On the Mechanism of the Metal Mediated Vinylic Cross Coupling Reactions. 1. Oxidative Addition: The Reaction of Vinyl Triflates with Zerovalent Platinum. Kinetics, Stereochemistry, and Molecular Structure

Peter J. Stang,* Mark H. Kowalski,[1] Melvyn D. Schiavelli,[2] and Desmond Longford[2]

Contribution from the Departments of Chemistry, The University of Utah, Salt Lake City, Utah 84112, and The College of William and Mary, Williamsburg, Virginia 23185. Received September 23, 1988

Abstract: The oxidative addition reaction of alkylvinyl triflates with $(Ph_3P)_4Pt$ and $(Ph_3P)_2Pt(C_2H_4)$ was investigated as a prototypical example of the first step of the Ni triad metal mediated vinylic cross coupling reactions. Kinetic, stereochemical, and variable temperature NMR experiments were carried out to establish the involvement of π-alkene complexes in these reactions. The proposed mechanism involves rate-determining formation of a π-alkene Pt complex, followed by rapid rearrangement to a σ-vinyl triflato-Pt(II) complex, and then addition of PPh_3 to yield a σ-vinyl cationic Pt(II) complex. Both σ-vinyl complexes were isolated and fully characterized, as stable crystalline species. A single crystal molecular structure determination is reported for the σ-(*trans*-2-butenyl)tris(triphenylphosphine)platinum(II) triflate complex.

Aliphatic conjugated dienes and enynes, *with stereodefined olefin geometries*, are among the most important aliphatic organic molecules known.[3-5] Because of the difficulty and nonspecificity of nucleophilic vinylic substitution (S_NV) reactions[6] few synthetic methods are available for the direct formation of carbon–carbon bonds between unsaturated units. Recently, a variety of metal mediated vinylic cross coupling reactions[7-10] have been developed that allow the ready formation, generally under mild conditions, of these desirable molecules and synthetic building blocks.

With the exception of the early Cu-promoted couplings[11] the great majority of these reactions employ the Nickel triad metals (Ni, Pd, Pt) and in particular Ni(0) and Pd(0) as the catalysts.[7-10] Until recently the electrophiles employed were vinyl halides,[7-10] whereas the nucleophiles consist of a wide variety of vinyl and alkynyl organometallic species such as Negishi's[12,13] alkenyl-zirconium and alkenylalanes, Suzuki's[14] vinylboranes, and Stille's[15] vinyl- and alkynylstannanes. Most recently vinyl triflates[16] have emerged as premier cross coupling partners.[17,18]

The gross features of the mechanism of these cross coupling reactions, as illustrated for an enol triflate and organostannane in Figure 1A[19] and generalized in Figure 1B, are understood.[3-5] Oxidative addition of substrate one ($S_1 \equiv$ electrophile) to the coordinatively unsaturated metal system results in complex I. Transmetalation by substrate two (S_2) in the form of a nucleophilic organometallic species results in the templated complex II. Subsequent, reductive elimination of complex II forms the coupled product S_1–S_2, regenerating the catalyst for the next cycle.

Most of the mechanistic insights into cross coupling processes are the result of early investigations on systems where at least one of the carbon ligands is a saturated sp^3-hybridized carbon group such as a benzyl, methyl, or alkyl.[20-22] Little is known about the details of cross coupling reactions where *both* partners are unsaturated (i.e., sp^2 or sp) carbon units[13,18,23] with virtually no information at all on enol triflates as coupling partners.[17,18] Hence it is the purpose of the current study, reported in this (oxidative addition) and the following (reductive elimination) paper,[24] to isolate the key intermediates and examine their formation and subsequent reductive elimination, with reference to metal mediated vinylic cross coupling reactions involving two *unsaturated* (sp^2- or sp-hybridized) carbon groups in general and enol triflates in particular.

Results and Discussion

One of our main objectives was to isolate and fully characterize key intermediates, therefore all reactions were carried out stoichiometrically. Moreover, we chose to examine the reactions of platinum rather than the much more reactive (and hence catalytically more active and desirable) nickel and palladium systems based upon the known[25] greater stability and kinetic unreactivity of platinum σ-carbon bonded compounds when compared to their

(1) Abstracted in part from Kowalski, M. H. Ph.D. Dissertation, The University of Utah, 1988.

(2) College of William and Mary.

(3) Nogradi, M. *Stereoselective Synthesis*; VCH Verlag: Weinheim, Federal Republic of Germany, 1986.

(4) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.

(5) *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981.

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

(7) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

(8) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

(9) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985.

(10) 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.

(11) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980. Posner, G. H. *Org. React.* **1975**, *22*, 253.

(12) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

(13) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.

(14) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178.

(15) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

(16) Stang, P. J.; Hanack, H.; Subramanian, L. R. *Synthesis* **1982**, 85.

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

(18) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

(19) Taken from ref 18, Scheme V.

(20) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360.

(21) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981, 4992.

(22) Ozawa, F.; Fujiomi, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144.

(23) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181. Negishi, E.; Akiyoshi, K.; Takahashi, T. *Chem. Commun.* **1987**, 477.

(24) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, following paper in this issue.

(25) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 471.
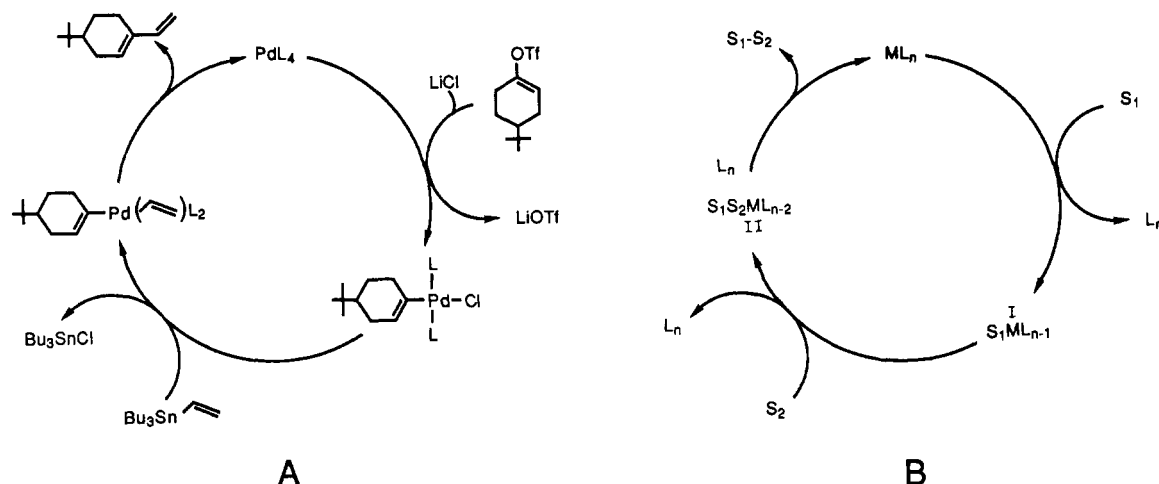
Figure 1. Mechanism for metal-catalyzed cross couplings: A,[19] for an enol triflate and organostannane; B, generalized.

palladium and nickel analogues.

Interaction of 3 equiv of vinyl triflates 1–4 with $Pt(PPh_3)_4$ in toluene at room temperature yields stable, crystalline $tris(PPh_3)Pt^{II}$ cations, 6–9, in 79–97% isolated yields (eq 1). The reaction of
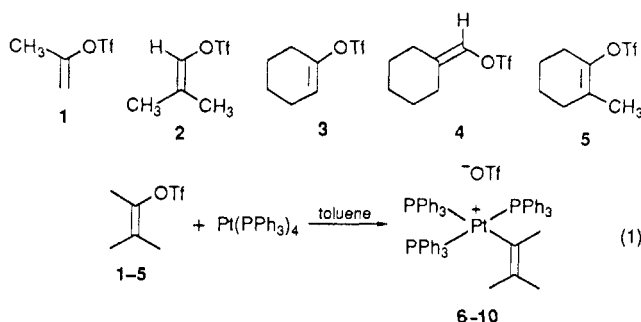
triflate 5 with $Pt(PPh_3)_4$ at 80° for 5 h gave 10 in 85% yield. The complexes can be isolated essentially pure as precipitated microcrystalline solids from the reaction flask and can be recrystallized from warm toluene/hexanes or CH_2Cl_2/Et_2O. Complexes 6–10 are stable crystalline, pale yellow, or colorless compounds. The complexes have been characterized by microanalysis, IR, NMR (^1H, ^{19}F, ^{31}P, ^{13}C), fast atom bombardment (FAB) mass spectroscopy, and conductance measurements.[26]

The IR spectra clearly establish the existence of an ionic triflate group in the solid state (KBr). Absorptions at 635 and 1270 cm^{-1} are assigned to the asymmetric stretch of the sulfonyl[27] and are distinguished from covalent triflates (absorptions at 645, 1215, and 1421 cm^{-1}) such as the organic vinyl triflate precursors. The vinyl double bond stretching frequency is too weak to be observed.

NMR spectra of compounds 6–10 are very complicated due to the abundance of NMR active nuclei present in the system: ^1H, ^{31}P, ^{195}Pt, and ^{19}F. ^{19}F spectra are the simplest; they are all singlets at −77.4 ppm (ref $CFCl_3$) in CD_3NO_2. The ionic triflate complexes in this study are shifted about 4 ppm upfield compared to the covalent triflate starting materials.

The ^{31}P NMR spectra display an A_2X splitting pattern, establishing the presence of two different PPh_3, with corresponding ^{195}Pt satellites.[28]

^{13}C NMR spectra are further complicated since the vinyl and aromatic carbons are coupled to both ^{31}P (two chemically different phosphorus atoms) and ^{195}Pt leading to complex resonances and significantly reduced signal-to-noise. Again, as in the ^{31}P spectra two different PPh_3 attached to Pt are indicated. The ipso, meta, and ortho carbons of the mutually trans PPh_3 appear as triplets due to virtual coupling.[29] The ipso, meta, and ortho carbons of

the PPh_3 trans to the vinyl group appear as doublets due to coupling to the single phosphorus of the trans PPh_3. All alkyl carbons of the vinyl groups are resolved; however, the β carbons of the σ-vinyl groups in complexes 8 and 10 are obscured by the aromatic resonances of the PPh_3. Likewise, the α carbons of complexes 7 and 9 are obscured by the aromatic resonances.

FAB mass spectra were very useful in confirming the structures of these cationic complexes.[30] Relative molecular masses are confirmed, and isotope patterns resulting from polyisotopic platinum are consistent with predictions. The molecular ions appear at m/z values corresponding to M^+ for the cation, not MH^+. The spectra show small intensities at $[M - vinyl]^+$. Other than the molecular cation the base peak, $[M - PPh_3]^+$, is key to confirming the presence of the σ-vinyl ligand. Conductance data obtained in CH_3NO_2 are indicative of 1:1 electrolytes. A final, unambiguous structure assignment, along with key structural features, are based upon a single-crystal X-ray determination (vide infra).

Cationic complexes 6–10 are of a unique structural type due to the lack of coordination of the triflate anion, with few analogous complexes known. Meek and Pidcock independently prepared the methyl fluorosulfonate derivative in the reaction of CH_3OSO_2F with $Pt(PPh_3)_3$.[31] The reactions of strong inorganic acids with Pt(0) phosphine complexes yield the analogous Pt(II) cationic hydrides.[32a] Substitution chemistry of various Pt(II) complexes and reactions of Pt(II) halides with silver salts in the presence of phosphines can also lead to Pt(II) tris(phosphine) cations.[32b,c] The interaction of vinyl triflates with $(Ph_3P)_4Pt$ amounts to a single-site addition of a "vinyl cation"[33] to Pt(0) yielding a stable σ-vinyl cation complex.

