3356 J. Am. Chem. Soc. 1989, 111, 3356-3362

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_2Cl_2) δ 0.57 (br s, $^3J_{\rm PtH}$ = 56 Hz, 3 H), 0.81 (br d, $^3J_{\rm HH}$ = 6.6 Hz, 3 H), 4.96 (complex q, $^3J_{\rm HH}$ = 6.6 Hz, $^3J_{\rm PtH}$ = 87 Hz, 1 H), 7.35–7.9 (aromatics, 30 H); ^{31}P NMR δ 27.5 (s, $^1J_{\rm PtP}$ = 3441 Hz). **19Z**: ^{1}H NMR (CD_2Cl_2) δ 1.16 (obscured d, 3 H), 1.18 (s, $^3J_{\rm PtH}$ = 55 Hz, 3 H), 4.23 (br d, $^3J_{\rm HH}$ = 5.4 Hz, $^3J_{\rm PtH}$ = 132 Hz, 1 H), 7.3–7.7 (aromatics, 30 H); ^{31}P NMR δ 27.6 (s, $^1J_{\rm PtP}$ = 3366 Hz).

Acknowledgment. Financial support by the NSF (CHE 8802622) and the generous loan of K_2PtCl_4 Pt by Johnson Matthey is gratefully acknowledged.

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

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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_3P 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.

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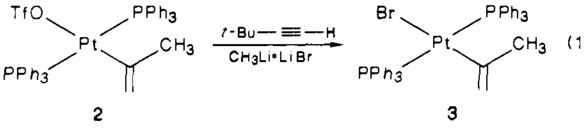
Table I. Summary of Crystallographic Data for **4** and **5**[a]

	4	**5**
mol formula	$C_{45}H_{44}P_2Pt$	$C_{45}H_{44}P_2Pt$
mol wt	841.89	841.89
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (14)	$P2_1/n$
cell dimensions		
a (Å), *b* (Å)	12.724 (6), 16.762 (5)	14.080 (3), 11.991 (4)
c (Å); *β* (deg)	18.779 (4), 97.91 (3)	22.602 (4), 90.50 (1)
V, Å^3	3966.9	3815.8
Z	4	4
d(calcd), g/cm^3	1.410	1.410
crystal dimensions, mm	0.38 × 0.25 × 0.20	0.30 × 0.28 × 0.20
radiation, Å	Mo Kα 0.71073	Mo Kα 0.71073
data collection method	$2\theta-\theta$	$2\theta-\theta$
scan speed, deg/min	variable (2.0–10.0)	variable (3.0–8.0)
reflcns measured	6858 *h*(0, 14), *k*(0, 11), *l*(−20, 20)	4508 *h*(0, 14), *k*(0, 11), *l*(−22, 22)
scan range	1.0°	$K_{\alpha 1}$ −1.0 to $K_{\alpha 2}$ +1.0
2θ limits, deg	3.0–42.0	3.0–42.0
total bkgd time/scan time	0.5	0.5
no. of reflcns between std	97	98
total unique data		4066
obsd data, $I > 3\sigma(I)$	4629	2378
abs coeff, (μ), cm^{-1}	36.80	38.26
min absorption correction	5.76	76.79
max absorption correction	99.99	99.99
no. of variables	433	418
R (averaging)		0.031, 0.022
max shift/error		0.01
R(*F*)	0.0449	0.0462
$R_w(F)$	0.0567	0.0539
goodness of fit	3.40	1.315

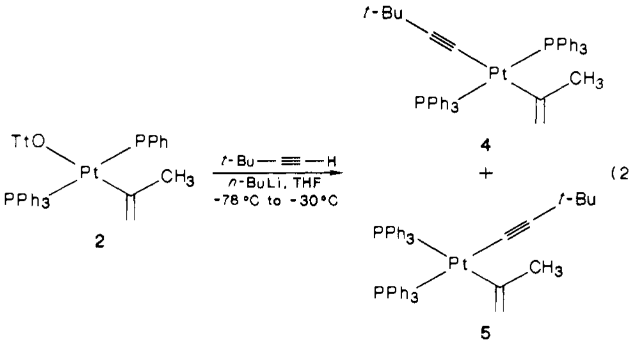
[a] Max. diff. Fourier peak 1.92 e/Å^3 about 1.002 Å from Pt for **4**. Max. diff. Fourier peak 1.678 e/Å^3 about 1.092 A from Pt for **5**.

