Interaction of $(Ph_3P)_4Pt$ with Alkynylvinyl Triflates: Stereochemistry and Mechanism of Formation of σ-Enynyl and σ-Butatrienyl Cationic Platinum(II) Complexes[†]

Peter J. Stang* and Arun K. Datta[1]

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

Received August 29, 1988

Reaction of alkynylvinyl triflates with $(Ph_3P)_4Pt$ results in σ-enynyl or σ-butatrienyl cationic platinum(II) complexes as reasonably stable microcrystalline solids in 63–84% isolated yields. Only hindered triflates give σ-butatrienyl complexes. Stereochemical studies established that a multistep process, involving initial π-acetylene formation, subsequent rearrangement to a σ-butatrienyl complex and attack by a second Pt species, to give the final σ-enynyl complexes best accounts for the observed results. Formation of the σ-butatrienyl complexes occurs stereospecifically with *inverted* olefin geometry whereas the formation of the enyne complexes occurs with partial stereoconvergence. These results are discussed and compared to the related reactions of iridium.

There is enormous current interest and research activity in the reactions of the zerovalent Nickel triad (Ni^0, Pd^0, Pt^0) metals with organic substrates and in particular with unsaturated molecules.[2,3] A great deal of this interest derives from the multitude of Ni-, Pd-, and Pt-catalyzed carbon–carbon bond forming reactions developed in the last two decades.[4–6] Of particular interest are σ-carbon metal species for they generally represent an obligatory step in the catalytic coupling processes. Moreover, such complexes are of inherent interest in their own right from the point of view of structure, bonding, and reactivity.[7] Although σ-allyl, σ-vinyl, and σ-allenyl complexes are reasonably well-known, little is known about σ-polyunsaturated organometallic species.[2,3,7]

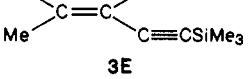
As part of an ongoing study[8,9] of organometallic compounds with polyunsaturated organic ligands we wish to report the reactions of $(Ph_3P)_4Pt$ with alkynylvinyl triflates and the ready formation and characterization of σ-enynyl and σ-butatrienyl cationic platinum(II) complexes.[10]

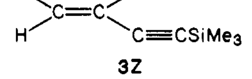
Results and Discussion

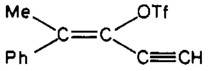
Alkynylvinyl triflates 1–4 were prepared by standard literature procedures from the corresponding alkynyl ketones.[10,11] Tetrakis(triphenylphosphine)platinum ($(Ph_3P)_4Pt$, **5**) was prepared from K_2PtCl_4 according to Ugo and co-workers.[12] Reaction of a 2–2.5 molar excess of alkynylvinyl triflates 1–4 with **5** in degassed benzene occurred at 25–80 °C in 0.5–6 h depending on the acetylenic substituent R. Vinyl triflates 1 and 3 gave enynyl cationic platinum(II) complexes **6** in 63–84% isolated yield whereas triflates 2 and 4 gave σ-butatrienyl complexes **7** in 72–85% isolated yield as outlined in Scheme I. Complexes **6** and **7** are reasonably stable, somewhat hygroscopic, pale yellow (off-white) microcrystalline or powdery solids.

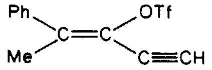
$Me_2C{=}C(OTf)C{\equiv}CR$ $\qquad$ $Ph_2C{=}C(OTf)C{\equiv}CH$

1a: R = H $\qquad$ **2**
b: R = Me
c: R = $SiMe_3$
d: R = *t*-Bu
e: R = Ph


3E


3Z


4E


4Z

Scheme I

$$\underset{\mathbf{1}}{Me_2C{=}C(OTf)C{\equiv}CR} + \underset{\mathbf{5}}{(Ph_3P)_4Pt} \xrightarrow[0.5\text{–}6\ h]{C_6H_6,\ 25\text{–}80\ °C} Me_2C{=}C(C{\equiv}CR)[Pt^+(PPh_3)_3{}^-OTf]$$

6a: R = H
6b: R= Me
6c: R = $SiMe_3$
6d: R = *t*-Bu
6e: R = Ph

$$\underset{\mathbf{2}:\ R\ =\ Ph;\ \mathbf{4E,Z}:\ R\ =\ Me}{PhRC{=}C(OTf)C{\equiv}CH} + \underset{\mathbf{5}}{(Ph_3P)_4Pt} \xrightarrow[30\ min]{C_6H_6,\ 25\ °C} PhRC{=}C{=}C{=}CH[Pt^+(PPh_3)_3{}^-OTf]$$

7a: R = Ph
7b: R = Me

Adducts **6** and **7** were characterized by spectral means. All the complexes **6** and **7** gave highly characteristic fragments in the FAB mass spectra corresponding to the cationic moiety and the corresponding protonated species,

---

[†] Dedicated to Professor Dietmar Seyferth on the occasion of his 60th birthday.

[1] Abstracted in part from: Datta, A. K. Ph.D. Dissertation, University of Utah, 1988.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[3] *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: London, 1985.

[4] Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

[5] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985.

[6] Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis. Practical Applications of Transition Metals*; Plenum: New York, 1984.

[7] *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6.

[8] Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720. White, M. R.; Stang, P. J. *Organometallics* **1983**, *2*, 1382. White, M. R.; Stang, P. J. *Organometallics* **1983**, *2*, 1654.

[9] Stang, P. J.; Dixit, V.; Schiavelli, M. D.; Drees, P. *J. Am. Chem. Soc.* **1987**, *109*, 1150.

[10] For a related study on the formation of (σ-butatrienyl)- and (σ-enynyl)cobaloxime complexes see: Stang, P. J.; Datta, A. K.; Dixit, V.; Wistrand, L. G. *Organometallics*, preceding paper in this issue.

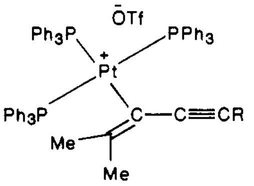
[11] Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438. Stang, P. J. Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

[12] Ugo, R.; Cariati, F.; LaMonica, G. *Inorg. Synth.* **1968**, *11*, 105.