Having achieved our first objective of isolating the oxidative addition product (Figure 1 and complex I) between a vinyl substrate and a zerovalent d^{10} nickel triad metal species (Pt(0)) we decided to (a) examine the mechanism of formation of I and (b) carry out a single-crystal X-ray structure determination of the oxidative addition product.

Mechanistic Considerations. Oxidative additions to low-valent group eight transition-metal complexes are usually considered to

(26) For a preliminary report of part of this work, see: Kowalski, M. H.; Stang, P. J. *Organometallics* **1986**, *5*, 2392.

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

(28) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266.

(29) Davies, J. In *The Chemistry of the Metal–Carbon Bond*: Hartley, F. R., Patai, S., Eds.; Wiley: London, 1982; Vol. 1, Chapter 21. Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.
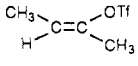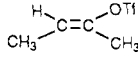
(30) Kowalski, M. H.; Sharp, T. S.; Stang, P. J. *Org. Mass. Spectrom.* **1987**, *22*, 642.

(31) (a) Eaborn, C.; Farrell, N.; Murphy, J. L.; Pidcock, A. *J. Organometl. Chem.* **1973**, *55*, C68. (b) Eaborn, C.; Farrell, N.; Murphy, J. L.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1976**, 58. (c) Peterson, J. L.; Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 8195.

(32) (a) Cariati, F.; Ugo, R.; Bonati, F. *Inorg. Chem.* **1966**, *5*, 1128. (b) Church, M. J.; Mays, M. J. *J. Chem. Soc. A* **1968**, 3074. (c) Pregosin, P. S.; Favez, R.; Roulet, R.; Boschi, T.; Michelin, R. A.; Ros, R. *Inorg. Chim. Acta* **1980**, *45*, L7.

(33) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. In *Vinyl Cations*; Academic Press: New York, 1979.

Table I. Rate Constants and Activation Parameters for the Reaction of Vinyl Triflates with $(Ph_3P)_4Pt$

compound	temperatures,[a] °C	k,[b] M^{-1} s^{-1}	n^c	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$(CH_3)_2C{=}C(OTf)CH_3$, **12**	25.0	0.0028 ± 0.0001	2	0.01	18.3	−8.9
	55.0	0.0645	1			
	60.0	0.066 ± 0.007	6			
	70.0	0.19 ± 0.05	4			
$(Et)_2C{=}CHOTf$	25.0^d	0.126		0.45	10.1	−29.1
	10.7	0.050 ± 0.006	2			
	11.5	0.054 ± 0.003	2			
	25.6	0.135 ± 0.02	4			
	30.6	0.164 ± 0.004	4			
11Z	25.0^d	0.257		0.91	16.9	−4.8
	15.0	0.0955 ± 0.007	2			
	20.0	0.163 ± 0.011	3			
	25.1	0.251 ± 0.03	2			
	26.2	0.265 ± 0.01	4			
	30.0	0.396 ± 0.02	3			
	35.0	0.738	1			
11E	25.0^d	0.372		1.32	17.1	−3.3
	14.9	0.130 ± 0.004	3			
	20.0	0.227	1			
	25.2	0.374 ± 0.008	3			
	30.0	0.620 ± 0.04	3			
	35.3	0.984 ± 0.08	2			
	40.0	1.57	1			
3	25.0^d	0.282		1.00	16.7	−5.2
	11.5	0.070 ± 0.01	10			
	16.3	0.12 ± 0.02	4			
	18.1	0.15 ± 0.005	2			
	25.6	0.28 ± 0.01	7			
$(CH_3)_2C{=}CHOTf$, **2**	25.0^d	0.331		1.17	18.4	0.9
	8.5	0.048 ± 0.001	2			
	11.5	0.080 ± 0.01	8			
	20.0	0.190 ± 0.003	2			
	21.1	0.21 ± 0.06	9			
	25.3	0.36 ± 0.03	10			
	27.9	0.44 ± 0.02	2			
$CH_2{=}C(OTf)CH_3$, **1**	25.0^d	7.4		26.2	11.5	−16.3
	3.0	1.50	1			
	5.0	1.89 ± 0.03	2			
	15.0	3.25	1			
	16.0	4.07	1			
CH_3I^e	25.0	0.0013		0.02		

[a] Temperature controlled to ±0.5 °C. [b] Average of runs. [c] Number of runs. [d] Calculated value. [e] From ref 36.

occur by one of four main processes:[7] (a) single electron transfer (SET); (b) three-centered concerted additions; (c) free-radical pathways; and (d) nucleophilic substitutions. SET processes are generally observed only with alkyl halides. There are no known SET processes with sulfonate esters[34] and triflates[35] in particular, and hence they are extremely unlikely in this case.

To probe the details of the mechanism of reaction of alkylvinyl triflates with Pt(0) we decided on four different approaches: (a) kinetics; (b) stereochemistry; (c) variable temperature (VT) NMR studies; and (d) single-crystal molecular structure determination.

Kinetics. The disappearance of starting material $Pt(PPh_3)_4$ was measured by following its visible absorption either at 358 nm or at 410 nm under pseudo-first-order conditions (20–40 equiv of triflate).[36] The second-order rate constants were calculated from the observable rate constants and the known concentrations of the triflate in each run. The data are summarized in Table I. Also included in Table I is the rate constant for the reaction of MeI with $Pt(PPh_3)_4$, for comparison.[36] Several observations can be made from this data. First, all the triflates except for the fully substituted 3-methyl-2-butenyl triflate (**12**) react much faster than MeI, hence there must be some rate enhancement due to the presence of the double bond on the triflate. Second, there is a definite dependence on substitution of the double bond. The

reactivity range between mono- and trisubstitution is greater than 2600. Whereas, all the disubstituted triflates, regardless of the exact substitution pattern, react at comparable rates (0.25–0.40, M^{-1} s^{-1}). Clearly, the rates of these reactions are highly dependent upon the steric environment of the vinyl triflate. For example, the *cis*-2-butenyl triflate reacts faster than the trans isomer. Likewise $Me_2C{=}CHOTf$ reacts faster than the more hindered $Et_2C{=}CHOTf$.

Stereochemistry. In order to examine the stereochemical course of the reaction triflates **13E** and **13Z** ((*E*)- and (*Z*)-2-phenyl-propenyl triflates) and **11E** and **11Z** ((*E*)- and (*Z*)-2-butenyl triflates) were prepared. Triflates **13E** and **13Z** were obtained as an 85:15 mixture, respectively, from *d,l*-2-phenylpropion-aldehyde and separated with HPLC. The stereochemistry of each was determined by comparison to previous work and confirmed by comparing the $^3J_{CH}$ coupling constants.[37,38] Triflates **11E** and **11Z** were prepared by HOTf addition to 2-butyne as a 35:65 (*E:Z*) mixture and separated by preparative GC.

The individual isomeric triflates **13E** and **13Z** were reacted overnight, with $Pt(PPh_3)_4$ in toluene, and the resulting product mixtures[39] were directly assayed by both ^1H and ^{31}P NMR in CD_3NO_2. The platinum oxidative addition products, **14E** and **14Z**, were found to be greater than 99% stereochemically pure by ^1H NMR (Scheme I). By using a similar procedure the reactions

(34) Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. Collman, J. P.; Finche, R. F.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.
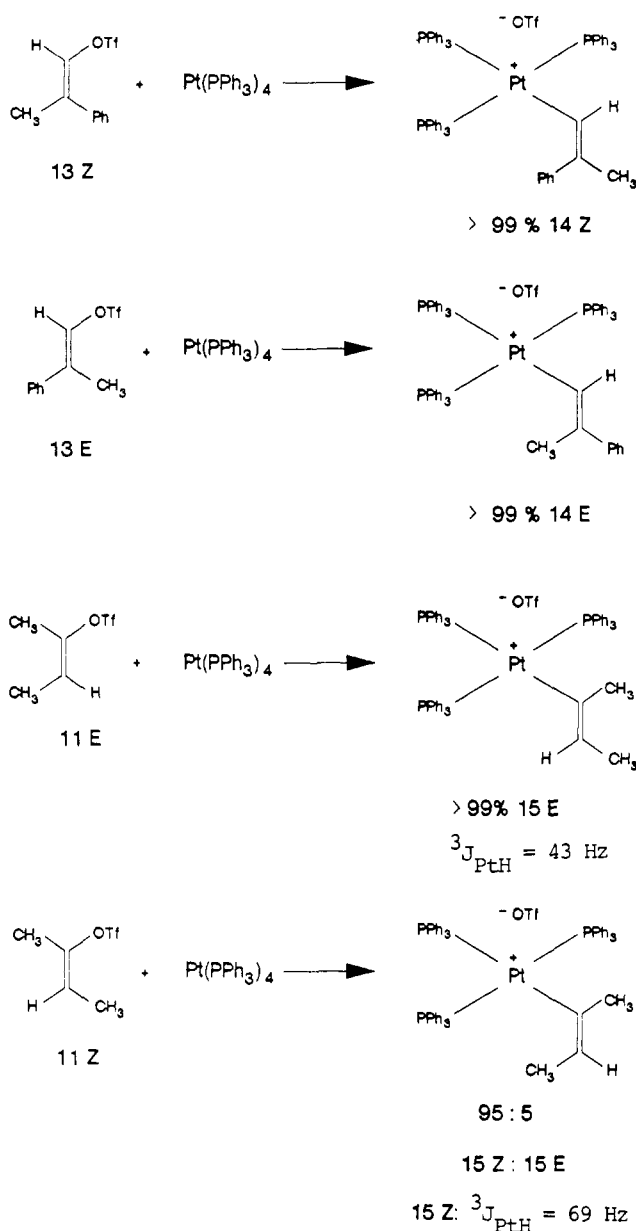
(35) Vinyl triflates have extremely high oxidation and reduction potentials as determined by recent microelectrochemical methods (to be published).

(36) Pearson, R. G.; Rajaram, J. *Inorg. Chem.* **1974**, *13*, 246. Franks, S.; Hartley, F. R. *Inorg. Chim. Acta* **1981**, *49*, 227.

(37) Kingsbury, C. A.; Draney, D.; Sopchik, A.; Rissler, W.; Durham, D. *J. Org. Chem.* **1976**, *41*, 3863.

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

(39) Besides the expected adducts no other products or impurities were detected. All analyses were carried out on the original reaction mixture prior to any workup.

Scheme I. Stereochemistry of Reaction of Vinyl Triflates **11** and **13** with (Ph₃P)₄Pt

13 Z

> 99 % **14 Z**

13 E

> 99 % **14 E**

11 E

>99% **15 E**

$$^3J_{PtH} = 43 \text{ Hz}$$

11 Z

95 : 5

15 Z : 15 E

15 Z: $^3J_{PtH} = 69$ Hz

of triflates **11E** and **11Z** with Pt(PPh₃)₄ were performed. Again, both of the reaction mixtures[39] were analyzed for stereochemical purity with ¹H NMR and ³¹P NMR in CD₃NO₂. The reaction of **11E** with Pt(PPh₃)₄ gave oxidative addition product **15E** in greater than 99% stereochemical purity, and reaction of **11Z** with Pt(PPh₃)₄ gave a 95:5 mixture of **15Z** and **15E** (Scheme I). Analysis of the supernatant toluene for unreacted triflate using ¹⁹F NMR found a resonance corresponding to only unreacted **11Z**. The two isomeric triflates are easily distinguished: their ¹⁹F NMR chemical shifts are 0.8 ppm apart. Therefore, under the conditions of the experiment, there is no isomerization of **11Z** to **11E**.

