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 55 Hz), 66.68 (*C*HMe, d, $^2J_{PC}$ = 38 Hz, $^1J_{PtC}$ = 113 Hz), 32.77 (d, J_{PC} = 3 Hz), 22.05, 21.65, 13.17, 15.41 (Me, d, $^3J_{PC}$ = 4 Hz), 6.35 ($^3J_{PC}$ = 3 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 18.61 ($^1J_{PtP}$ = 3750 Hz, $^2J_{PP}$ = 16 Hz), 14.66 ($^1J_{PtP}$ = 4275 Hz, $^2J_{PP}$ = 16 Hz); ^{19}F NMR (CDCl$_3$) δ −78.2 ppm; FAB MS *m/z* 829 (100, M − OTf), 719 (92, Pt(PPh$_3$)$_2$), 642, 456 (15, PtPPh$_3$), 377, 302. Anal. Calcd for C$_{45}$H$_{43}$PtP$_2$SO$_3$F$_3$: C, 55.27; H, 4.43. Found: C, 55.56; H, 4.52.

Reaction of 1 with Propynyl(phenyl)iodonium Triflate (4). Method C. Bis(triphenylphosphine)platinum ethylene complex 1 (7.5 mg, 0.010 mmol) was added to a dried NMR tube. The tube was sealed with a rubber septum, evacuated, and flushed with nitrogen. Deuteriobenzene (0.5 mL) was added and ethylene bubbled through the solution for 5 min. A solution of propynyl(phenyl)iodonium triflate,[18] 4 (0.010 mmol, 3.9 mg), in deuteriobenzene (0.5 mL) was added slowly while ethylene was continuously bubbled through the solution. This reaction resulted in a 78:22 ratio of the σ-alkynyl complex to the η^3-allenyl complex, as determined by ^{31}P NMR. Because of the low percentage of the desired η^3-allenyl complex, no attempts to isolate the product were made. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 23.64 (**5**, $^1J_{PtP}$ = 2710 Hz), 19.66 (**7**, $^1J_{PtP}$ = 3800 Hz, $^2J_{PP}$ = 20 Hz), 14.21 (**7**, $^1J_{PtP}$ = 4326 Hz, $^2J_{PP}$ = 20 Hz).

[(PPh$_3$)$_2$Pt(η^3-CH$_3$CHC≡CCH$_3$)]OTf (7). Bis(triphenylphosphine)platinum ethylene complex, 1 (74.7 mg, 0.100 mmol), was dissolved in 10 mL of dry degassed methylene chloride and 1-((trifluoromethyl)sulfonyl)-3-pentyne, **6** (35 mg, 0.15 mmol), was added. The reaction was complete within 30 min, as determined by ^{31}P NMR. Dry degassed hexanes (20 mL) was slowly added to the solution, resulting in the precipitation of the product. The resulting white powder was filtered out and washed with additional hexanes and the product **7** dried overnight in vacuo (83.4 mg, 89% yield): mp 121–123 °C dec; IR (thin film CCl$_4$) 3073, 3056, 3007, 2921, 1481, 1436, 1271 (OTf), 1223 (OTf), 1150 (OTf), 1096, 1031, 999, 753, 694, 636 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38–7.06 (m, 30H), 3.37–3.21 (m, 1H), 1.30 (d, J = 2.44; $^3J_{HH}$ = 5.1 Hz), 1.02 (t, J = 6.5 Hz; d, J = 3.9 Hz; J_{PtH} = 12 Hz) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 133.93 (*ortho*, d, $^2J_{PC}$ = 12 Hz, $^2J_{PtC}$ = 21 Hz), 133.28 (*ortho*, d, $^2J_{PC}$ = 12 Hz, $^2J_{PtC}$ = 27 Hz), 131.62 (*para*, d, $^4J_{PC}$ = 2 Hz), 131.43 (*para*, d, $^4J_{PC}$ = 2 Hz), 128.77 (*meta*, d, $^3J_{PC}$ = 11 Hz), 128.74 (*meta*, d, $^3J_{PC}$ = 11 Hz), 129.67 (*ipso*, d, $^1J_{PC}$ = 59 Hz, $^2J_{PtC}$ = 35 Hz), 128.83 (*ipso*, d, $^1J_{PC}$ = 57 Hz, $^2J_{PtC}$ = 32 Hz), 120.95 (OTf, q, $^1J_{CF}$ = 321 Hz), 100.47 (*C*–CH$_3$, d, $^2J_{PC}$ = 3 Hz; d, $^2J_{PC}$ = 48 Hz, $^1J_{PtC}$ = 132 Hz), 96.56 (C*C*C, d, $^2J_{PC}$ = 4 Hz; d, $^2J_{PC}$ = 6 Hz, $^1J_{PtC}$ = 54 Hz), 66.13 (*C*HMe, d, $^2J_{PC}$ = 38 Hz, $^1J_{PtC}$ = 114 Hz), 15.25 (Me, d, $^3J_{PC}$ = 4 Hz, $^2J_{PtC}$ = 12 Hz), 6.35 (CH$_3$, d, $^3J_{PC}$ = 3 Hz) ppm; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 18.68 ($^1J_{PtP}$ = 3743 Hz, $^2J_{PP}$ = 16 Hz), 14.79 ($^1J_{PtP}$ = 4277 Hz, $^2J_{PP}$ = 16 Hz) ppm; ^{19}F NMR (CDCl$_3$) δ −78.2 ppm; FAB MS *m/z* 786 (100, M − OTf), 719 (66, Pt(PPh$_3$)$_2$), 642, 455 (16, PtPPh$_3$), 378, 307, 154, 136. Anal. Calcd for C$_{42}$H$_{37}$PtP$_2$SO$_3$F$_3$: C, 53.90; H, 3.98. Found: C, 54.13; H, 4.05.