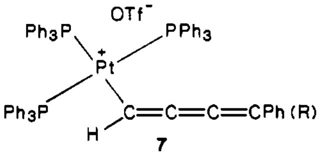
0276-7333/89/2308-1024$01.50/0

i.e. $MH^+ - OTf$ and $M^+ - OTf$ clearly indicative of 1:1 adducts. The infrared of adducts **6** showed a weak absorption between 2050 and 2160 cm^{-1} characteristic of the C≡C bond, whereas this band was absent in complexes **7**. The presence of triflate, and hence the cationic nature of these species, was confirmed by two strong bands in the infrared centered at 1265 and 630 cm^{-1} and a singlet in the ^{19}F NMR at -77.6 ∓ 0.2 ppm. These infrared absorptions and ^{19}F NMR signal are highly characteristic of ionic, or weakly coordinated, triflate species.[13] The ^1H NMR of all compounds were consistent with the proposed structures.

Most valuable in the structure determinations were the ^{31}P and ^{13}C NMR. The ^{31}P NMR showed two distinct signals along with the assoicated Pt satellites. Specifically the trans phosphorus gave rise to a triplet centered at 14.3 ± 0.3 ppm with $J_{P-P} = 21.5 \pm 0.5$ Hz and $J_{Pt-P} = 1875 \pm 30$ Hz, whereas the two equivalent cis phosphorus gave a doublet centered at 16.0 ± 1.0 ppm with $J_{P-P} = 21.5 \pm 0.5$ Hz and $J_{Pt-P} = 2980 \pm 140$ Hz for **6**. Likewise, in **7** the trans phosphorus appeared as a triplet centered at 15.5 ± 0.3 ppm and $J_{P-P} = 19.5 \pm 1.5$ Hz and $J_{Pt-P} = 2110 \pm 40$ Hz, and the cis phosphorus signal occurred at 16.5 ± 0.5 ppm with $J_{P-P} = 19.5 \pm 0.5$ Hz and $J_{Pt-P} = 2930 \pm 95$ Hz (for the exact signals of the individual compounds of **6** and **7**, see Experimental Section). Similarly, in the ^{13}C NMR the signals due to the C≡C carbons of **6** were in the standard acetylenic range[14] of 85–110 ppm, whereas the signals due to the central sp-hybridized carbons of the butatrienyl moiety in **7** were in the characteristic[15] low-field range of 157–165 ppm. Therefore, these data unambiguously establish the structures of **6** as a σ-enynyl square-planar cationic complex and **7** as a σ-butatrienyl square-planar cationic complex. To our knowledge both **6** and **7**, but in particular **7** with the extended unsaturation of a σ-butatrienyl ligand, are unique and represent the first platinum examples of their kind.



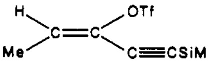
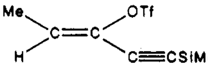
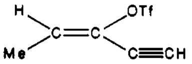
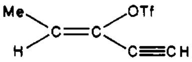
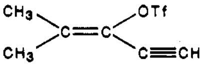
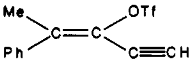
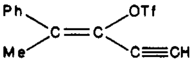
6



7

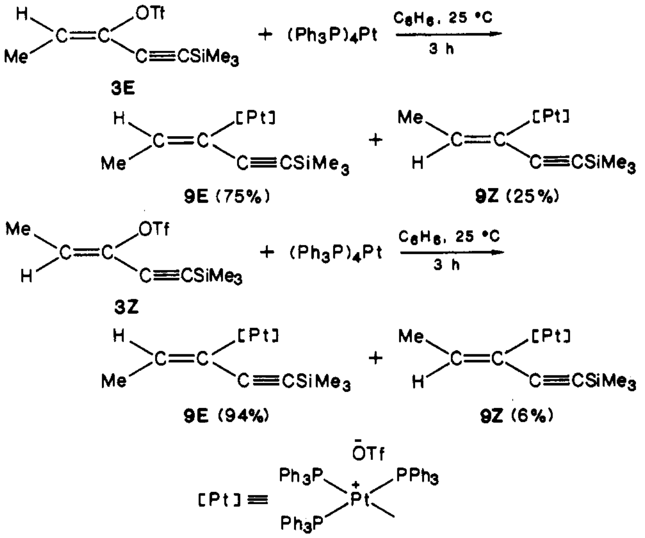
Mechanistic Considerations. The specific reaction conditions (see Experimental Section) required for the formation of **6** establish a qualitative order of reactivity that is strongly dependent upon the terminal substituent R in the starting alkynylvinyl triflates **1**: with H ≫ Me > $SiMe_3$ > Ph ≫ *t*-Bu. This order of reactivity approximates the relative size of the various substituents and suggests a strong dependence of the reaction upon steric factors. A similar dependence of rate upon steric factors was observed in the reaction of **1** with Vaska's complex, where in fact the *t*-Bu compound **1d** did not react at all.[9] Although this might imply a similarity of mechanisms for the reactions of Pt and Ir with **1**, we decided to get further insight into this question by a detailed stereochemical investigation.

Table I. Summary of Stereochemically Relevant Spectral Data for 3 and 4 and Related Compounds[a]

compd	^{13}C	^1H			
	Me	Me	C=CH	C≡CH	$^3J_{C-H}$, Hz
 **3E**	13.77	1.90	6.09		9.3
 **3Z**	12.41	1.86	5.97		2.1
 **8E**	13.21	1.9	6.2	3.5	9.15
 **8Z**	12.02	1.8	6.05	3.2	2.06
	19.1 21.4	1.9 2.0		3.4	
 **4E**	19.23	2.26		3.21	
 **4Z**	21.38	2.33		3.60	

[a] Chemical shifts in ppm.

Scheme II



Stereochemical Studies. The isomeric alkynylvinyl triflates **3** were separated by preparative GC and **4** by HPLC in greater than 99% isomeric purity. The relevant spectral data upon which the stereochemical assignment of **3E** and **3Z** are based along with related compounds are summarized in Table I. Two characteristic features of the NMR data allow firm assignments of the olefin geometries of the individual isomers. A considerable body of evidence[16] indicates that the long-range vicinal carbon–hy-