There was at this point little doubt that the reaction was stereospecific with retention of double bond geometry. However, firm proof of the stereochemistry of the resultant complexes was clearly necessary. Confirmation of olefin geometry came from the ¹H NMR spectra of the crude products. In analogy to $^3J_{HH}$ alkene coupling constants, trans $^3J_{PtH}$ are always greater than cis $^3J_{PtH}$ between isomers of platinum vinyl complexes with β-vinyl protons.[40] The observed values for the stereoisomeric adducts

15 were **15E**, $^3J_{PtH} = 43$ Hz, and **15Z**, $^3J_{PtH} = 69$ Hz. The coupling constant arguments for stereochemical assignments were further confirmed by X-ray analysis (vide infra). The small amount of stereorandomization in the reaction of **11Z** with (Ph₃P)₄Pt might be due to β-hydride elimination, with formation of (Ph₃P)₃Pt⁺H and 2-butyne, followed by readdition of the platinum hydride to the alkyne. This hypothesis is supported by the fact that only in the reaction of **11Z**, where the β-hydrogen and Pt are in the proper anti orientation for elimination, was a small amount of randomization observed.

Both the kinetic and stereochemical results rule out a free-radical process as such a mechanism would most likely result in stereorandomization. Moreover, the more substituted triflate resulting in the more stable radical should have reacted faster, contrary to observations. A concerted three-centered process is also extremely unlikely as such processes are usually only observed with homonuclear substrates[41] such as O₂ and H₂, and although there are a few known[42] examples with alkyl halides there are none known with triflates.

A direct in-plane S$_N$2-like nucleophilic attack is also ruled out by (i) the extremely high energy required for such a process,[43] and (ii) it requires inversion of alkene geometry that is contrary to observations. A nucleophilic vinylic substitution (S$_N$V)[6] by an addition–elimination process, although consistent with the observed stereospecificity of the reaction, is also unlikely. Such processes only occur with "activated" substrates, and, with the exception[38] of the reaction of the super nucleophilic [Co(dmgH)₂py]⁻ anion, there are no known examples of *simple alkylvinyl* substrates reacting by such a mechanism.[6] Moreover, simple alkylvinyl triflates do not react[38] at carbon with ordinary nucleophiles more powerful than (Ph₃P)₄Pt such as PhS⁻.

The most likely mechanism for the oxidative addition reaction of vinyl substrates with the Ni triad zerovalent metals is π-complex formation between substrate and catalyst. Such a mechanism has been widely proposed for the oxidative addition of unsaturated (vinyl, aryl, acetylenic) substrates to Ni(0), Pd(0), and Pt(0), but little *direct* evidence has been provided for the existence of these π-complexes.[7,44] Hence, we set out to establish the involvement of such π-alkene complexes in the oxidative addition of vinyl triflates.

Attempts To Isolate a π-Complex. Since it was very likely that the reactive intermediate species in these reactions is the "-(PPh₃)₂Pt" fragment (**16**), the ethylene π complex (PPh₃)₂Pt-(C₂H₄) (**17**) was reacted with 2-propenyl triflate (**1**) in hopes of isolating the π complex of the vinyl triflate. Reaction of 1.1 equiv of **1** with **17** in toluene at room temperature gives within a few minutes a white microcrystalline precipitate. The solid was isolated in 84% yield based on starting platinum, assuming a 1:1 platinum–triflate complex. However, rather than the π complex, the isolated product was instead a new oxidative addition product, **18**, with coordination of the triflate (eq 2). Complex **18** is a stable

$$\text{(2)}$$

1   **18**
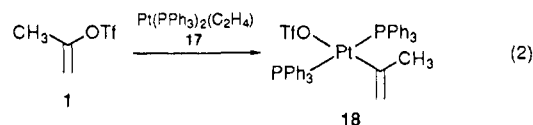
microcrystalline compound that can be recrystallized from CH₂Cl₂/Et₂O or CH₂Cl₂/hexanes solutions to yield colorless rods. Suitable X-ray quality crystals were grown, but were twinned and therefore not usable. The complex is sensitive to moisture in solution as bubbling wet argon through a CDCl₃ solution of **18** led to broad resonances in the ¹H NMR presumably due to rapid H₂O/triflate exchange.

(40) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961.

(41) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.
(42) Wong, P. K.; Stille, J. K. *J. Organomet. Chem.* **1974**, *70*, 212. Lau, K. S. Y.; Becker, Y.; Baenziger, N.; Huang, F.; Stille, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 5664 and references therein.
(43) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1953.
(44) Stille, J. K. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: London, 1985; Vol. 2, Chapter 9, pp 625–787, and references therein.

Scheme II. Stereochemistry of Reaction of Vinyl Triflates **11** with $(Ph_3P)_2Pt(C_2H_4)$

> 99% **19E**

$^3J_{PtH} = 87$ Hz

15E

> 99% E

95 : 5

19Z:19E

15Z

95 : 5

Z : E

19Z: $^3J_{PtH} = 132$ Hz
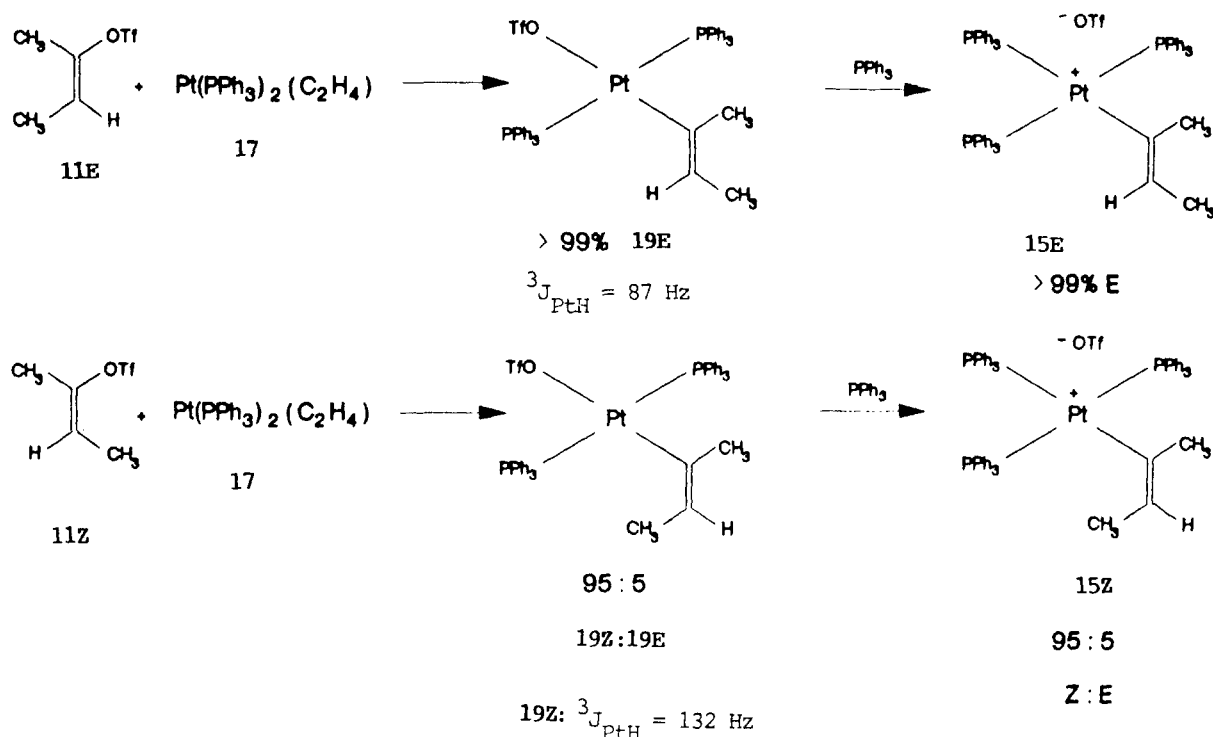
The IR data distinguish **18** from the purely ionic triflate complexes: there are triflate resonances (CF_3 and SO_2) at 1313, 1200, 1091, and 620 cm^{-1}. The NMR data are straightforward with trans stereochemistry clearly established. The propenyl resonances in the ^1H NMR are broad pseudotriplets due to ^{195}Pt satellites. The ^{31}P NMR is a singlet with satellites. The ^{13}C NMR confirms the geometry around platinum, and all resonances are accounted for. The key vinyl resonances are found at δ 28.8 (CH_3), δ 114.3 (β-vinyl), and δ 135.2 (α-vinyl).

Since the attempt to isolate the triflate π-olefin complex led to insertion product **18**, the chance to test the stereochemical course of this reaction also existed; hence, the reactions with stereoisomers **11E** and **11Z** and $Pt(PPh_3)(C_2H_4)$ were carried out. In each reaction the products **19E** and **19Z** were easily distinguished by ^1H NMR; the ^{31}P NMR signals of each product were coincident at 27.5 ppm. Reaction of **11E** with **17** yields complex **19E** with greater than 99% retention of double bond geometry according to ^1H NMR (Scheme II). The reaction of **11E** with **17** yields a mixture of **19Z** and **19E** with a 95:5 ratio according to ^1H NMR (Scheme II), the same ratio as found in the reaction of **11Z** with $Pt(PPh_3)_4$ to yield **15Z** and **15E** (Scheme I). The reaction of **19E** with PPh_3 in CD_2Cl_2 yields **15E** quantitatively. The reaction of the 95:5 mixture of **19Z** and **19E** with PPh_3 gave a 95:5 mixture of **15Z** and **15E** without any isomerization of the vinyl ligands (Scheme II). Just as with the complexes **15E** and **15Z**, the $^3J_{PtH}$ coupling constants were used to assign the stereochemistry of the resultant compounds (for **19E** $^3J_{PtH} = 87$ Hz and for **19Z** $^3J_{PtH} = 132$ Hz).

The origin of the stereorandomization in the reactions of **11Z** with Pt(0) is not easily explained. One possibility may be inferred from the fact that traces of triflic acid causes each pure isomer to equilibrate to a 87:13 (**19Z:19E**) mixture at 22.5 °C (eq 3). The same type of equilibrium could not be established betwen complexes **15E** and **15Z**.

$$(3)$$

19Z   87:13   **19E**
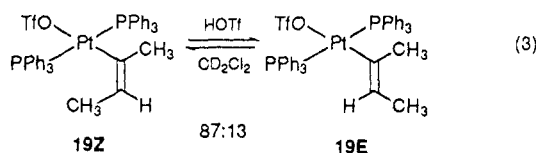
The fact that *catalytic* amounts of HOTf can create an equilibrium between **19Z** and **19E** is interesting. Reger and

co-workers have demonstrated the acid-catalyzed isomerization of σ-vinyl Fe complexes.[45] Just as the π intermediate can rearrange to **19Z**, it may also rearrange with *anti* elimination of HOTf to possibly yield the acetylene complex **20** (eq 4). This

$$(4)$$

20
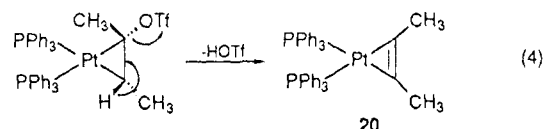
possible side reaction does not seem to be significant on a stoichiometric scale, since no evidence for formation of **20** is found in the products, but may explain the loss of stereospecificity for this *single* reaction. The presence of free HOTf in catalytic amounts could isomerize the products. In the other reactions anti elimination is not possible, and no loss of stereospecificity is found.