[(PPh$_3$)$_2$Pt(η^3-CH$_3$CHC≡C-*n*-C$_4$H$_9$)]OTf (16). Bis(triphenylphosphine)platinum ethylene complex, 1 (74.7 mg, 0.100 mmol), was dissolved in 10 mL of dry degassed methylene chloride, and 1-((trifluoromethyl)sulfonyl)-3-octyne, **15** (41.5 mg, 0.15 mmol), was added. The reaction was complete within 30 min, as determined by ^{31}P NMR. Dry degassed hexanes (20 mL) was slowly added to the solution, resulting in the precipitation of the product. The resulting white powder was filtered out and washed with additional hexanes and the product dried overnight in vacuo. (83.3 mg, 85% yield). See the previous procedure for the analytical data.

1-((Trifluoromethyl)sulfonyl)-3-pentyne (6). Sodium carbonate (2.76 g, 25 mmol) was dried for 3 h at 200 °C under vacuum. This was then added to methylene chloride (30 mL) and triflic anhydride (8.4 mL, 50 mmol) in a dry Schlenk flask. The reaction mixture was then cooled to −45 °C. Next, 3-pentyn-1-ol (3.7 mL, 40 mmol) was added dropwise over 15 min. The reaction mixture was stirred for 2 h and then was allowed to warm slowly to 0 °C. Stirring was maintained for an additional 1 h. The reaction was then quenched with water (20 mL). The organic layer was separated from the aqueous layer and dried over magnesium sulfate (1 g). The product was concentrated by rotary evaporation and distilled at room temperature under reduced pressure (20–25 °C/200 mmHg). The purified product **6** is a colorless oil (3.5 g, 64%): ^{1}H NMR (CDCl$_3$) δ 4.53–4.48 (CH$_2$OTf, m, 2H), 2.67–2.62 (CH$_2$, m, 2H), 1.77–1.75 (CH$_3$, m, 3H) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 118.55 (OTf, q, $^1J_{CF}$ = 320 Hz), 79.35 (αC), 74.47 (CH$_2$-OTf), 71.66 (βC), 20.19 (CH$_2$), 3.32 (CH$_3$).

1-((Trifluoromethyl)sulfonyl)-3-octyne (15). Sodium carbonate (2.76 g, 25 mmol) was dried for 3 h at 200 °C under vacuum. This was then added to methylene chloride (30 mL) and triflic anhydride (8.4 mL, 50 mmol) in a dry Schlenk flask. The reaction mixture was cooled to −45 °C. Next, 3-octyn-1-ol (5.0 mL, 40 mmol) was added dropwise over 15 min. The reaction mixture was stirred for 2 h and then was allowed to warm slowly to 0 °C. Stirring was maintained for an additional 1 h. The reaction was quenched with water (20 mL). The organic layer was separated from the aqueous layer and dried over magnesium sulfate (1 g). The product was concentrated by rotary evaporation and distilled at room temperature using reduced pressure (20–27 °C/200 mmHg). The purified product **13** is a colorless oil (4.3 g, 65%): ^{1}H NMR (CDCl$_3$) δ 4.51 (CH$_2$OTf, t, $^3J_{HH}$ = 7 Hz, 2H), 2.70–2.64 (CH$_2$, m, 2H), 2.15–2.10 (m, 2H), 1.47–1.35 (m, 4H), 0.91–0.81 (CH$_3$, t, $^3J_{HH}$ = 7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 118.57 (OTf, q, $^1J_{CF}$ = 320 Hz), 84.04 (αC), 74.52 (CH$_2$OTf), 72.42 (βC), 30.71, 21.89, 20.25, 18.27, 13.55 (CH$_3$).

Acknowledgment. We are grateful to the NSF (CHE9101767) for financial support and to Johnson-Matthey for the generous loan of K$_2$PtCl$_4$.

Supplementary Material Available: Tables of crystal data, bond distances and angles, torsion angles, least squares planes, and displacement parameters (*B*'s and *U*'s) (14 pages). Ordering information is given on any current masthead page.

OM930558Y