Results and Discussion

The fact that vinyl Pt(II) halides are unreactive toward lithium reagents is well illustrated in the first experimental attempt to react *t*-BuC≡C$^-$ (**1**) with triflate complex **2**. Generation of *t*-BuC≡C$^-$ **1** by reaction of CH_3Li (LiBr complex) and *t*-BuC≡CH in THF, then addition of **2**, warming to room temperature, and stirring overnight led to exclusive formation of complex **3** (eq 1). No evidence for acetylide transmetalation was found. LiBr, part of the lithium reagent complex, seems to react preferentially with the starting triflate complex to yield the bromide product before it can react with the acetylide.



It was then imperative that not only did the organolithium reagent have to be free of halide but also starting **2** had to be as well. Since complex **2** as recrystallized from CH_2Cl_2/Et_2O contained a CH_2Cl_2 solvate, nonrecrystallized **2** had to be used. Addition of **2** to a solution of **1** (1.2 equiv), generated from *t*-BuC≡CH and *halide free n*-BuLi at −78 °C, led to a heterogeneous solution. Warming to −30 °C gave a pink homogeneous solution. Workup yielded a pale yellow solid that was approximately a 4:1 mixture of trans and cis transmetalation complexes **4** and **5** as determined by ^{31}P NMR (eq 2). Following the reaction by ^{31}P NMR (THF, unlocked) shows reaction as low as −78 °C. No significant change in product ratio occurs after warming the reaction to −30 °C. However, warming the solution above 0 °C led to yellow solutions and some decomposition. Pure cis complex **5** was ultimately isolated and purified by crystallization from acetone and then recrystallized from Et_2O/hexanes in 14% isolated yield.



Complex **5** is a colorless crystalline solid that has been fully characterized by IR, multinuclear NMR, and elemental analysis. The IR spectrum shows a weak absorption at 2112 cm^{-1} due to the C≡C stretch. NMR data clearly distinguish **5** from its trans isomer **4**. The ^1H NMR has a singlet resonance at 0.67 ppm corresponding to the *tert*-butyl of the alkynyl ligand. The methyl of the 2-propenyl σ-vinyl ligand at 1.80 ppm is a doublet of multiplets, due to coupling to the *trans*-PPh_3, the *cis*-PPh_3, and the vinyl protons. The vinyl protons have similar multiplicity. The ^{31}P NMR exhibits two doublets, since the square-planar complex is not symmetric, with the expected ^{195}Pt satellites. The ^{13}C NMR is even more complicated, yet all resonances can be assigned (see Experimental Section). Alkynyl and vinyl carbons are easily distinguished and have multiplicities consistent with the cis stereochemistry of the complex.

The solid-state structure of complex **5** was confirmed by single-crystal X-ray diffraction. Suitable crystals were grown by

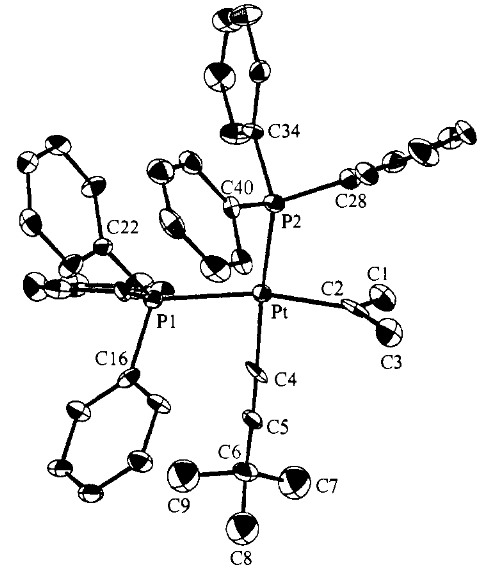


Figure 1. ORTEP representation of complex **5**.