NMR Observation of a π-Alkene Complex. In order to possibly observe a vinyl triflate π-complex variable temperature NMR experiments were carried out on the Pt(0) system. Due to the low solubility of $Pt(PPh_3)_4$ in toluene the more soluble precursor **17** was chosen. It was hoped that the vinyl triflate would simply displace the π-ethylene and give the desired π vinyl triflate complex.

Reaction of **5** equiv of **1** with **17** at -78 °C with a stream of argon bubbling through an NMR tube for 1 h produced no new products. Warming to -63 °C with bubbling for 1 h again produced no new products. The same procedure at -40 °C produced a small amount of product resonance as a singlet at 26.5 ppm with Pt satellites, attributable to the oxidative addition product **18**. Further warming gave total conversion to **18**. Addition of 1 equiv of PPh_3 to **18** in the C_7D_8 solution at room temperature led to rapid precipitation of a white solid. The solid was dissolved by adding CD_2Cl_2 (ca. 0.3 mL). Both ^1H and ^{31}P NMR confirmed the identity of the solid to be the cationic complex **6**. Therefore, as suspected, addition of PPh_3 to **18** leads to quantitative conversion to **6** (eq 5).
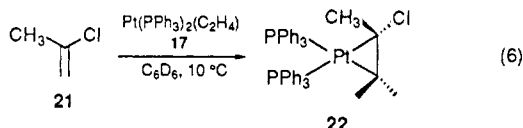
$$(5)$$

18   **6**

(45) Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305.
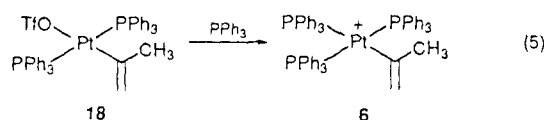
Table II. NMR Data for π-Olefin Pt Complexes **22** and **24**

compd	^{1}H NMR^a	^{31}P NMR^b	^{13}C NMR^c
22	2.06 (d, $^3J_{PH}$ = 8.0 Hz, $^3J_{PtH}$ = 48 Hz), 2.18 (m, $^2J_{PtH}$ = 62 Hz), 2.82 (m, $^2J_{PtH}$ = 62 Hz)	26.3 (d, $^2J_{PP}$ = 43 Hz, $^1J_{PtP}$ = 2982 Hz), 30.1 (d, $^2J_{PP}$ = 43 Hz, $^1J_{PtP}$ = 3910 Hz)	
24	2.18 (d, $^3J_{PH}$ = 8.0 Hz, $^2J_{PtH}$ = 48 Hz), 2.22 (m, $^2J_{PtH}$ = 62 Hz), 3.00 (m, $^2J_{PtH}$ = 62 Hz)	23.9 (d, $^2J_{PP}$ = 43 Hz, $^1J_{PtP}$ = 3013 Hz), 27.6 (d, $^2J_{PP}$ = 43 Hz, $^1J_{PtP}$ = 3893 Hz)	30.5 (br m, CH_3), 42.6 (dd, $^2J_{PC}$ = 36 Hz, $^2J_{PC}$ = 5.5 Hz β-C), 64.6 (dd, $^2J_{PC}$ = 61 Hz, $^2J_{PC}$ = 9.0 Hz α-C)

^{a} At 300 MHz. Complex **22**: in C_6D_6 ref to C_6D_5H at 7.15 ppm. Complex **24**: in C_7D_8 ref to $C_6D_5CD_2H$ at 2.09 ppm. ^{b} At 121 MHz ref to external H_3PO_4 at 0.00 ppm. ^{c} At 75 MHz ref to CD_3 resonance of C_7D_8 at 20.4 ppm.

Having failed to observe a π complex of 2-propenyl triflate, two less reactive leaving groups were tried, chloride and bromide. The only previously reported π-complexes that led to oxidative addition insertion products were those of perhalo olefins.[46] The less reactive 2-propenyl chloride (**21**) was tried first. To a solution of $(PPh_3)_2Pt(C_2H_4)$ in C_6D_6 in a NMR tube was added 30 equiv of **21** at 10 °C. A slow stream of argon was bubbled through the solution for 20 min in order to drive any liberated ethylene out of solution. The solution was kept cool so the volatile vinyl chloride would not evaporate. The reaction gave complex **22** (eq 6), and

$$CH_3\diagdown Cl \quad \xrightarrow[\text{C}_6\text{D}_6,\ 10\ °C]{\text{Pt(PPh}_3)_2(C_2H_4)} \quad \overset{CH_3}{\underset{PPh_3}{PPh_3}}\diagdown \overset{Cl}{\underset{Pt}{}} \quad (6)$$

21   **22**

both ^{1}H and ^{31}P NMR spectra (Table II) were taken of the product mixture. While the ^{1}H NMR of the mixture (Figure 2) is dominated by resonances due to free vinyl chloride, the ^{31}P NMR is clear of starting materials. Complex **22** appears as two doublets at 30.1 and 26.3 ppm with $^2J_{PP}$ = 43 Hz with satellites. The vinyl protons of **21** are shifted substantially upfield from 4.18 and 4.94 ppm (free vinyl chloride) to 2.82 and 2.18 ppm and appear as complex multiplets with satellites due to coupling to each other, the methyl of the ligand, two nonequivalent phosphorus nuclei, and ^{195}Pt. Attempts to isolate the π complex were unsuccessful and led to complex mixtures which did include both cis and trans oxidative addition insertion products. These reactions were not pursued further.

Likewise, addition of 5 equiv of **23** to a C_7D_8 solution of **17** below −20 °C in an NMR tube with argon bubbling for 1 h gives a solution of essentially pure π-vinyl bromide complex (**24**) (eq 7). Observation at −20 °C allowed ^{1}H, ^{31}P, and ^{13}C NMR spectra

$$CH_3\diagdown Br \quad \xrightarrow[\text{toluene-}d_8,\ -20\ °C]{\text{Pt(PPh}_3)_2(C_2H_4)} \quad \overset{CH_3}{\underset{PPh_3}{PPh_3}}\diagdown \overset{Br}{\underset{Pt}{}} \quad (7)$$

23   **24**
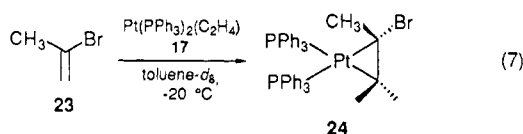
to be taken (Table I). The ^{1}H NMR shows significant upfield shifts of the vinyl protons from 5.06 and 5.15 ppm to 3.00 and 2.12 ppm as complex multiplets similar to **22**. The methyl group as in **22** is a doublet with satellites. The ^{31}P NMR of **24** shows signals due to a small amount of cis oxidative addition product but mostly π complex as two doublets at 27.6 and 23.9 ppm with $^2J_{PP}$ = 43 Hz.

The ^{13}C NMR proved much more difficult to obtain at −20 °C, but the key "vinyl" resonances are found. There is a remarkable upfield shift of the vinyl carbon signals from 137 and 117 ppm to 64.6 and 42.6 ppm. Each resonance appears as a doublet of doublets due to coupling to both *trans*- and *cis*-phosphorus nuclei. Unfortunately, the ^{195}Pt satellites are not resolved. The large upfield shift (shielding) of both the vinylic proton and the olefinic carbon signals in **24** is clearly indicative of a significant back donation by the d-electrons in Pt into the LUMO π*-orbital of the alkene. It further suggests that the structure of **22** and **24** is best represented as a platinacyclopropane-like species. Once

(46) (a) Bland, W. J.; Burgess, J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1968**, *14*, 201. (b) Bland, W. J.; Burgess, J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1968**, *15*, 217. (c) Bland, W. J.; Kemmitt, R. D. W. *J. Chem. Soc. A* **1968**, 127. (d) Green, M.; Osborn, R. B. L.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2525.

Table III. Summary of Crystallographic Data for **15Z**·$(CH_2Cl_2)_{1/2}$^{a}

mol formula	$C_{60}H_{53}P_3F_3O_3SClPt$
mol wt	1234.70
crystal system	triclinic
space group	$P\bar{1}$
cell dimensions	
a, Å	12.670 (4)
b, Å	19.928 (6)
c, Å	12.904 (4)
α, deg	80.81 (3)
β, deg	66.65 (2)
γ, deg	73.51 (2)
V, Å^3	2864.1
Z	2
d_{calcd}, g/cm^3	1.431
crystal dimensions, mm	0.22 × 0.25 × 0.30
radiation, Å	Mo Kα 0.71073
data collection method	2θ:θ
scan speed, deg/min	2.0
reflcns measd	11189, h(0,11),k(0,18),l(−20,20)
scan range	$K_{\alpha1}$ −1.0 to $K_{\alpha2}$ +1.0
total bkdg. time/scan time	0.5
no. of reflcns between std	97
total unique data	9894
obsd data, $I > 3\sigma(I)$	8024
abs. coeff, (μ), cm^{-1}	26.403
no. of variables	360
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.069
$R_w = [\sum w\|\|F_o\| - \|F_c\|\|^2/w(F_o)^2]^{1/2}$	0.075

^{a} Highest peak in the final fourier map 1.2 e/Å^3 about 0.801 Å from Pt atom.

Table IV. Selected Bond Distances for **15Z**·$(CH_2Cl_2)_{1/2}$^{a}

	distance (Å)		distance (Å)
Pt–C(2)	2.07 (1)	Pt–P(3)	2.333 (3)
Pt–P(2)	2.372 (3)	Pt–P(1)	2.376 (3)
P(1)–C(11)	1.81 (1)	P(1)–C(5)	1.84 (1)
P(1)–C(17)	1.87 (1)	P(2)–C(23)	1.82 (1)
P(2)–C(29)	1.83 (1)	P(2)–C(35)	1.84 (1)
P(3)–C(41)	1.82 (1)	P(3)–C(53)	1.83 (1)
P(3)–C(47)	1.84 (1)	C(1)–C(3)	1.43 (6)
C(2)–C(3)	1.24 (5)	C(2)–C(4)	1.61 (3)

^{a} Numbers in parentheses are estimated standard deviations in the least significant digit.

Table V. Selected Bond Angles for **15Z**·$(CH_2Cl_2)_{1/2}$^{a}

	angle (deg)		angle (deg)
C(2)–Pt–P(3)	84.7 (4)	C(2)–Pt–P(2)	175.3 (6)
C(2)–Pt–P(1)	83.0 (3)	P(3)–Pt–P(2)	96.2 (1)
P(3)–Pt–P(1)	166.82 (9)	P(2)–Pt–P(1)	96.4 (9)
C(3)–C(2)–C(4)	120.0 (24)	C(3)–C(2)–Pt	124.0 (249)
C(4)–C(2)–Pt	116.0 (13)	Pt–C(2)–C(1)	93.0 (10)
C(2)–C(3)–C(1)	123.0 (25)		

^{a} Numbers in parentheses in the columns label angle (deg) are estimated standard deviations in the least significant digits.

again the π-complex **24** could not be isolated, and the oxidative addition chemistry of the bromide was not explored further.