---

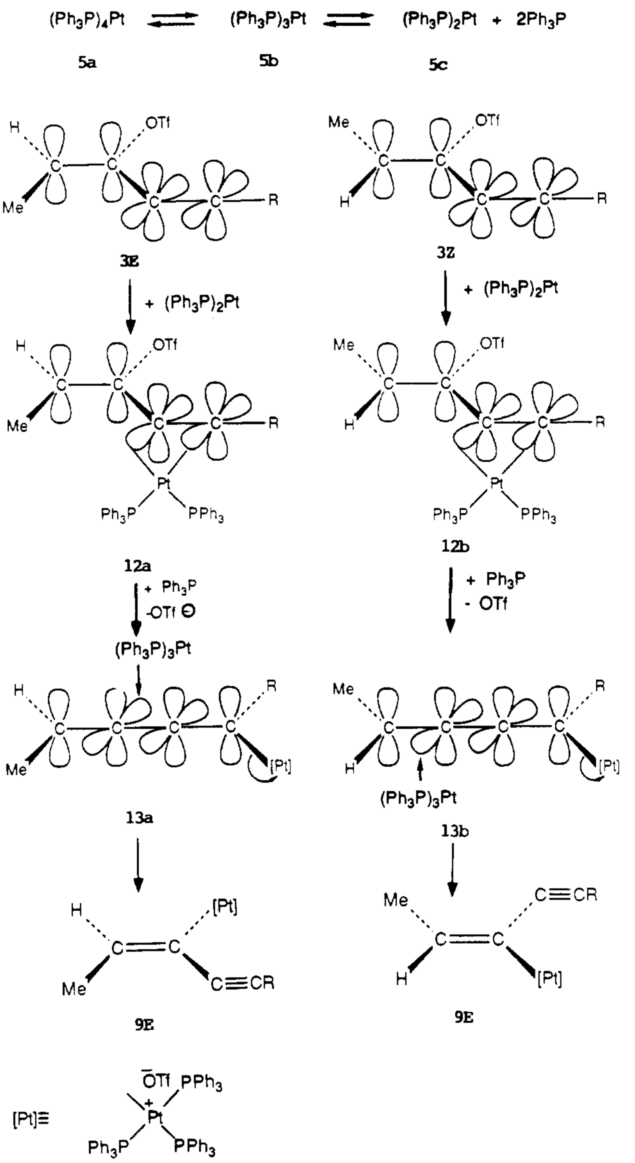
(13) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(14) Levi, G. C.; Lighter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; pp 90–95.

(15) Hopf, H. *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley-Interscience: London, 1980; Chapter 20, pp 779–901. Murray, M. *Methoden Org. Chem. (Houben-Weyl), 4th Ed.* **1977**, *2a*, 963–1076.

(16) Marshall, J. L.; Seiwell, R. *J. Magn. Reson.* **1974**, *15*, 150. Anderson, J. E. *Tetrahedron Lett.* **1975**, *46*, 4079. Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617. Kingsbury, C. A.; Draney, D.; Sopchick, A.; Rissler, W.; Durham, D. *J. Org. Chem.* **1976**, *41*, 3863. Garratt, D. G.; Beaulieu, P. *Can. J. Chem.* **1979**, *57*, 119. Letcher, R. M.; Acheson, R. M. *Org. Magn. Reson.* **1981**, *16*, 316. Lin, T.-Y.; Cromwell, N. H.; Kingsbury, C. A. *J. Heterocycl. Chem.* **1985**, *22*, 21. Ito, S.; Ziffer, H.; Bax, A. *J. Org. Chem.* **1986**, *51*, 1130.

Scheme III



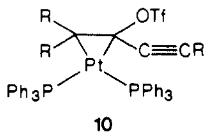
drogen coupling is always larger in the trans arrangement than the cis one: $^3J_{C,H}$(trans) > $^3J_{C,H}$(cis). Indeed this holds for alkynylvinyl triflates **3** (as well as **8E** and **8Z**) with $^3J_{C,H}$ = 9.3 Hz and 2.1 Hz for **3E** and **3Z**, respectively. Moreover, abundant data indicate[17] that the carbon-13 chemical shifts of carbon atoms in perturbed (spatially crowded) alkyl groups are further *upfield* than the resonances of similar carbons in a less perturbed or uncrowded environment. This effect, along with the proton chemical shifts of the respective vinylic hydrogens, confirms the stereochemical assignments of **3E** and **3Z**.

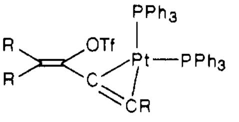
The results of the reactions of the *individual* isomeric alkynylvinyl triflates **3E** and **3Z** with $(Ph_3P)_4Pt$ are summarized in Scheme II. The structural assignments of **9E** and **9Z** were made on the basis of spectral data as discussed above and described in the Experimental Section. The stereochemical assignments of **9E** and **9Z** were based on the Pt–H coupling constants. Specifically, it has been demonstrated that in platinoalkene species the trans $^3J_{Pt-H}$ is always significantly greater than the corresponding $^3J_{Pt-H}$ cis coupling.[18] Homonuclear decoupling experiments[1] established a $^3J_{Pt-H}$ = 85 Hz for **9Z** and a $^3J_{Pt-H}$ = 56 Hz for **9E**, respectively.

As the data in Scheme II indicate the reaction of alkynylvinyl triflates with $(Ph_3P)_4$ occurs with partial stereoconvergence. This is in contrast to the analogous reactions of related alkynylvinyl triflates with Ir[9] (Vaska's complex) and Co[10] ($[Co(dmgH)_2py]^-$) that occurred with complete stereospecificity. Control experiments established that the isomeric starting triflates **3** as well as the products **9** were stable to the reaction conditions.

A direct nucleophilic vinylic substitution (S_NV) via a stepwise addition–elimination process[19] might account for these results. Such a mechanism readily accounts for the partial stereoconvergence observed in the reaction[20] of simple alkylvinyl triflates MeCH=CHOTf with $[Co(dmgH)_2py]^-$. However, since Pt is some 10^7 *less* nucleophilic[21] than Co and since organic nucleophiles more nucleophilic than Pt do not react[22] with alkynylvinyl triflates **1**, this is an unlikely process. Moreover, such a process with **1** would require loss of conjugation between the alkene–alkyne π-bond, an unlikely event.

A much more likely mechanism is initial formation of a π-olefin complex between **1** and the coordinatively unsaturated $(Ph_3P)_3Pt$ or $(Ph_3P)_2Pt$. It is of course well-known[23] that $(Ph_3P)_4Pt$ rapidly dissociates to form $(Ph_3P)_3Pt$ and $(Ph_3P)_2Pt$. Moreover, π-alkene and π-alkyne platinum complexes are well established.[7,24] In the case of **1** either a π-alkene, **10**, or a π-alkyne, **11**, platinum complex might be formed: Although a π-alkene complex,


10


11

10, could more directly account for the formation of enyne complexes **6** and **9** than the alkyne complex **11** (vide infra), it would also, however, require stereospecificity with retention of olefin geometry. Analogous Pd reactions are well-known[25] to give stereospecific products in vinylic cross-coupling reactions.[26] Moreover, the reaction of the isomeric β-styryl halides with $(Ph_3P)_4Pt$ was shown to proceed with complete retention of olefin geometry.[27] Likewise, the reaction of the isomeric MeCH=CMeOTf with $(Ph_3P)_4Pt$ to give the analogous σ-vinyl cationic platinum complexes proceeds with complete retention of olefin geometry.[28]

---

(17) Pochat, F. *Tetrahedron* **1986**, *42*, 3537. Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315. Woolfenden, W. R.; Grant, D. M. *Ibid.* **1966**, *88*, 1496. deHaan, J. W.; Van deVen, L. J. M. *Org. Magn. Reson.* **1973**, *5*, 147. Lippmaa, E.; Pehk, T.; Andersson, K.; Rappe, C. *Ibid.* **1970**, *2*, 109. Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* 1971, *36*, 2757. Uriac, P.; Bonnic, J.; Huet, J. *Tetrahedron* **1985**, *41*, 5051.