Table II. Selected Bond Distances for **5**[a]

	distance (Å)		distance (Å)
Pt-P1	2.340 (4)	C4-C5	1.22 (2)
Pt-P2	2.286 (4)	C5-C6	1.46 (2)
Pt-C2	2.05 (2)	C6-C7	1.40 (3)
Pt-C4	1.97 (2)	C6-C8	1.44 (4)
C1-C2	1.43 (3)	C6-C9	1.42 (4)
C2-C3	1.37 (2)		

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

Table III. Selected Bond Angles for **5**[a]

	angle (deg)		angle (deg)
P1-Pt-P2	100.3 (1)	C1-C2-C3	122 (2)
P1-Pt-C2	167.2 (4)	C4-C5-C6	175 (2)
P1-Pt-C4	83.1 (5)	C5-C6-C7	116 (2)
P2-Pt-C2	92.3 (5)	C5-C6-C8	106 (2)
P2-Pt-C4	176.6 (4)	C5-C6-C9	111 (2)
C2-Pt-C4	84.3 (7)	C7-C6-C8	105 (2)
Pt-C2-C1	114.7 (3)	C7-C6-C9	119 (3)
Pt-C2-C3	123.4 (9)	C8-C6-C9	96 (3)
Pt-C4-C5	176 (2)		

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

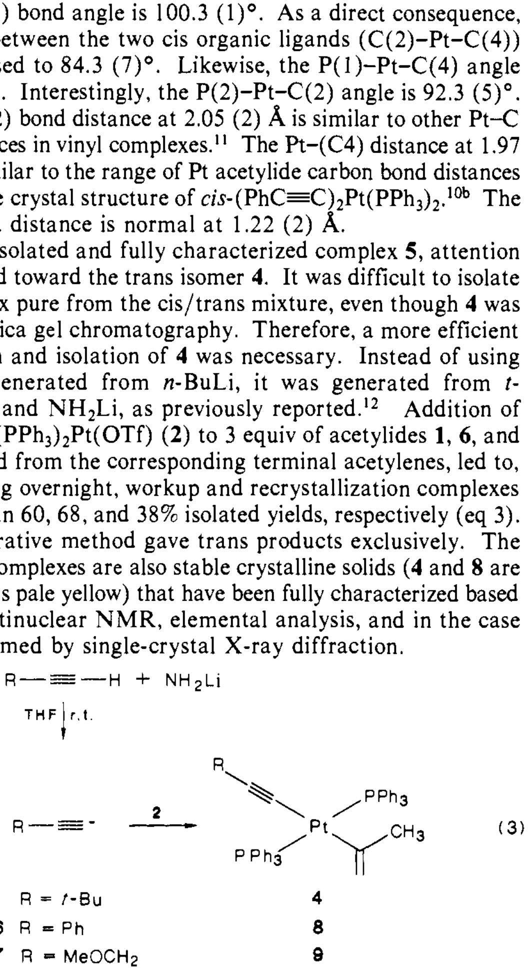
Table IV. Selected Bond Distances for **4**[a]

	distance (Å)		distance (Å)
Pt-P1	2.293 (3)	C4-C5	1.21 (2)
Pt-P2	2.296 (3)	C5-C6	1.46 (2)
Pt-C2	2.10 (1)	C6-C7	1.48 (3)
Pt-C4	2.04 (1)	C6-C8	1.47 (2)
C1-C2	1.48 (2)	C6-C9	1.51 (3)
C2-C3	1.36 (2)		

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

slow evaporation from acetone. An ORTEP representation of **5** is shown in Figure 1. Crystal data (Table I), bond lengths (Table II), and bond angles (Table III) are presented. All atoms are within ±0.03 Å from the calculated plane. Complex **5** as revealed from the X-ray structure has several interesting features. Bond angles around the Pt atom are distinctly distorted from 90°. As a result of relieving strain between the *cis*-phosphines, the P(1)-Pt-P(2) bond angle is 100.3 (1)°. As a direct consequence, the angle between the two cis organic ligands (C(2)-Pt-C(4)) is compressed to 84.3 (7)°. Likewise, the P(1)-Pt-C(4) angle is 83.1 (5)°. Interestingly, the P(2)-Pt-C(2) angle is 92.3 (5)°. The Pt-C(2) bond distance at 2.05 (2) Å is similar to other Pt-C bond distances in vinyl complexes.[11] The Pt-(C4) distance at 1.97 (2) Å is similar to the range of Pt acetylide carbon bond distances found in the crystal structure of *cis*-$(PhC{\equiv}C)_2Pt(PPh_3)_2$.[10b] The C≡C bond distance is normal at 1.22 (2) Å.