Single-Crystal Molecular Structure Determination. Suitable single crystals of **15Z** were grown from CH_2Cl_2/Et_2O solutions yielding colorless rods as 0.5 CH_2Cl_2 solvate. An ORTEP representation is shown in Figure 3. Crystal data (Table III), selected bond lengths (Table IV), and selected bond angles (Table V) are

Reaction of Vinyl Triflates with Zerovalent Pt

J. Am. Chem. Soc., Vol. 111, No. 9, 1989 3353
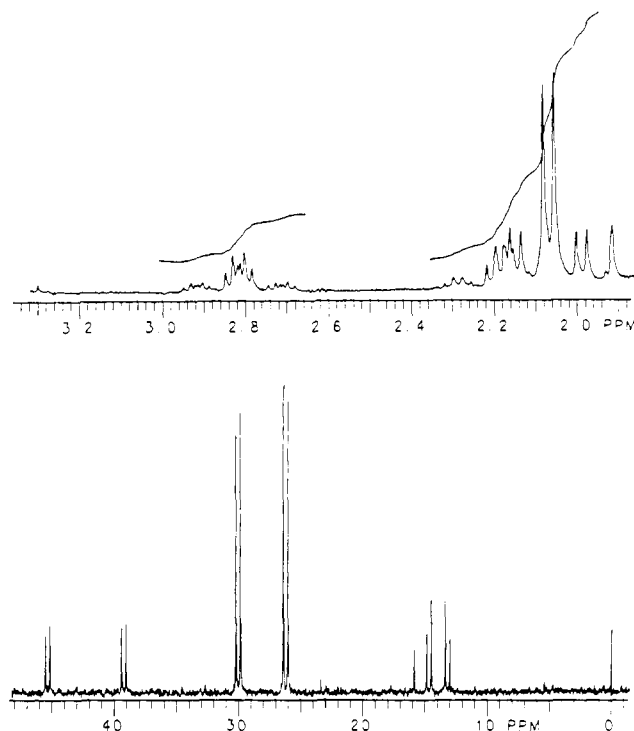
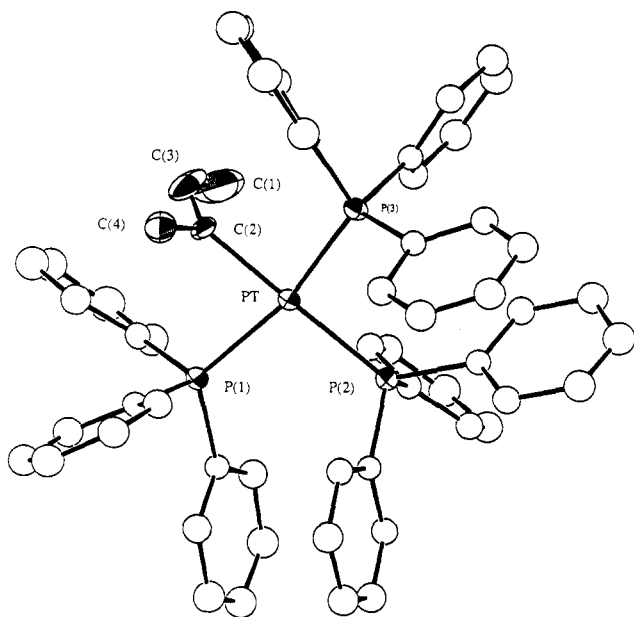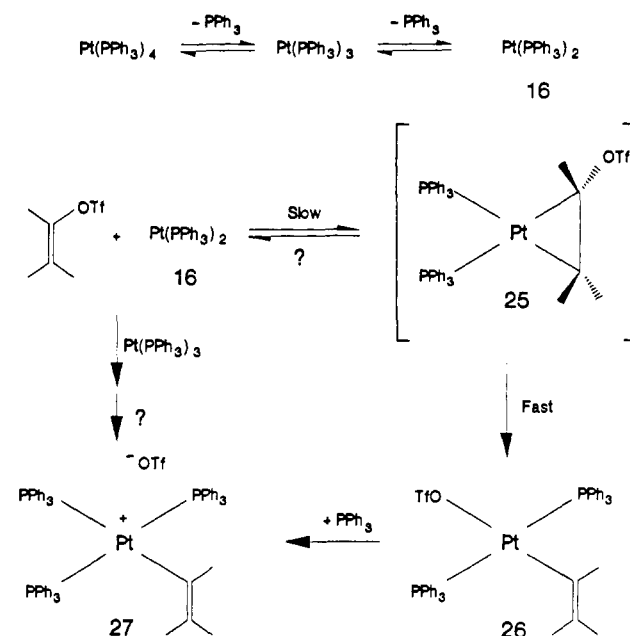**Figure 2.** ^{1}H NMR (top) and ^{31}P NMR (bottom) of π-olefin Pt complex **22**.

Figure 3. ORTEP of complex **15Z**. For clarity and disordered triflate and CH_2Cl_2 solvate are omitted.

presented. Complex **15Z** is approximately square planar. The bulky *trans*-PPh$_3$ distorts the two *cis*-PPh$_3$ toward the relatively small vinyl group so that the acute angle between P(1)–Pt–P(3) is 166.82 (9)°. The Pt–C(2) bond length of 2.07 (1) Å appears to be normal for platinum vinyl carbon bonds.[47] Angles around atom C(2) are 120 ± 4°, and the C(2)–C(3) bond length is 1.24 (5) Å. The triflate counterion is highly disordered and hence is not shown in the ORTEP.

Since to our knowledge there are no known molecular structures for any σ-vinyl cationic complexes comparable to **15Z**, it is difficult

(47) (a) Cardin, C. J.; Cardin, D. J.; Lappert, M. F. *J. Organomet. Chem.* **1973**, *60*, C70. (b) Cardin, C. J.; Muir, K. W. *J. Chem. Soc., Dalton trans.* **1977**, 1593. (c) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46. (d) Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1986**, 2315.

Scheme III. Summary of Mechanism of Oxidative Addition of Vinyl Triflates to Pt(0)

to make exact comparisons with the known[47,48] *trans*-halo(σ-vinyl)bis(triphenylphosphine)platinum(II) species. However, the broad features of the two types of complexes are similar.

Conclusions. The mechanism of oxidative addition of vinyl triflates to Pt(0) may be summarized as outlined in Scheme III. Disassociation of $(Ph_3P)_4Pt$ to $(Ph_3P)_3Pt$ and $(Ph_3)_2Pt$ is well established.[7] Rate-determining, possibly reversible, reaction of $(Ph_3P)_2Pt$ with the vinyl triflate results in the stereospecific formation of a π-olefin platinum complex **25** that undergoes *rapid* rearrangement to the σ-vinyl, coordinated-triflate complex **26**. The formation of π-complex **25** is supported by the negative entropies of activation (Table I) and the analogous complexes **22** and **24** observed spectrally. Reaction of **26** with triphenylphosphine present in solution in turn forms the σ-vinyl cationic platinum(II) complex **27**. Complex **27** may also be formed more directly via the reaction of $(Ph_3P)_3Pt$ with vinyl triflate. Either the coordinated complex **26** or the cationic complex **27**, or both, represent the final oxidative addition species essential for the transmetalation step and subsequent reductive coupling. In contrast to the interaction of the highly reactive vinyl triflates, the vinyl halides appear to react with Pt(0) via the rapid, perhaps reversible, formation of the π-alkene complex and its *slow*, rate-determining rearrangemewnt to the σ-vinyl, halo-platinum species analogous to **26**.

In this study we presented kinetic, stereochemical, and spectral evidence for the intermediacy of a π-alkene complex **25** and isolated and fully characterized, including a molecular crystal structure determination of **27**, the σ-vinylplatinum complexes **26** and **27**, resulting from oxidative addition. Although our reactions were carried out stoichiometrically and employed Pt(0) rather than the catalytically much more active Pd(0) and Ni(0) species, we believe that this system is an excellent model for Ni triad metal mediated vinylic cross coupling reactions.

Experimental Section

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

reported in ppm relative to the carbon resonance of the deuterated NMR solvent. All ^{31}P NMR spectra were recorded in a Varian XL-300 at 121 MHz with broadband ^{1}H decoupling with the magnet locked on the deuterated solvent and chemical shift reported relative to external 85% H_3PO_4 at 0.00 ppm. All ^{19}F NMR spectra were obtained on a Varian XL-300 at 283 MHz with CFCl$_3$ as the internal standard at 0.00 ppm.

Fast atom bombardment mass spectra were obtained with a VG Analytical 7070-E mass spectrometer. Analytical GC was performed on a Hewlett-Packard 5711A flame ionization detector GC equipped with a Hewlett-Packard 3380A integrator, with a 0.125 in. × 6 ft UCW-98 on 80/100 Chromosorb W analytical column. Preparative GC work was performed on a Varian Aerograph 90-P, with a 0.25 in. × 20 ft 15% QF-1 preparative column. High-pressure liquid chromatography (HP-LC) was performed by using a Varian 500 liquid chromatograph with Varian Micropak columns and a variable wavelength UV detector (U-V-100).

Conductance measurements were made according to Angelici[49] using doubly distilled CH_3NO_2 and metal complex solutions of approximately 10^{-4} M and using a Radiometer-Copenhagen CDM3 conductance bridge. The cell constant was calculated to be 0.252.

Materials. In general, solvents were either reagent grade or were purified according to known procedures.[50] Specifically, THF (Fischer, Baker) was predried with CaCl$_2$, refluxed over CaH$_2$, distilled from LAH with triphenylmethane as an indicator, and distilled again from potassium/benzophenone (ketyl radical). Hydrocarbon solvents (hexanes, pentane, and toluene) were stirred over H_2SO_4, distilled from CaH$_2$, and then stored over 4 Å molecular sieves.

Deuterated NMR solvents (Aldrich or Norell) were purified by drying over P_2O_5 (CDCl$_3$, CD$_2$Cl$_2$), then freeze-pump-thawed three times, and then vacuum transferred. CD$_3$NO$_2$ was used as packaged with small amounts of water impurity.

Trifluoromethanesulfonic acid (3 M) was converted to the anhydride Tf$_2$O, by the method of Anderson.[51] *N*-Phenyl triflimide was prepared according to the method of Hendrickson and crystallized from hexanes.[52] *N,N*-Diisobutyl-2,4-dimethyl-3-pentylamine was purchased from Fluka or the free base recovered from the triflic acid salt and then distilled. PPh$_3$ was recrystallized from hexanes and vacuum dried. Triflates were prepared according to known procedures.[16,53] Isomeric (*E*)- and (*Z*)-2-butenyl triflates (**11**) were separated by preparative GC. Isomeric (*E*)-and (*Z*)-phenylpropenyl triflates (**13**) were separated by using preparative HPLC. 2-Propenyl bromide and 2-propenyl chloride were purchased from Aldrich and distilled from CaH$_2$ prior to use.

K$_2$PtCl$_4$ (Strem, Johnson-Matthey) was used as shipped or prepared in three steps from platinic acid.[54] Pt(PPh$_3$)$_4$[55] and Pt(PPh$_3$)$_2$Pt(C$_2$H$_4$)[56] were prepared according to literature procedure.

3-Methyl-2-butenyl Triflate (12).[57] A mixture of isomers was prepared from 3-methyl-2-butanone (12.9 g, 150 mmol), Tf$_2$O (48.7 g, 173 mmol), and *N,N*-diisobutyl-2,4-dimethyl-3-pentylamine (37.5 g, 165 mmol) giving 13.9 g (42%) in a 66:34 ratio as measured by GC. Five grams (7.56 mmol of the kinetic isomer) of the mixture of triflates were added to 100 mL of freshly distilled THF in a 250-mL, round-bottomed flask. PPh$_3$ (2.08 g, 7.94 mmol) was added with stirring and a slow stream of bubbling argon. Pd(PPh$_3$)$_4$ (0.184 g, 0.160 mmol, 2 mol %) was added, and the reaction stirred at reflux for 1 h. The brown THF solution was filtered through a short column of silica gel, and the THF was distilled leaving a brown liquid residue. The residue was bulb-to-bulb distilled yielding 2.2 g (65% recovery of desired triflate) which was greater than 99.5% devoid of the other triflate and greater than 99% pure by GC.