(18) Clark, H. C.; Ferguson, G.; Goal, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961. Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* 1971, 2667. Mann, B. E.; Shaw, B. L.; Tucker, N. I. *Chem. Commun.* **1970**, 1333.

(19) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. Modena, G. *Ibid.* **1971**, *4*, 73.

(20) Stang, P. J.; Datta, A. K. *J. Am. Chem. Soc.* **1989**, *111*, 1358.

(21) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

(22) Dixit, V. Ph.D. Dissertation, The University of Utah, 1985.

(23) Cook, C. D.; Jauhal, G. S. *Can. J. Chem.* **1967**, *45*, 301. Ugo, R.; Cariati, F.; Monica, G. L. *Chem. Commun.* **1966**, 868.

(24) Green, M.; Osborn, R. B. L.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2525. Ashley-Smith, J.; Green, M.; Wood, D. C. *Ibid.* **1970**, 1847. Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 759. Rochon, F. D.; Theophanides, T. *Can. J. Chem.* **1972**, *50*, 1325. Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1291.

(25) Stille, J. K. in ref 3, Vol. 2, Chapter 9, pp 625–787.

(26) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.

(27) Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103.

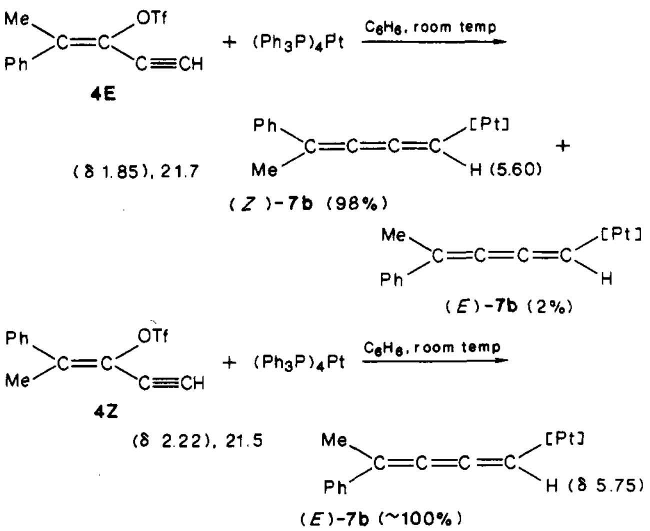
(28) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.*, in press.

Hence, we propose that the most likely mechanism to account for all observations involves a number of steps and intermediates as outlined in Scheme III. Specifically, interaction of coordinativaly unsaturated $(Ph_3P)_2Pt$ (**5c**) with **3E** and **3Z** on the *less* hindered face of the acetylene (i.e. the side opposite the OTf group) results in π-acetylene complexes **12a** and **12b**, respectively. Further reaction (i.e. rearrangement) gives σ-cumulenyl cationic platinum complexes **13a** and **13b**, respectively. In-plane attack, *from the less hindered side* (away from the Me group) of **13a** and **13b**, respectively by a second molecule of platinum, i.e. $(Ph_3P)_3Pt$, results in the formation of **9E** in *both* cases. Hence, this mechanism predicts net *retention* of olefin geometry for **3E** and inversion of **3Z**. This is observed experimentally, albeit not stereospecifically; **3E** gives predominantly retention (75%) and **3Z** results in predominantly (94%) inversion of olefin geometry. The minor amount of stereoconvergence (i.e. "wrong" product) may be accounted for by either (a) nonstereospecific π-complexes formation or (b) nonstereospecific attack (i.e. preferential but not *exclusive* attack from the less hindered side) upon **13a** and **13b**.

This mechanism involves three major facets: (a) initial π-complex formation; (b) rearrangement to a σ-butatrienyl complex; (c) attack by a second nucleophile. π-Complex formation is consistent with (but not necessarily proven) the qualitative kinetic observations whereby the least hindered system (R = H in **1**) reacts fastest and the most hindered one (R = *t*-Bu in **1**) the slowest. It is well-known that the more hindered (i.e. substituted) an alkene or acetylene the less they form π-complexes.[2,7] The last point (i.e. a second nucleophilic attack) is facilitated by the cationic nature of the Pt in **13**, that in fact makes it an excellent nucleofuge and hence predesposed to departure.[29]

We have of course attempted to obtain *direct* evidence for the involvement of π-complexes **12** and σ-butatrienyl complexes **13** in these reactions. However, at least in the former case our attempts have been twarted to date. Low-temperature reaction and/or continuous NMR monitoring of the interaction of **1** with **5** either gives no reaction (low temperature) or rapidly forms, without the observation of intermediates, product **6**. Attempts to react **1** with the (π-ethylene)platinum complex $(C_2H_4)Pt(PPh_3)_2$, under a variety of conditions, in hopes of displacing the ethylene and isolating or observing a π-complex resulted only in tar and polymer formation. In contrast, our efforts to form and study σ-butatrienyl cationic platinum complexes proved successful. As already indicated above, reaction of the more hindered β,β-diphenylalkynylvinyl triflate **2** gave a 72% isolated yield of the σ-butatrienyl complex **7a**. To get an idea of the stereochemistry of the butatriene forming reaction we examined the interaction of isomeric alkynylvinyl triflates **4** with **5**. Triflates **4E** and **4Z** were separated by HPLC in greater than 99% isomeric purity. As these triflates are tetrasubstituted olefins, assigning stereochemistry to the individual geometric isomers presents a problem. Currently there are no known definitive methods, short of X-ray determination, for assigning stereochemistry to tetrasubstituted alkenes. However, careful examination of the spectral data summarized in Table I and in particular the consistent trends in both ^{13}C and ^{1}H chemical shifts between stereochemically related isomers allows for a reasonable assignment. Specifically, we assign the first (**F**) and major fraction **4F** from the HPLC as the **4E** isomer and the second (**S**) and minor fraction **4S** = **4Z** based on the following considerations. In all instances, both in the ^{13}C and ^{1}H spectra, the chemical shift of the β-methyl group on the same side as the acetylene moiety is *lower* than when the methyl is on the side of the triflate. Likewise, the chemical shift of the terminal acetylenic hydrogen is *lower* when the alkyne and methyl groups are syn than vice versa. Since the stereochemical assignments of the trisubstituted analogues **3** and **8** are secure on the basis of the long-range, $^{3}J_{C-H}$, cis and trans carbon–hydrogen coupling constants, as discussed above, we have reasonable confidence in the assignments of **4E** and **4Z**.