Having isolated and fully characterized complex **5**, attention was directed toward the trans isomer **4**. It was difficult to isolate this complex pure from the cis/trans mixture, even though **4** was stable to silica gel chromatography. Therefore, a more efficient preparation and isolation of **4** was necessary. Instead of using acetylide generated from *n*-BuLi, it was generated from *t*-BuC≡CH and NH_2Li, as previously reported.[12] Addition of 2-propenyl$(PPh_3)_2Pt(OTf)$ (**2**) to 3 equiv of acetylides **1**, **6**, and **7**, generated from the corresponding terminal acetylenes, led to, after stirring overnight, workup and recrystallization complexes **4**, **8**, and **9** in 60, 68, and 38% isolated yields, respectively (eq 3). This preparative method gave trans products exclusively. The new trans complexes are also stable crystalline solids (**4** and **8** are colorless, **9** is pale yellow) that have been fully characterized based on IR, multinuclear NMR, elemental analysis, and in the case of **4**, confirmed by single-crystal X-ray diffraction.



(3)

The spectral data clearly establish the complexes to have trans stereochemistry. The ^{31}P NMR resonances are singlets with the usual ^{195}Pt satellites. ^1H NMR resonances are also pseudotriplets with some unresolved splitting of the 2-propenylvinyl protons. The arylphosphine resonances in the ^{13}C NMR are triplets due to virtual coupling. The alkynyl ^{13}C NMR chemical shifts vary considerably from complex to complex. ^{195}Pt satellites are generally not found in the ^{13}C spectra. An IR spectrum of **4** shows a weak absorption at 2112 cm^{-1} due to the C≡C stretch, whereas complexes **8** and **9** have a C≡C stretch that is very prominent at 2102 and 2108 cm^{-1}, respectively.

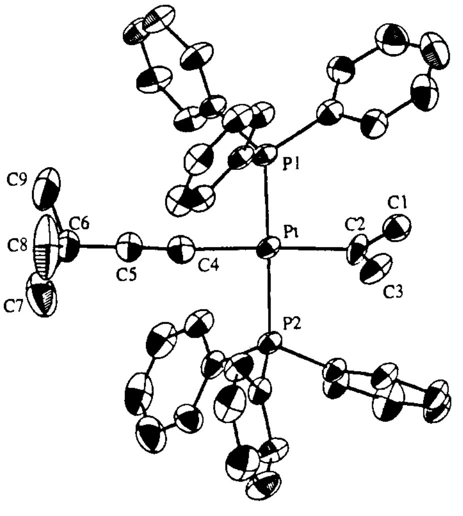


Figure 2. ORTEP representation of complex **4**.

Table V. Selected Bond Angles for **4**[a]

	angle (deg)		angle (deg)
P1-Pt-P2	174.5 (1)	C1-C2-C3	123 (1)
P1-Pt-C2	90.2 (3)	C4-C5-C6	178 (1)
P1-Pt-C4	89.5 (4)	C5-C6-C7	112 (1)
P2-Pt-C2	90.8 (4)	C5-C6-C8	110 (1)
P2-Pt-C4	88.9 (4)	C5-C6-C9	110 (1)
C2-Pt-C4	173.0 (5)	C7-C6-C8	110 (2)
Pt-C2-C1	119.8 (8)	C7-C6-C9	109 (2)
Pt-C2-C3	118 (1)	C8-C6-C9	106 (2)
Pt-C4-C5	176 (1)		

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

The solid-state structure of **4** is illustrated in Figure 2. Crystal data, bond lengths, bond angles, and atomic coordinates are found in Tables I, IV, and V. The geometry is close to square planar according to the calculated least-squares plane. In contrast to the above discussed cis isomer **5** the angles about the Pt center in **4** are normal at 90 ± 1°. The vinyl carbon-Pt bond length of 2.10 (1) Å and alkynyl carbon-Pt bond length of 2.04 (1) Å are similar to those in the analogous vinyl alkynyl complexes.[13]