2-Methyl-1-cyclohexenyl Triflate (5). This compound was prepared according to Scott and Crisp[58] as a 97:3 mixture of the desired triflate and its corresponding "kinetic" isomer. This minor isomer was removed by using the method described with 3-methyl-2-butenyl triflate from the mixture of triflates (244 mg, 1.00 mmol), PPh$_3$ (26 mg, 0.10 mmol), and Pd(PPh$_3$)$_4$ (12 mg, 0.01 mmol).

(49) Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry*. W. B. Saunders: Philadelphia, PA, 1969, p 17.

(50) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. W. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1966.

(51) Anderson, A. G. Ph.D. Dissertation, The University of Utah, 1977.

(52) Hendrickson, J. B.; Bair, K. W.; Bergeron, R.; Giga, A.; Skipper, D. L.; Sternbach, D. D.; Wareing, J. A. *Org. Prep. Proc.* **1977**, *9*, 173.

(53) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.

(54) (a) Keller, R. N. *Inorg. Synth.* **1946**, *2*, 247. (b) Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1963**, *7*, 240.

(55) Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* **1968**, *11*, 105.

(56) Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1978**, *18*, 121.

(57) Summerville, R. H.; Senkler, C. A.; Schleyer, P. v. R.; Deuber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 1100.

(58) Crisp, G. T.; Scott, W. J. *Synthesis* **1985**, 335.

General Procedure for the Preparation of σ-Vinyl Cationic Platinum Complexes: 2-Propenyl(PPh$_3$)$_3$Pt(OTf) (6). To 100 mL of argon-degassed toluene solution was added 1.0 g (0.80 mmol) of Pt(PPh$_3$)$_4$. The yellow homogeneous solution was degassed further by bubbling argon for 10 min. 2-Propenyl triflate (1) (460 mg, 2.4 mmol) was added all at once via syringe. Within 10 min the solution became colorless, and a white precipitate started forming. Dry hexanes (150 mL) were added to the reaction solution after 30 min to continue the precipitation, and the flask was then stored in the refrigerator for 1 h. Filtration of the solid and washing with toluene and hexanes gave 862 mg (88%) of a white microcrystalline solid of **6** as a ^{1}/$_2$ mol toluene solvate according to ^{1}H NMR: mp 175–178 °C (dec): IR 3059 m, 1584 w, 1571 w, 1480 m, 1432 s, 1268 s, 1141 s, 1092 s, 1023 s, 742 s, 693 s, 631 s; ^{1}H NMR (CD$_3$NO$_2$) δ 0.99 (br d, $^4J_{PH}$ = 5.5 Hz, $^3J_{PtH}$ = 28 Hz, 3 H), 4.85 (dd, $^4J_{PH}$ = 8.4 Hz, $^2J_{HH}$ = 1.5 Hz, $^3J_{PtH}$ = 39 Hz, 1 H), 5.04 (dd, $^4J_{PH}$ = 19 Hz, $^2J_{HH}$ = 1.5 Hz, $^3J_{PtH}$ = 83 Hz, 1 H) 7.1–7.7 (aromatics, 45 H); ^{31}P NMR δ 19.7 (d, $^2J_{PP}$ = 19.6 Hz, $^1J_{PtP}$ = 3054 Hz), 18.4 (t, $^1J_{PtP}$ = 1718 Hz); ^{13}C NMR δ 30.6 (br s), 122.4 (q, $^1J_{CF}$ = 320 Hz), 123.4 (br s), 129.5 (overlapping dt), 130.6 (d, $^1J_{PC}$ = 56 Hz)^d, 130.6 (t, $^1J_{PC}$ = 28 Hz), 132.0 (s), 132.3 (s), 135.6 (d, $^2J_{PC}$ = 12 Hz), 136.3 (t, $^2J_{PC}$ = 6 Hz), 156.3 (dt, $^2J_{PC}$ = 85 Hz, $^2J_{PC}$ = 11 Hz); FAB MS, RMM$^+$ (1022), M$^+$ (3.0), [M − PPh$_3$]$^+$ (100); conductance (Ω_M) 88 cm^2 ohm^{-1} mol^{-1}. Anal. Calcd for C$_{61.5}$H$_{54}$P$_3$F$_3$O$_3$SPt: C, 60.63; H, 4.48; P, 7.62. Found: C, 60.57; H, 4.67; P, 7.79.

2-Methyl-1-propenyl(PPh$_3$)$_3$Pt(OTf) (7). This complex was prepared according to the general procedure from Pt(PPh$_3$)$_4$ (1.24 g, 1.00 mmol) and 2-methyl-1-propenyl triflate 2 (0.613 g, 3.00 mmol) in 100 mL of toluene by stirring overnight yielding 1.03 g (0.87 mmol, 87%) of product without a toluene solvate according to ^{1}H NMR: mp 244–245 °C (dec); IR 3060 m, 1588 w, 1573 w, 1482 m, 1435 s, 1270 s, 1143 s, 1092 s, 1027 s, 742 s, 695 s, 635 s; ^{1}H NMR (CD$_3$NO$_2$) δ 0.67 (br s, 3 H), 0.97 (br s, 3 H), 5.39 (m, 1 H), 7.1–7.7 (aromatics, 45 H); ^{31}P NMR δ 19.8 (overlapping dt, $^2J_{PP}$ = 18.4 Hz, $^1J_{PtP}$ = 2952 Hz, $^2J_{PtP}$ = 1901 Hz); ^{13}C NMR δ 26.5 (s, $^3J_{PtC}$ = 83 Hz), 29.4 (d, $^4J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 61 Hz), 122.4 (q, $^1J_{CF}$ = 320 Hz), 129.7 (t, $^3J_{PC}$ = 5 Hz), 130.0 (d, $^3J_{PC}$ = 10 Hz), 131.6 (t, $^1J_{PC}$ = 27 Hz), 131.6 (d, $^1J_{PC}$ = 54 Hz), 132.4 (s), 136.0 ($^2J_{PC}$ = 10 Hz), 136.3 (t, $^2J_{PC}$ = 5 Hz), 139.0 (br s); FAB MS, RMM$^+$ (1036), M$^+$ (1.5), [M − PPh$_3$]$^+$ (100); conductance (Ω_M) 95 cm^2 ohm^{-1} mol^{-1}. Anal. Calcd for C$_{59}$H$_{52}$P$_3$F$_3$O$_3$SPt: C, 59.74; H, 4.42; P, 7.83. Found: C, 59.38; H, 4.34; P, 7.89.

1-Cyclohexenyl(PPh$_3$)$_3$Pt(OTf) (8). This complex was prepared from Pt(PPh$_3$)$_4$ (1.24 g, 1.00 mmol) and 1-cyclohexenyl triflate 3 (0.690 g, 3.00 mmol) in 100 mL of toluene by using the general procedure and stirring overnight yielding 1.21 g (0.97 mmol, 97%) as a ^{1}/$_3$ mol toluene solvate according to ^{1}H NMR: mp 195–197 °C (dec); IR 3059 w, 1605 w, 1588 w, 1572 w, 1480 m, 1433 s, 1270 vs , 1141 s, 1091 s, 1029 s, 745 s, 695 s, 635 s; ^{1}H NMR (CD$_3$NO$_2$) δ 0.10 (m, 2 H), 0.21 (m, 2 H), 1.18 (m, 2 H), 1.72 (m, 2 H), 5.53 (br d, $^4J_{PH}$ = 10 Hz, $^3J_{PtH}$ = 37 Hz, 1 H), 7.0–7.8 (aromatics, 45 H); ^{31}P NMR δ 20.6 (d, $^2J_{PP}$ = 19.5 Hz, $^1J_{PtP}$ = 3139 Hz), 18.6 (t, $^1J_{PP}$ = 1692 Hz); ^{13}C NMR δ 22.0 (s), 25.4 (s, J_{PtC} = 36 Hz), 30.6 (d, J_{PC} = 9 Hz, J_{PtC} = 50 Hz), 37.8 (s), 122.4 (q, $^1J_{CF}$ = 320 Hz), 129.5 (overlapping dt), 131.0 (d, $^1J_{PC}$ = 56 Hz), 131.0 (t, $^1J_{PC}$ = 28 Hz), 131.9 (s), 132.1 (s), 135.7 (d, $^2J_{PC}$ = 11 Hz), 136.2 (t, $^2J_{PC}$ = 5 Hz), 146.7 (dt, $^2J_{PC}$ = 85 Hz, $^2J_{PC}$ = 12 Hz); FAB MS, RMM$^+$ (1062), M$^+$ (2.5), [M − PPh$_3$]$^+$ (100); conductance (Ω_M) 85 cm^2 ohm^{-1} mol^{-1}. Anal. Calcd for C$_{63.2}$H$_{56.6}$P$_3$F$_3$O$_3$SPt: C, 60.51; H, 4.55; P, 7.39. Found: C, 60.85; H, 4.62; P, 7.34.

Cyclohexylidenyl(PPh$_3$)$_3$Pt(OTf) (9). This complex was prepared from Pt(PPh$_3$)$_4$ (0.50 mg, 0.40 mmol) and cyclohexylidenyl triflate 4 (0.29 g, 1.2 mmol) in 40 mL of toluene by stirring overnight to yield 453 mg (0.35 mmol, 88%) of a ^{1}/$_3$ mol toluene solvate according to ^{1}H NMR: mp 175–178 °C; IR 3060 m, 1589 w, 1573 w, 1482 m, 1435 s, 1269 s, 1143 s, 1091 s, 1027 s, 744 s, 695 s, 635 s; ^{1}H NMR (CD$_3$NO$_2$) δ 0.70 (m, 2 H), 0.91 (m, 2 H), 1.05 (m, 4 H), 1.81 (m, 2 H), 4.82 (m, 1 H), 7.1–7.7 (aromatics, 45 H); ^{31}P NMR δ 18.7 (d, $^2J_{PP}$ = 19.5, $^1J_{PtP}$ = 2982 Hz), 19.2 (t, $^1J_{PtP}$ = 1914); ^{13}C NMR 26.8 (s), 27.2 (s), 27.3 (s), 36.7 (s, $^3J_{PtC}$ = 32 Hz), 41.2 (d, $^4J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 51 Hz), 122.4 (q, $^1J_{CF}$ = 320 Hz), 129.5 (t, $^3J_{PC}$ = 5 Hz), 129.6 (d, $^3J_{PC}$ = 10 Hz), 131.0 (d, $^1J_{PC}$ = 58 Hz), 131.0 (t, $^1J_{PC}$ = 29 Hz), 132.1 (s), 135.8 (d, $^2J_{PC}$ = 11 Hz), 136.1 (t, $^2J_{PC}$ = 6 Hz), 143.6 (br s); FAB MS, RMM$^+$ (1076), M$^+$ (5.0), [M − PPh$_3$]$^+$ (100). Anal. Calcd for C$_{64.3}$H$_{58.6}$P$_3$F$_3$O$_3$SPt: C, 61.46; H, 4.71; P, 7.39. Found: C, 61.17; H, 4.99; P, 7.71.