Scheme IV



The results of the reaction of the *individual* isomeric alkynylvinyl triflates **4E** and **4Z** are summarized in Scheme IV.

The structural assignments of **7b** were based on spectral data as discussed above and detailed in the Experimental. Stereochemistry was assigned on the basis of the ^{1}H and ^{13}C chemical shifts summarized in Scheme IV. Since the substituents of even carbon cumulenes are all in the same plane, as in alkenes, one might expect similar pertubations by various groups upon the chemical shifts in the two classes of compounds albeit perhaps diminished in magnitude in butatrienes compared to alkenes. This is indeed the case. Specifically, the cumulenic hydrogen in the *E* isomer ((*E*)-**7b**) experiences a 0.15 ppm van der Waals induced[30] *downfield* shift (when on the side of the larger phenyl) compared to (*Z*)-**7b**. Likewise, the methyl group is at 0.37 ppm lower field, also due to van der Waals compression effects[30] due to the bulky Pt group, in (*E*)-**7b** than in (*Z*)-**7b**. As expected,[17] and consistent with the proton NMR data the ^{13}C shifts are in the opposite direction, albeit the differences are very small. Hence the stereochemistry of these products are reasonably secure.

The stereochemical results in Scheme IV reveal two interesting points: (a) the reaction is highly (essentially completely) stereospecific; (b) with *inversion* of olefin geometry. Both of these observations are consistent with the overall mechanism proposed in Scheme III. Formation of a π-acetylene complex from the *less* hindered side and subsequent rearrangement to the σ-butatrienyl complex must occur by inversion of alkene geometry. The small amount of retention (2%) in the interaction of the **4E**

---

[29] The ability of metal centers to function as leaving groups is not widely recognized. For a recent cogent example see: Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 215 and references therein.

[30] Laszlo, P., Stang, P. J. *Organic Spectroscopy, Principles and Application*; Harper & Row Publishers: New York, 1971.

isomer might be accounted for by complexation on the side of the triflate and methyl groups due to the larger size of the β-phenyl group than the β-methyl group.[31] Moreover, the stereospecific π-complex formation observed with **4** must mean that the partial stereoconvergence observed in the enyne formation from **3** (Scheme II) must be the result of the second step: attack by a second Pt on the initially formed σ-butatrienyl complexes (Scheme III).

Conclusion. Reaction of enynyl triflates with $(Ph_3P)_4Pt$ gives isolable, reasonably stable σ-enynyl or σ-butatrienyl cationic platinum(II) complexes depending upon the substitution pattern of the starting alkynylvinyl triflate. Stereochemical studies establish that a multistep mechanism involving initial stereospecific formation of a π-acetylene complex that rearranges to a σ-butatrienyl complex which in turn suffers an in-plane attack by a second Pt species best accounts for these results. It is interesting to compare the reactions of the same alkynylvinyl triflates with Pt and Ir.[9] Vaska's complex gives *exclusively* (σ-butatrienyl)iridium complexes with complete stereospecificity and retained *olefin* geometry. Platinum in contrast results in σ-butatrienyl complexes of *inverted* olefin geometry, and in less substituted cases only (σ-enynyl)platinum complexes are isolated. These differences can be accounted for by different pathways in the reactions of the two systems due to differences in the character of the two metal systems. Iridium reacts via a syn-S_N2' process,[9] whereas platinum reacts by initial π-complexation. Moreover, the order of magnitude greater nucleoplicity of Pt[21] compared to Ir coupled with the better nucleofugacity[29] of the cationic platinum compared to the neutral iridium in the respective σ-butatrienyl complexes nicely accounts for a second attack by Pt, but not by Ir, and the concomitant formation of predominantly σ-enyne complexes with Pt, but only σ-butatrienyl complexes with Ir. Further studies with Rh and other metal systems as well as the chemistry of these novel polyunsaturated transition-metal complexes are under way and will be the subject of future reports.

Experimental Section

General Data. All reactions were carried out under an argon atmosphere. All boiling and melting points are uncorrected. Ir spectra were recorded on either a Perkin-Elmer 289 or a Nicolet 600 Ft spectrophotometer. NMR were recorded on a Varian EM-360 or 390, FT80A, or XL-300 spectrometer and are reported in parts per million (ppm) relative to internal Me_4Si (0.00); for ^{13}C NMR the locks were on deuteriated solvents. Mass spectra were obtained on a Varian MAT112 or a VG Micromass spectrometer. Analytical GC was carried out with a HP-5710A flame ionization GC with a HP-3380-A integrator. Preparative GC utilized a Varian-Aerograph 90P chromatograph. Solvents and reagents were purified and dried by standard procedures immediately prior to use. Preparative HPLC was performed on a Varian 5000 LC using a normal phase Varian micropack column. All ^{31}P NMR are relative to 85% H_3PO_4 and ^{19}F NMR relative to $CFCl_3$.

Analytical data were not obtained due to stability considerations and problems with reliable analyses of certain triflates due to the simultaneous presence of fluorines and sulfur. Structure determinations are based upon exhaustive spectral data (mass spectrum, IR, ^1H, ^{19}F, ^{13}C, ^{31}P NMR) and comparison to the analogous Co and Ir species. Purity was assest by ^{19}F and ^{31}P NMR.

Starting Materials. Tetrakis(triphenylphosphine)platinum (5). This compound was prepared from 1.1 g (2.45 mmol) of K_2PtCl_4 (Johnson Matthey) and 3.23 g (12.4 mmol) of triphenylphosphine in an alkaline ethanol solution according to a standard literature procedure.[12] Recrystallization afforded 2.52 g (81%) of **5** as a bright yellow powder. Alkynylvinyl triflates **1**, **2**, and **4** are known compounds and were prepared as previously described.[9,10] Isomeric vinyl triflates **3** were prepared from known[9,32] 1-(trimethylsilyl)pentyn-3-one as follows.