Some insight into the differences in thermodynamic stability may be inferred from the X-ray data. Electronic and steric factors obviously contribute to the relative ground-state energies of each isomer. Most if not all bis-alkyl and bis-aryl Pt(II) complexes exist with the cis isomer as the more stable of the pair.[7] This can be explained on the basis of electronic effects, where the trans influence of the strong σ donor ligands weaken the Pt ligand bonds trans to themselves. More simply put, the more labile phosphine ligands (much weaker σ donors) are aligned trans to the strong σ donors, so the σ organic ligands do not have to compete for orbital electronic density. In contrast the thermodynamic isomer in all *bis*-alkynyl Pt(II) compounds appear to be the trans isomers. This last fact is substantiated by the observation of isomerization reactions of some these complexes from cis to trans.[10c] Steric factors must be more important here. All attempts to isomerize the pure isolated complexes **4** (trans) and **5** (cis) to the other isomer failed. The two geometric isomers could not be interconverted by addition of PPh_3, LiCl, $HgCl_2$, or polar solvents such as acetone and DMSO at room temperature. The clear analogy of the *trans*-bis-alkynyl complexes, the fact that most reactions using organometallic reagents yield thermodynamic isomers, and the observation of significant steric strain in the cis isomer in the solid state all are highly suggestive that the cis is the kinetic and the trans is the thermodynamic product in the reaction of acetylides with σ-vinylbis(triphenylphosphine)Pt(II) triflate (**2**).

Studies on the Reductive Elimination of (σ-Alkynyl)(σ-vinyl)platinum(II) Complexes. Bis-organo Pt(II) complexes that do not

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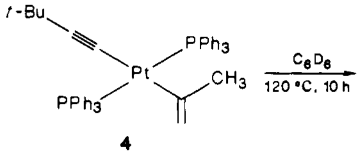
contain β hydrogens on the organic groups are relatively stable toward thermal decomposition.[14] These complexes in contrast to the Pd(II) and Ni(II) analogues[6,14,15] are much more reluctant to undergo reductive elimination. Herein lies the utility of the new (σ-alkynyl)(σ-vinyl)Pt(II) complexes: they can be isolated and fully characterized as models, yet also undergo reductive elimination reactions.

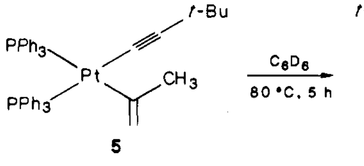
The best Pt(II) analogue to complexes **4** and **5** that undergoes reductive elimination is *cis*-$(Ph)_2Pt(PPh_3)_2$ studied by Braterman and Cross.[16] The thermolysis of a series of (bis-aryl)(bis-PPh_3)Pt^{II} complexes has demonstrated the requirement that the complexes have cis geometry. Experimental data suggest that the reaction proceeds via a concerted process, as evidenced by the absence of crossover products or products derived from radical intermediates and isomeric scrambling.

Initially, complexes **4** and **5** were submitted to thermal decomposition by heating C_6D_6 solutions in sealed NMR tubes. Complex **4** coupled at 120 °C, and ^1H NMR showed the disappearance of starting Pt(II) complex with concomitant formation of enyne **10** (eq 4). The aromatic region was extremely complicated, and the ^{31}P NMR showed no distinct phosphorus-containing compounds, implying that a large amount of decomposition of the platinum-containing products occurred. The volatile compounds were vacuum transferred to another NMR tube, and the resulting ^1H NMR spectrum showed a clean spectrum of **10**.



(4)

Authentic **10** was prepared by reaction of $t\text{-BuC}{\equiv}C^-$ with acetone to yield ynol **11**, $(CH_3)_2C(OH)C{\equiv}CBu\text{-}t$, which was dehydrated and distilled from $KHSO_4$. The ^1H NMR spectrum in C_6D_6 was identical with that obtained from the decomposition and coupling of complex **4**. In contrast to the harsh conditions required for reaction of the trans isomer **4**, the cis complex **5** decomposed to completion to give an orange solution and coupled product **10** at 80 °C in 5 h (eq 5).