2-Methyl-1-cyclohexenyl(PPh$_3$)$_3$Pt(OTf) (10). To a 20-mL degassed solution of Pt(PPh$_3$)$_4$ (200 mg, 0.161 mmol) in toluene was added 118 mg (0.483 mmol) of triflate 5 at room temperature. The round-bottomed flask was fitted with a reflux condensor, and the solution was heated to 80 °C (oil bath) for 5 h. The pale yellow solution was slowly cooled to room temperature, and a white solid began to precipitate. The mixture was added to 60 mL of dry hexanes, cooled in the refrigerator, and filtered. The white solid was washed with cold toluene and then with

Reaction of Vinyl Triflates with Zerovalent Pt

J. Am. Chem. Soc., Vol. 111, No. 9, 1989 3355

hexanes yielding 184 mg (85%) with no toluene solvate: mp 194–196 °C dec; IR 3057 m, 1585 w, 1572 w, 1479 m, 1432 s, 1269 vs, 1141 s, 1090 s, 1025 s, 742 s, 694 s, 632 s; ^{1}H NMR (CD$_3$NO$_2$) δ 0.03 (m, 2 H), 0.25 (m, 2 H), 1.07 (m, 2 H), 1.90 (m, 2 H), 1.90 (br s, 3 H), 7.0–7.6 (aromatics, 45 H); ^{31}P NMR δ 19.2 (d, $^2J_{PP}$ = 17.5 Hz, $^1J_{PtP}$ = 3145 Hz), 15.6 (t, $^1J_{Pt}$ = 1583 Hz); ^{13}C NMR δ 22.0 (s), 24.8 (br s), 30.2 (d, $^4J_{PC}$ = 6 Hz, $^3J_{PtC}$ = 50 Hz), 35.6 (br d, $^4J_{PC}$ = 8 Hz), 40.4 (s), 122.4 ($^1J_{CF}$ = 320 Hz), 129.2 (overlapping dt), 131.2 (d, $^1J_{PC}$ = 54 Hz), 131.2 (t, $^1J_{PC}$ = 27 Hz), 131.7 (s), 132.3 (s), 136.0 (d, $^2J_{PC}$ = 11 Hz), 136.3 (t, $^2J_{PC}$ = 6 Hz), 141.8 (dt, $^2J_{PC}$ = 84 Hz, $^2J_{PC}$ = 10 Hz); FAB MS, RMM$^+$ (1076), M$^+$ (0.5), [M – PPh$_3$]$^+$ (100).

2-Propenyl(PPh$_3$)$_2$Pt(OTf) (18). To 748 mg (1.00 mmol) of (PPh$_3$)$_2$Pt(C$_2$H$_4$) in 10 mL of toluene, degassed by bubbling argon through a pipet for 15 min, was added 209 mg (1.10 mmol) of 2-propenyl triflate all at once. Degassing by bubbling was continued. A white precipitate began falling out of the solution almost immediately. The reaction appeared to be over in 10 min. The round-bottomed flask was stoppered and placed in the freezer for 1 h. The white solid was filtered on a medium porosity scintered glass filter funnel and washed with toluene (30 mL) and then liberally with dry hexanes yielding 800 mg (0.837 mmol, 84%) of **18** as $^1/_2$ mol toluene solvate according to ^{1}H NMR: mp 142–143 °C dec; 3067 w, 1585 w, 1479 m, 1429 s, 1313 s, 1200 s, 1091 s, 1005 s, 852 m, 744 s, 689 s, 620 s; ^{1}H NMR (CD$_2$Cl$_2$) δ 0.65 (br s, $^3J_{PtH}$ = 54 Hz, 3 H), 4.58 (br s, $^3J_{PtH}$ = 78 Hz, 1 H), 4.77 (br s, $^3J_{PtH}$ = 162 Hz, 1 H), 7.4–7.8 (aromatics, 30 H); ^{31}P NMR δ 26.9 (s, $^1J_{PtP}$ = 3362 Hz); ^{13}C NMR δ 28.8 (br s, $^2J_{PtC}$ = 57 Hz), 114.3 (br s), 128.0 (t, $^3J_{PC}$ = 5.8 Hz), 129.4 (t, $^1J_{PC}$ = 28 Hz), 131.1 (s), 135.2, (t, $^2J_{PC}$ = 7.2 Hz), 135.4 (t, $^2J_{PC}$ = 6.5 Hz). Anal. Calcd for C$_{43.5}$H$_{39}$P$_2$F$_3$O$_3$SPt: C, 54.66; H, 4.12; P, 6.48. Found C, 54.39; H, 4.16; P, 6.79.

VT NMR Observation of the Reaction between 2-Propenyl Triflate and (PPh$_3$)$_2$Pt(C$_2$H$_4$). Ten mg (0.0134 mmol) of (PPh$_3$)$_2$Pt(C$_2$H$_4$) was weighed into a 5-mm NMR tube, and the tube was evacuated. Dry oxygen free C$_7$D$_8$ (0.5 mL) was added to the tube, and then the tube was sealed with a rubber septum. The solution was cooled to –78 °C, and 12.7 mg (0.0669 mmol) of 2-propenyl triflate was added. A ^{31}P NMR was taken at –80 °C. Only starting ethylene complex (31.5 ppm) was observed at this temperature. Dry argon was bubbled through the solution for a period of 1 h at both –78 °C and –63 °C with no reaction at either temperature as determined by ^{31}P NMR. At –40 °C after bubbling for 1 h the resonance of a small amount of oxidative addition product could be observed at 26.5 ppm. Warming to –23 °C then 0 °C led to clean conversion to only one product (13). One equivalent of PPh$_3$ (3.5 mg) was added to the reaction mixture. Immediately a white precipitate formed. About 0.3 mL of CD$_2$Cl$_2$ was added which dissolved the product, which was confirmed to be complex **6** by ^{1}H and ^{31}P NMR.

VT NMR Observation of the Reaction between 2-Propenyl Chloride and (PPh$_3$)$_2$Pt(C$_2$H$_4$). Ten mg (0.0134 mmol) of (PPh$_3$)$_2$Pt(C$_2$H$_4$) was weighed into a 5-mm NMR tube, and the tube was evacuated. Dry oxygen free C$_6$D$_6$ (0.5 mL) was added to the tube. About 30 equiv (ca. 30 mg, 0.40 mmol) of 2-propenyl chloride was added. A slow stream of argon was bubbled through the solution for 20 min. The solution was kept at 10 °C to keep the chloride from evaporating. Both ^{1}H NMR and ^{31}P NMR spectra were taken of the mixture (Figure 2, Table II).

VT NMR Observation of the Reaction between 2-Propenyl Bromide and (PPh$_3$)$_2$Pt(C$_2$H$_4$). Ten mg (0.0134 mmol) of (PPh$_3$)$_2$Pt(C$_2$H$_4$) was weighed into a 5-mm NMR tube, and the tube was evacuated. Dry oxygen free C$_7$D$_8$ (0.5 mL) was added to the tube. The solution was cooled to –23 °C with a CCl$_4$/dry ice bath. 2-Propenyl bromide (6.0 μL, 0.067 mmol) was added. A slow stream of argon bubbled through the solution for 1 h. ^{1}H, ^{31}P, and ^{13}C NMR spectra were taken of the mixture at –20 °C (Table II).

Kinetic Studies of the Reaction between Vinyl Triflates and Pt(0). Stock solutions (4.0 × 10^{-4} M) were made by dissolving 12.4 mg (0.0100 mmol) of Pt(PPh$_3$)$_4$ in a 25-mL volumetric flask with freshly distilled degassed (nitrogen) toluene. The UV–vis cells were oven dried, cooled under nitrogen atmosphere, sealed with rubber septa and parafilm, and were loaded with the Pt(0) solution (ca. 4.2 mL) with a cannula under nitrogen atmosphere. Triflates (20–40 equiv) were degassed with nitrogen before use, weighed, and added via syringe. The absorption of Pt(PPh$_3$)$_4$ 358 nm or at 410 nm compared to the absorption of a blank cell containing toluene was followed as the Pt(PPh$_3$)$_4$ reacted and disappeared.[36] Pseudo-first-order rate constants were calculated by using a nonlinear least-squares treatment of the data. Reactions were followed to at least 4 half-lives. Reported values for the second-order rate constants were calculated from the first-order rate constants and the known concentration of triflate in each run and were generally averaged from multiple runs (see Table I).

The Reaction of (*E*)-2-Phenylpropenyl Triflate (13E) with Pt(PPh$_3$)$_4$. To 20 mL of an argon-degassed solution of Pt(PPh$_3$)$_4$ (200 mg, 0.161 mmol) was added 128 mg (0.483 mmol) of pure (*E*)-2-phenylpropenyl

triflate (**13E**). The reaction was stirred for 15 h, and the solvent was stripped under reduced pressure and then dried under high vacuum (<-0.01 Torr). The residue was washed liberally with dry hexanes and again dried on the high vacuum. This yielded complex **14E** as a white powdery solid (204 mg). The crude solid was analyzed by both ^{1}H and ^{31}P NMR (CD$_3$NO$_2$) and found to have a 1.0 mol solvate of toluene according to ^{1}H NMR (recovery was 95% based on starting platinum). No **14Z** could be detected by searching for the vinyl methyl resonances (1.54 ppm) in the ^{1}H NMR: ^{1}H NMR (CD$_3$NO$_2$) δ 1.18 (br s, 3 H), 6.56 (m, vinyl, 1 H), 7.1–7.6 (aromatics, 48 H), 7.71 (m, phenyl, 2 H); ^{31}P NMR δ 16.5 (t, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 1893 Hz), 19.1 (d, $^1J_{PtP}$ = 2952 Hz).

The Reaction of (*Z*)-2-Phenylpropenyl Triflate (13Z) with Pt(PPh$_3$)$_4$. This reaction was performed as the above on a smaller scale: 30 mg (0.024 mmol) of Pt(PPh$_3$)$_4$ and 10.4 mg (0.0391) of pure (*Z*)-2-phenylpropenyl triflate **13Z**. The crude solid **14Z** was analyzed by ^{1}H and ^{31}P NMR (CD$_3$NO$_2$) and found to have a 1.0 mol toluene solvate according to ^{1}H NMR (recovery was 93% base on starting platinum). No **14E** can be detected by searching for the vinyl methyl (1.18 ppm) in the ^{1}H NMR: ^{1}H NMR (CD$_3$NO$_2$) δ 1.54 (br s, 3 H), 6.27 (m, phenyl, 2 H), 6.41 (m, vinyl, 1 H), 6.79–6.90 (m, phenyl, 3 H), 7.1–7.7 (aromatics, 48 H); ^{31}P NMR δ 15.8 (t, $^2J_{PP}$ = 19 Hz, $^1J_{PtP}$ = 1923 Hz), 19.1 (d, $^1J_{PtP}$ = 2927 Hz).