1-(Trimethylsilyl)-3-penten-1-yn-3-yl Triflates (3). Reaction of 5.78 g (37.5 mmol) of 1-(trimethylsilyl)pentyn-3-one with 15.9 g (56.3 mmol) of triflic anhydride[33] and 13.2 g (47 mmol) of *N,N*-diisobutyl-2,4-dimethyl-3-pentylamine (Fuluka) in 500 mL of dry CH_2Cl_2, by standard procedure,[32] gave 8.1 g (75%) of a 54:46 *mixture* of **3E** and **3Z**: bp (mixture) 45–48 °C (0.4 mm). The two isomers were separated by preparative GC on a 0.25 in. × 15 ft 15% SF-96 on 45/60 Chromosorb W column. For **3E** (major isomer): IR (neat) 3060, 2960, 2160 (C≡C), 1645 (C=C), 1420, 1210, 1135 (OSO_2CF_3), 840 ($SiMe_3$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9, $SiMe_3$), 1.90 (d, J = 7.5 Hz, 3, Me), 6.09 (q, J = 7.5 Hz, 1, C=CH); ^{13}C NMR ($CDCl_3$) δ 0.56 ($SiMe_3$), 13.77 (Me), 93.06, 104.93 (C≡C), 118.90 (q, OSO_2CF_3), 128.16 (β-vinyl C), 131.02 (α-vinyl C). For **3Z** (minor isomer): IR (neat) 3050, 2960, 2155 (C≡C), 1655 (C=C), 1415, 1220, 1150, (OSO_2CF_3), 840 ($SiMe_3$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9, $SiMe_3$), 1.86 (d, J = 7.3 Hz, 3, Me), 5.97 (q, J = 7.3 Hz, 1, C=CH); ^{13}C NMR ($CDCl_3$) δ 0.63 ($SiMe_3$), 12.41 (Me), 95.08, 99.22 (C≡C), 118.80 (q, OSO_2CF_3), 127.52 (β-vinyl C), 130.88 (α-vinyl C).

General Procedure for the Reaction of Alkynylvinyl Triflates 1–4 with $(Ph_3P)_4Pt$ (5). Tetrakis(triphenylphosphine)platinum (**5**; 200 mg, 0.16 mmol) was dissolved in carefully degassed benzene (10 mL) and then 0.3–0.4 mmol of the appropriate triflate added all at once. The homogenous mixture was stirred for a given period at the indicated temperatures. The extent of the reaction could be qualtitatively monitored by the color change from the intense yellow of **5** to pale yellow, off-white as the reaction progressed. Workup consisted of adding the entire solution to 100 mL of petroleum ether and filtering the precipate. Recrystallization of this crude material from benzene–petroleum ether or chloroform–petroleum ether gave pure products as colorless (off-white) or pale yellow microcrystalline solids.

Enyne Complex 6a. Stirring of enyne triflate **1a** (90 mg, 0.4 mmol) with $(Ph_3P)_4Pt$ (200 mg, 0.16 mmol) at room temperature for 30 min and workup gave 122 mg (63%) of **6a**: mp 105–107 °C dec; MS *m/e* 1061 (MH^+ - OTf, 11.4), 1060 (M^+ - OTf, 10.7) 981 (5), 798 (100), 719 (64), 642 (16), 456 (55), 378 (64), 359 (44); IR (KBr) 3300 (C≡CH), 3050, 2950, 2050 (C≡C), 1585, 1570, 1480, 1435, 1270, 1220, 1140, 1090, 1025, 1000, 740, 690, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (m, 3, Me), 1.24 (m, 3, Me), 3.12 (s, 1, C≡CH), 7.0–7.80 (m, 45); ^{31}P NMR δ 15.1 (d, J_{P-P} = 21.80, J_{Pt-P} = 2944 Hz), 14.7 (t, J_{P-P} = 21.80, J_{Pt-P} = 1906 Hz); ^{13}C NMR δ 24.9 (d, J_{CP} = 8, J_{CPt} = 52 Hz, Me), 28.0 (d, J_{CP} = 4.5, J_{CPt} = 50 Hz, Me), 86.8, 88.9 (C≡C), 121.0 (q, J_{CF} = 320 Hz, OSO_2CF_3), 127.7, 128.1, 128.9, 129.5, 130.7, 130.9, 134.1, 148.8; ^{19}F NMR δ -77.62.

Enyne Complex 6b. Reaction of 100 mg (0.42 mmol) of triflate **1b** with **5** (200 mg, 0.16 mmol) for 1.5 h at 60 °C gave 160 mg (80%) of **6b**. This product consisted of a 80:20 mixture of **6b** and a rearranged isomer identified[1] by its spectra as $(CH_3)_2CHC{\equiv}CC[Pt]{=}CH_2$. The two isomers could not be separated by chromatography or crystallization. All spectra were obtained on the mixture; hence the mass spectra, IR, and ^{13}C NMR are given for the mixture and all other spectra are for **6b** only: MS *m/e* 1075 (MH^+ - OTf, 17.5), 1074 (M^+ - OTf, 18.3), 981 (11.6), 812 (100), 719 (70), 642 (18), 456 (65), 378 (71); IR (KBr) 3060, 2900, 1585, 1570, 1480, 1435, 1270, 1220, 1150, 745, 695, 635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (m, 3, Me), 1.20 (s, 3, Me), 1.85 (s, 3, Me), 7.07–7.55 (m, 45); ^{31}P NMR δ 16.5 (d, J_{P-P} = 21.10, J_{Pt-P} = 3018 Hz), 14.5 (t, J_{P-P} = 21.10, J_{Pt-P} = 1873 Hz); ^{13}C NMR ($CDCl_3$) δ 5.30, 21.9, 23.0, 25.2, 27.60, 85.0, 95.2, 102.0, 114.6, 121.0, 127.6, 128.0, 128.1, 128.2, 129.4, 130.6, 130.7, 131.0, 134.0, 134.6, 144.1, 144.2; ^{19}F NMR δ -77.62.

Enyne Complex 6c. Reaction of triflate **1c** (100 mg, 0.35 mmol) with **5** (200 mg, 0.16 mmol) for 2 h at 60 °C gave 155 mg (76%) of **6c**: mp 150–155 °C dec; MS *m/e* 1133 (MH^+ - OTf, 5.5), 1132 (M^+ - OTf, 5.9), 981 (2), 870 (100), 792 (6.2), 719 (48), 642 (8.3), 608 (11), 514 (23.6), 456 (32), 378 (42), IR (KBr) 3050, 2950, 2095 (C≡C), 1585, 1570, 1480, 1430, 1265, 1220, 1140, 1090,

---

(31) The respective *A* values for C_6H_5 and CH_3 are 3.0 and 1.7. See: Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

(32) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438.