(5)

Having demonstrated the formation of conjugated enynes from both *trans*- and *cis*-(σ-alkynyl)(σ-vinyl)Pt(II) complexes, a more detailed investigation into the nature of these reductive coupling reactions was undertaken. The reaction process could be conveniently followed by ^1H NMR. The *tert*-butyl group of the σ-alkynyl ligand provided a convenient NMR handle separate from the rest of the organic resonances. Both the disappearance of starting material (**4** and **5**) and appearance of product (**10**) could be followed at variable temperatures by using this technique. The rates of decomposition of colorless solutions of **4** and **5** (ca. 10^{-2} M) were followed to at least 3 half-lives. Unfortunately, a comprehensive kinetic study of these reductive elimination reactions was precluded by somewhat erratic rates, the details of which will be described below.[17] However, even though the actual kinetic data is not absolute, several observations have been made which give considerable insight into the nature of the reactions. Specific rate constants and derived data are reported within the constraints of the experiments performed.

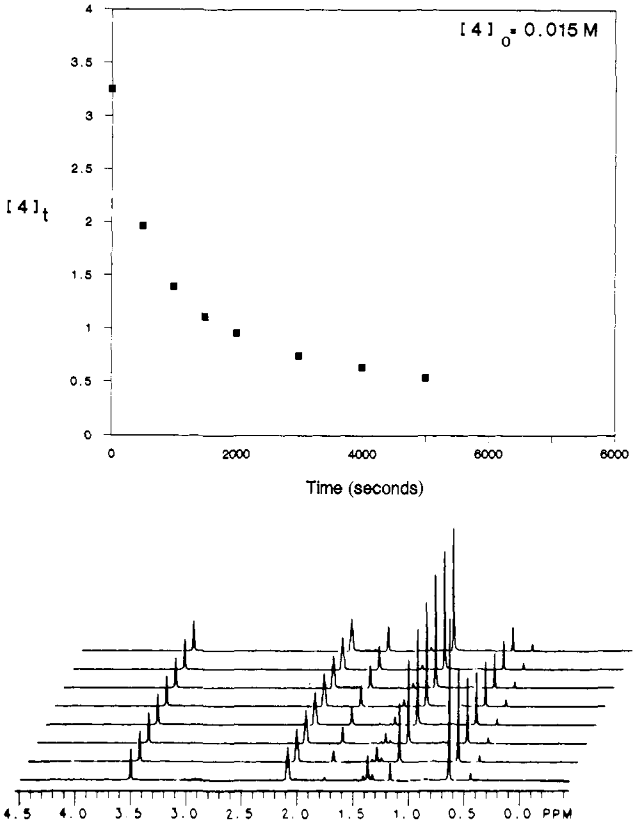


Figure 3. Plot of [4] vs time and arrayed ^1H NMR spectra (signals at 2.1 ppm are due to the residual H in C_7D_8 and at 0.4 and 3.5 ppm are added internal standard).

The formation of enyne **10** from *trans*-**4** in toluene was followed at 105.5 °C. Clean decomposition and coupling was observed with *no evidence for any intermediates* derived form the σ organic ligands. However, the reaction profile and arrayed spectra show a reaction rate distinctly deviant from first order (Figure 3): the rate of decomposition clearly slows as a function of time.

Next, the coupling reaction of **4** was performed with added PPh_3. Addition of PPh_3 (0.5–10 equiv) severely inhibited the reaction rate. At 110 °C no detectable reaction could be observed even after 20 min. Indeed, even after heating at 120 °C for 18 h with 10 equiv of PPh_3 only 33% of **4** had disappeared. The addition of dimethyl maleate also inhibited the reaction. A mixture of 5 equiv of dimethyl maleate and 1 equiv of **4** in toluene-d_8 did not react at all at 120 °C after observation for 30 min. Hence, addition of electron donor molecules strongly inhibit the rate of reaction of the coupling of *trans*-**4**.

Even though **4** decomposes to yield **10** at elevated temperatures, it must first rearrange to an intermediate capable of reductive elimination. The σ ligands must be adjacent to each other in order for reductive elimination to occur. Theoretical studies clearly show that reductive elimination from d^8 complexes must occur from a cis or trigonal planar orientation.[19] The inhibition observed

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(15) (a) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (b) Scott, W. J.; Pena, M. R.; Sward, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302. (c) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (d) Negishi, E. I.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (e) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. (f) Miyaura, N.; Suzuki, A. *J. Organomet. Chem.* **1981**, *213*, C53. (g) Miyaura, N.; Suginome, H.; Suzuki, A. *Tetrahedron Lett.* **1981**, *22*, 127.

(16) (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306. (b) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1310. (c) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892.