The Reaction of (*E*)-2-Butenyl Triflate (11E) with Pt(PPh$_3$)$_4$. To 5 mL of an argon-degassed solution of Pt(PPh$_3$)$_4$ (51 mg, 0.041 mmol) was added 25 mg (0.12 mmol) of pure (*E*)-2-butenyl triflate (**11E**) all at once. The reaction was stirred for 18 h and turned colorless. The solvent was stripped under reduced pressure and then dried under high vacuum (<-0.01 Torr). The residue was washed liberally with dry hexanes and again dried on the high vacuum. This yielded complex **15E** as a white powdery solid (45 mg). The crude solid was analyzed by both ^{1}H and ^{31}P NMR (CD$_3$NO$_2$) and found to have a 0.5 mol solvate of toluene (recovery was 89% based on starting platinum). No **15Z** can be detected by searching for the vinyl methyl resonance (1.59 ppm) in the ^{1}H NMR: mp 174–177 °C dec; IR 3057 m, 1585 w, 1572 w, 1479 m, 1432 s, 1269 vs, 1141 s, 1090 s, 1025 s, 742 s, 694 s, 632 s; ^{1}H NMR δ 0.54 (br s, 3 H), 0.80 (br d, $^4J_{PH}$ = 5.8 Hz, 3 H), 5.22 (m, $^3J_{PtH}$ = 43 Hz, 1 H), 7.1–7.75 (aromatics, 45 H); ^{31}P NMR δ 18.5 (t, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 1722 Hz), 19.9 (d, $^1J_{PtP}$ = 3117 Hz).

The Reaction of (*Z*)-2-Butenyl Triflate (11Z) with Pt(PPh$_3$)$_4$. To 20 mL of an argon-degassed toluene solution of Pt(PPh$_3$)$_4$ (203 mg, 0.163 mmol) was added pure (*Z*)-2-butenyl triflate (**11Z**) (100 mg, 0.490 mmol). The reaction was stirred for 18 h, and the workup was identical with that for **15E**. The crude solid (185 mg) was then characterized by ^{1}H and ^{31}P NMR (CD$_3$NO$_2$). Integration of the vinyl methyl resonances at 1.59 ppm (**15Z**) and 0.54 ppm (**15E**) gives a 95:5 ratio of **15Z:15E**. Complex **15Z** had no toluene solvate (yield based on starting platinum was 96%). In a separate experiment on the same scale a 0.7-mL aliquot of the supernatant toluene was transferred to a NMR tube. Searching for isomerized triflate **11E** by ^{19}F NMR (–73.2 ppm) showed one resonance corresponding to starting triflate **11Z** (–74.0 ppm) was present in the mixture: mp 170–173 °C dec; IR (KBr) 3060 m, 1588 w, 1573 w, 1482 m, 1435 s, 1270 s, 1143 s, 1092 s, 1027 s, 742 s, 695 s, 635 s; ^{1}H NMR δ 1.12 (br d, $^4J_{PH}$ = 5.3 Hz, 3 H), 1.59 (br d, $^3J_{HH}$ = 6.7 Hz, 3 H), 5.05 (br m, $^3J_{PtH}$ = 67 Hz, 1 H), 7.05–7.65 (aromatics, 45 H); ^{31}P NMR δ 17.2 (t, $^2J_{PP}$ = 19 Hz, $^1J_{PtP}$ = 1669 Hz), 18.5 (d, $^1J_{PtP}$ = 3057 Hz); ^{13}C NMR δ 21.8 (d, $^2J_{PC}$ = 4.8 Hz), 31.6 (br s), 127.9 (overlapping dt), 129.1 (t, $^1J_{PC}$ = 29 Hz), 130.7 (s), 131.2 (s), 134.1 (d, $^2J_{PC}$ = 11 Hz), 134.6 (t, $^2J_{PC}$ = 5.9 Hz), 145.3 (dt, $^2J_{PC}$ = 81 Hz, $^2J_{PC}$ = 11 Hz).

Single-Crystal X-ray Diffraction Analysis of 15Z. Colorless crystals of **15Z** were obtained by diffusion crystallization from CH$_2$Cl$_2$/Et$_2$O in the refrigerator to yield colorless rods as a $^1/_2$ mol CH$_2$Cl$_2$ solvate. X-ray data were collected on a Syntex P$\bar{1}$ automated diffractometer as summarized in Table III. The structure was solved by treating the phenyl rings of the PPh$_3$ as rigid bodies and other standard heavy atom techniques using the UCLA Crystallographic Package.

The Reactions of (*E*)- and (*Z*)-2-Butenyl Triflates (11E and 11Z) with Pt(PPh$_3$)$_2$(C$_2$H$_4$). These reactions were performed similarly to the reactions between pure isomeric **11E and 11Z** and Pt(PPh$_3$)$_4$. Pt(PPh$_3$)$_2$(C$_2$H$_4$) (150 mg, 0.200 mmol) was dissolved in 10 mL of dry degassed toluene. Degassing by bubbling argon continued. The individual purified triflates **11E** and **11Z** (100 mg, 0.490 mmol) were both added via syringe to each flask. After stirring for 15 h the toluene was stripped under reduced pressure, and the residue was pumped on the high vacuum overnight (<0.01 Torr) in order to remove both solvent and excess triflate to yield white powders in each flask. ^{1}H NMR in CD$_2$Cl$_2$ shows each product **19E** and **19Z** to have $^2/_3$ mol toluene solvates. ^{1}H NMR analysis of the solid obtained from the reaction of **11E** shows no evidence for the presence of complex **19Z** (1.16–1.18 ppm, overlapping resonances). In contrast, analysis of the reaction involving triflate **11Z** shows by integration of the methyl groups at 0.57 and 0.81 ppm to be

a 95:5 mixture of **19Z:19E**. Crystallization of either product proved to be too difficult since the complexes decomposed in chlorocarbon solvents. **19E**: ^{1}H NMR (CD$_2$Cl$_2$) δ 0.57 (br s, $^3J_{PtH}$ = 56 Hz, 3 H), 0.81 (br d, $^3J_{HH}$ = 6.6 Hz, 3 H), 4.96 (complex q, $^3J_{HH}$ = 6.6 Hz, $^3J_{PtH}$ = 87 Hz, 1 H), 7.35–7.9 (aromatics, 30 H); ^{31}P NMR δ 27.5 (s, $^1J_{PtP}$ = 3441 Hz). **19Z**: ^{1}H NMR (CD$_2$Cl$_2$) δ 1.16 (obscured d, 3 H), 1.18 (s, $^3J_{PtH}$ = 55

Hz, 3 H), 4.23 (br d, $^3J_{HH}$ = 5.4 Hz, $^3J_{PtH}$ = 132 Hz, 1 H), 7.3–7.7 (aromatics, 30 H); ^{31}P NMR δ 27.6 (s, $^1J_{PtP}$ = 3366 Hz).

On the Mechanism of the Metal Mediated Vinylic Cross Coupling Reactions. 2. Reductive Elimination: Preparation, Molecular Structure, and Thermal Chemistry of (σ-Alkynyl)(σ-vinyl)platinum(II) Complexes

Peter J. Stang* and Mark H. Kowalski[1]

Contribution from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112. Received September 23, 1988

Abstract: Reaction of RC≡CLi with CH$_2$=C(CH$_3$)Pt(PPh$_3$)$_2$(OTf) results in *cis*- and *trans*-(σ-alkynyl)(σ-vinyl)platinum(II) complexes. The cis isomer is the kinetic product and the trans one the thermodynamic one. X-ray crystal structures of both the cis and trans isomers are reported. The cis isomer is distorted around the Pt with a P–Pt–P angle of 100° and a C–Pt–C angle of only 84°, whereas the trans isomer has normal bond angles of 90 ± 1° around the central platinum. Kinetic studies establish that the cis isomer undergoes reductive elimination at much lower temperatures than the corresponding trans isomer. Added Ph$_3$P essentially inhibits the reductive coupling of the trans isomer but has little effect upon the coupling reaction of the cis isomer. The data strongly suggest that the trans isomer undergoes reductive coupling by a prior dissociative pathway, whereas the cis couples by a concerted process. These results and their implication for the mechanism of the Nickel triad metal mediated vinylic cross coupling reactions are discussed.

The widely accepted catalytic cycle proposed for the metal mediated cross coupling reactions has three important, distinct parts: (i) oxidative addition; (ii) transmetalation; and (iii) reductive elimination.[2] In the preceding paper[3] we addressed the issue of the oxidative addition of alkylvinyltriflates to Pt(0); in this paper we wish to discuss the details of the transmetalation and reductive elimination.

In catalytic cross coupling reactions the oxidative addition step provides the cationic coupling partner. Just as importantly, the anionic equivalent must be attached to the metal template in order for coupling (reductive elimination) to occur. In most cases this is accomplished with lithium, Grignard, or tin reagents. Some reactions, namely Heck olefination type reactions, require 1 equiv of base to provide an anionic coupling equivalent.[4]

The superior leaving group ability of the triflate group translates to exceptional lability of triflate transition-metal complexes.[5] Therefore, a wide variety of new complexes derived from the vinyl Pt(II) triflate complexes may be prepared by simple metathesis reactions of the labile triflate complexes. Most importantly, the transmetalation reaction, a required step in coupling reactions, can be reproduced[6] to give unsaturated bis-organo Pt(II) compounds.

Other than our new oxidative addition reactions of vinyl triflates to Pt(0) described in the preceding paper,[3] there are few, if any, systematic preparative methods for vinyl Pt(II) complexes and derivatives. The addition of organometallic species to σ-vinyl

Pt(II) cations giving bis-organo Pt(II) complexes is potentially the most significant of these substitution reactions.

There are numerous bis-organo Pt(II) complexes known. Typical transformations include the reactions of excess lithium or Grignard reagents with platinum dichlorides.[7] There are well known and useful pathways used to prepare bis-aryl, bis-alkyl, and metallocyclic Pt(II) complexes. A few mixed organic ligand species have been reported.[8] Notably absent from the various types of bis-organo Pt(II) complexes are bis-vinyl and mixed alkynyl vinyl derivatives. Those that have been prepared[9] are derived from bis-alkynyl complexes[10] and reactions with strong acids or with hydrazine. In the case of vinyl organometallic reagents and reactions with platinum dichlorides the reaction stops at the single addition product.[11] Therefore, there appeared to be a large gap in the preparative methods and as a result the chemistry of vinyl Pt(II) complexes and derivatives. Hence, attention was directed toward lithium acetylide reagents and labile vinyl triflate Pt(II) compounds with hopes of preparing and isolating (σ-alkynyl)(σ-vinyl)Pt(II) complexes and examining their coupling reactions.

(1) Abstracted in part from Kowalski, M. H. Ph.D. Dissertation, University of Utah, 1988.

(2) For reviews, see: (a) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (c) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749.

(3) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, preceding paper in this issue.

(4) Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691.

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

(6) (a) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174 and references therein. (b) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181.

(7) (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705. (b) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 4020. (c) Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808.

(8) (a) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. (b) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

(9) (a) Bell, R. A.; Chisholm, M. H.; Cristoph, G. C. *J. Am. Chem. Soc.* **1976**, *98*, 6046. (b) O'Flynn, K. H. P.; McDonald, W. S. *Acta Crystallogr.* **1976**, *B32*, 1596.

(10) (a) Collamati, A.; Furlani, A. *J. Organomet. Chem.* **1969**, *17*, 457. (b) Bonamico, M.; Dessy, G.; Fares, V.; Russo, M. V.; Scaramuzza, L. *Cryst. Struct. Commun.* **1977**, *6*, 39. (c) Sonogashira, K.; Fujikura, Y.; Yatake, N.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101. (d) Russo, M. V.; Furlani, A. *J. Organomet. Chem.* **1979**, *165*, 101. (e) Cross, R. J.; Davidson, M. F. *Inorg. Chim. Acta* **1985**, *97*, L35.

(11) (a) Cardin, C. J.; Cardin, D. J.; Lappert, M. F. *J. Organomet. Chem.* **1973**, *60*, C70. (b) Cardin, C. J.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1977**, 1593. (c) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46. (d) Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1986**, 2315.