(33) Stang, P. J.; Dueber, T. E. *Organic Syntheses* **1974**, *54*, 79.

1025, 995, 840, 745, 695, 630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.1 (s, 9, SiMe$_3$), 0.82 (m, 3, Me), 1.26 (s, 3, Me), 6.95–7.52 (m, 45); ^{31}P NMR δ 16.4 (d, J_{P-P} = 21.64, J_{Pt-P} = 2968 Hz), 14.4 (t, J_{P-P} = 21.64, J_{Pt-P} = 1894 Hz); ^{13}C NMR (CDCl$_3$) δ 0.3 (SiMe$_3$), 24.9, 28.2 (Me), 101.8, 109.9 (C≡C), 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$), 127.1, 128.0, 129.1, 130.1, 130.7, 130.9, 134.3, 134.6, 148.7; ^{19}F NMR δ −77.62.

Enyne Complex 6d. Reaction of triflate **1d** (115 mg, 0.4 mmol) with **5** (200 mg, 0.16 mmol) for 6 h at 80 °C gave 168 mg (83%) of **6d**: mp 195–198 °C dec; MS *m/e* 1117 (MH$^+$ − OTf, 3.7), 1116 (M$^+$ − OTf, 6.5), 981 (2), 854 (100), 719 (50), 456 (60), 378 (60); IR (KBr) 3050, 2960, 2150 (C≡C), 1585, 1570, 1480, 1430, 1265, 1220, 1140, 1090, 1025, 740, 690, 630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.67 (m, 3, Me), 1.08 (s, 9, *t*-Bu), 1.33 (s, 3, Me), 6.96–7.53 (m, 45); ^{31}P NMR δ 17.0 (d, J_{P-P} = 21.40, J_{Pt-P} = 3011 Hz), 14.1 (t, J_{P-P} = 21.40, J_{Pt-P} = 1845 Hz); ^{13}C NMR (CDCl$_3$) δ 24.5, 28.1 (Me, 28.5, 31.3 (*t*-Bu), 84.0, 102.0 (C≡C), 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$), 127.8, 128.0, 129.4, 130.5, 130.8, 134.2, 134.5, 144.1; ^{19}F NMR δ −77.62.

Enyne Complex 6e. Reaction of triflate **1e** (120 mg, 0.4 mmol) with **5** (200 mg, 0.16 mmol) for 3 h at 70 °C gave 170 mg (84%) of **6e**: mp 185–186 °C dec; MS *m/e* 1137 (MH$^+$ − OTf, 0.83), 1136 (M$^+$ − OTf, 1), 981 (2), 874 (57), 719 (52), 642 (12), 455 (80), 378 (100); IR (KBr) 3060, 2900, 2160, (C≡C), 1585, 1570, 1480, 1435, 1270, 1220, 1150, 1095, 1030, 745, 695, 635 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.81 (m, 3, Me), 1.26 (s, 3, Me), 6.95–7.60 (m, 50); ^{31}P NMR δ 16.4 (d, J_{P-P} = 21.60, J_{Pt-P} = 2975 Hz), 14.6 (t, J_{P-P} = 21.60, J_{Pt-P} = 1906 Hz); ^{13}C NMR (CDCl$_3$) δ 25.2, 28.1 (Me), 94.6, 98.0 (C≡C), 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$), 124.5, 127.3, 127.8, 128.0, 128.2, 129.1, 130.2, 130.5, 130.6, 130.9, 134.1, 134.5, 147.2; ^{19}F NMR δ −77.62.

σ-Butatrienyl Complex 7a. Reaction of triflate **2** (100 mg, 0.28 mmol) with **5** (200 mg, 0.16 mmol) for 30 min at room temperature gave 154 mg (72%) of **7a** as a pale yellow solid: mp 180–182 °C dec; MS *m/e* 1185 (MH$^+$ − OTf, 30), 1184 (M$^+$ − OTf, 34), 981 (5), 922 (100), 719 (64), 642 (23), 456 (60), 378 (73); IR (KBr) 3050, 1586, 1578, 1565, 1430, 1265, 1220, 1140, 1090, 1025, 737, 690, 630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.96 (m, J_{P-H} = 8.6, J_{Pt-H} = 53 Hz, 1, C=CH), 7.0–7.68 (m, 55); ^{31}P NMR δ 15.92 (d, J_{P-P} = 21.30, J_{Pt-P} = 2835 Hz), 15.25 (t, J_{P-P} = 21.30, J_{Pt-P} = 2149 Hz); ^{13}C NMR (CDCl$_3$) δ 119.1 (α-butatriene C), 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$), 126.9, 127.6, 127.9, 128.4, 128.6, 129.3, 131.0, 131.2, 131.3, 131.8, 134.1, 134.2, 134.4, 139.8, 140.2, 157.5 (C$_{sp}$), 167.8 (C$_{sp}$); ^{19}F NMR δ −77.58.

Reaction of 3E with 5. A solution of **3E** (100 mg, 0.35 mmol) and **5** (200 mg, 0.16 mmol) in degassed benzene (10 mL) was stirred at room temperature for 3 h under an argon atmosphere. The solvent was removed on a rotary evaporator and the residue washed with petroleum ether and dried under vacuum to give 170 mg (84%) of a pale yellow solid. Careful integration of the ^{1}H and ^{31}P NMR spectra showed a 75:25 mixture of **9E** and **9Z**. All spectra were obtained on the mixture (as they could not be separated by chromatography, HPLC, or crystallization). However, since the isomer ratio was 3:1, the signals in the ^{1}H, ^{13}C, and ^{31}P NMR are reported for the individual isomers: IR (KBr, mixture), 3050, 2095 (C≡C), 835 (SiMe$_3$), 1255, 630 (OSO$_2$CF$_3$). For major isomer **9E**: ^{1}H NMR (CDCl$_3$) δ 0.2 (s, 9, SiMe$_3$), 0.59 (m, J_{H-H} = 6.2 Hz, 3, Me), 4.96 (m, J_{H-H} = 6.2, J_{P-H} = 8.6, J_{Pt-H} = 56 Hz, 1, C=CH), 7.02–7.50 (m, PPh$_3$); ^{31}P NMR δ 18.27 (d, J_{P-P} = 21.50, J_{Pt-P} = 2943 Hz), 17.32 (t, J_{P-P} = 21.50, J_{Pt-P} = 1954 Hz); ^{13}C NMR (CDCl$_3$) δ 0.44 (SiMe$_3$), 19.65 (s, Me), 104.80, 107.30 (C≡C), 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$) 128.1, 129.2, 130.9, 134.1, 134.5, 144.5; ^{19}F NMR (mixture) δ −77.62. For minor isomer **9Z**: ^{1}H NMR (CDCl$_3$) δ 0.1 (s, 9, SiMe$_3$), 1.07 (m, J_{H-H} = 7.6 Hz, 3, Me), 5.74 (m, J_{H-H} = 7.6, J_{P-H} = 17.2, J_{Pt-H} = 85 Hz, 1, C=CH), 7.0–7.53 (m, PPh$_3$); ^{31}P NMR δ 16.10 (d, J_{P-P} = 20.25, J_{Pt-P} = 2918 Hz), 1490 (t, J_{P-P} = 20.25, J_{Pt-P} = 1910 Hz); ^{13}C NMR (CDCl$_3$) δ 0.51 (SiMe$_3$), 21.86 (Me), 96.2, 111.67 (C≡C), 121.0, 128.0, 129.2, 131.0, 134.0, 134.7, 142.5. Analysis of the excess unreacted starting triflate **3E** by analytical GC on a 0.125 in. × 6 ft 10% UCW-982 on 80/100 Chromosorb W column at 130 °C indicated no isomerization.

Reaction of 3Z with 5. A solution of **3Z** (100 mg, 0.35 mmol) and **5** (200 mg, 0.16 mmol) in degassed benzene (10 mL) was stirred at room temperature for 3 h under argon. The solvent was removed on a rotary evaporator and the residue washed with petroleum ether and dried under vacuum to give 167 mg (82%) of a pale yellow solid. ^{1}H, ^{31}P, and ^{13}C NMR all indicated a mixture of 94:6 of **9E**/**9Z** (by integration of the ^{1}H and ^{31}P NMR) with the *major isomer* (**9E**) being *identical* with the major isomer from the reaction of pure triflate **3E**. The spectral properties have been reported above. GC analysis of the unreacted starting triflate **3Z** as above indicated no isomerization. Heating this or the above mixture of isomers in benzene did not change the respective isomer ratios of products **9E**/**9Z** resulting from the pure starting individual triflates **3E** or **3Z**. However, carrying out the reaction itself at 40 °C (i.e. predissolving **5** at 40 °C and then adding **3**) gave slightly different product ratios, from **3E**, **9E**/**9Z** = 57:43, and from **3Z**, **9E**/**9Z** = 91:9, for reaction at 40 °C for 45 min.

Reaction of 4E (4F) with 5. Reaction of **4F** (fraction 1 from HPLC, **4E**, see text) (70 mg, 0.24 mmol) with **5** (150 mg, 0.12 mmol) for 30 min at room temperature gave 125 mg (82%) of product consisting of a 98:2 mixture of (*Z*)-**7b** and (*E*)-**7b**. For (*Z*)-**7b**: IR (KBr) 3050, 2060 (C=C=C=C), 1265, 630 (OSO$_2$CF$_3$) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.85 (s, 3, Me), 5.60 (m, J_{P-H} = 8.90, J_{Pt-H} = 53 Hz, =C=CH), 6.95–7.75 (m, 50): ^{31}P NMR δ 15.82 (d, J_{P-P} = 19.9, J_{Pt-P} = 2873 Hz), 15.36 (t, J_{P-P} = 19.9, J_{Pt-P} = 2153 Hz); ^{13}C NMR (CDCl$_3$) δ 21.7 (d, J_{CP} = 2.7, J_{Pt-C} = 23 Hz, Me), 112.7, 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$), 125.3, 127.1, 128.4, 130.0, 131.0, 131.1, 131.4, 134.2, 140.0, 158.2, 165.3 (C$_{sp}$); ^{19}F NMR δ −77.58.

Reaction of 4Z (4S) with 5. Reaction of **4S** (fraction 2 from HPLC, **4Z**, see text) (70 mg, 0.24 mmol) with **5** (150 mg, 0.12 mmol) for 30 min at room temperature gave 130 mg (85%) of pure (*E*)-**7b**: IR (KBr) 3055, 2055 (C=C=C=C), 1270, 635 (OSO$_2$CF$_3$); ^{1}H NMR (CDCl$_3$) δ 2.22 (3, Me), 5.75 (m, J_{P-H} = 8.5, J_{Pt-H} = 58 Hz, 1, =C=CH), 6.97–7.57 (m, 50); ^{31}P NMR δ 17.02 (d, J_{P-P} = 18, J_{Pt-P} = 2839 Hz), 15.80 (t, J_{P-P} = 18, J_{Pt-P} = 2125 Hz); ^{13}C NMR (CDCl$_3$) δ 21.5 (d, J_{CP} = 4.3, J_{Pt-C} = 25 Hz, Me) 111.6, 121.0 (q, J_{CF} = 320 Hz, OSO$_2$CF$_3$), 125.8, 126.8, 128.3, 130.0, 130.9, 131.0, 131.1, 134.2, 139.6, 159.3, 163.6 (C$_{sp}$); ^{19}F NMR δ −77.58.

Acknowledgment. Financial support by the NSF (CHE-8802622) is gratefully acknowledged. We wish to thank Johnson Matthey for a generous loan of K$_2$PtCl$_4$. P.J.S. thanks Drs. Z. Majerski (Institute Ruder Boskovič) and Dr. Sunko (University of Zagreb) for their kind hospitality as a Fulbright-Hayes Scholar.

Registry No. **1a**, 71451-07-5; **1b**, 100109-00-0; **1c**, 71451-04-2; **1d**, 75700-32-2; **1e**, 100108-99-4; **2**, 71451-08-6; **3E**, 119072-32-1; **3Z**, 119072-33-2; **4E**, 119072-34-3; **4Z**, 119072-35-4; **5**, 14221-02-4; **6a**, 119109-33-0; **6b**, 119109-35-2; **6c**, 119109-37-4; **d**, 119109-39-6; **6e**, 119109-41-0; **7a**, 119109-43-2; **7b**, isomer 1, 119109-47-6; **7b**, isomer 2, 119237-77-3; **8E**, 106211-71-6; **8Z**, 106211-72-7; **9E**, 119109-45-4; **9Z**, 119237-75-1; K$_2$PtCl$_4$, 10025-99-7; 1-(trimethylsilyl)pentyn-3-one, 18387-58-1.