(17) The main problem is strong complexation of the liberated organometallic fragment, "$(Ph_3P)_2Pt$" with the alkyne moiety in both the starting material and the coupled product **10**. This is of course a function of time as well as concentration and hence results in somewhat eratic kinetics. In other studies the liberated metal species was scavanged with added $PhC{\equiv}CPh$ to avoid interference in the coupling process.[18] However, in our case this was not feasable as the existing alkyne moiety in **4**, **5**, and **10** effectively competed with *any* externally added scavenging agent.

(18) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

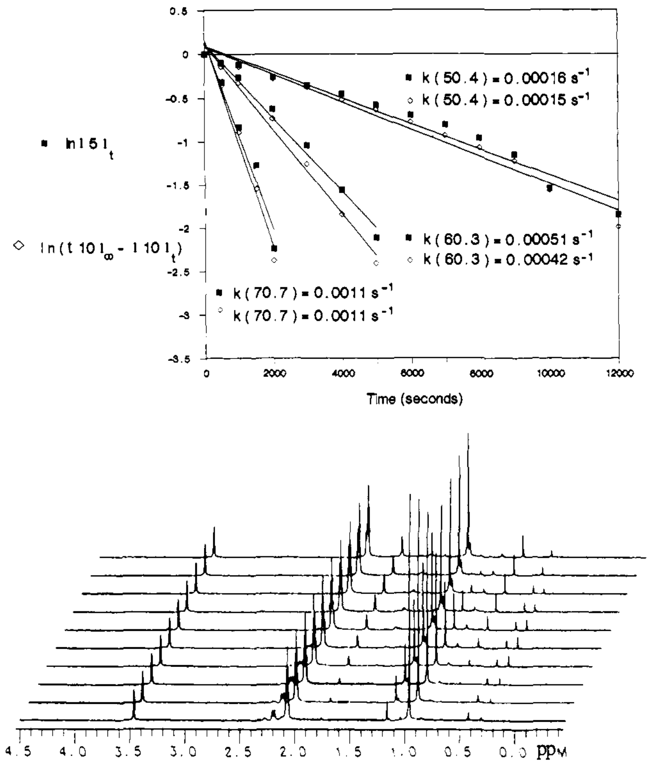


Figure 4. Top: plot of ln [**5**] and ln ([**10**]$_\infty$ − [**10**]$_t$) vs time at 50.4 °C, 60.3 °C, and 70.7 °C. Bottom: typical arrayed ^{1}H NMR spectra (signals at 3.5 ppm are due to added internal standard and at 2.1 ppm to the residual H in C_7D_8).

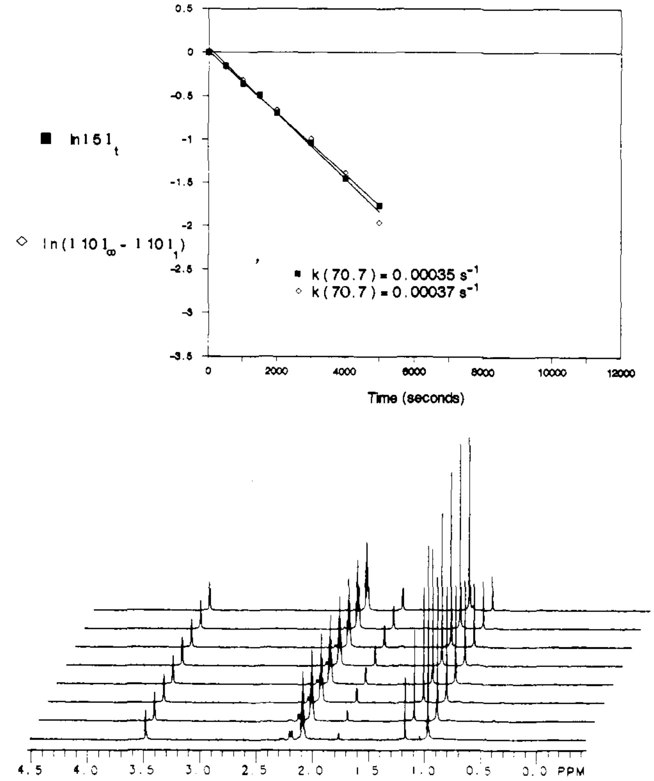
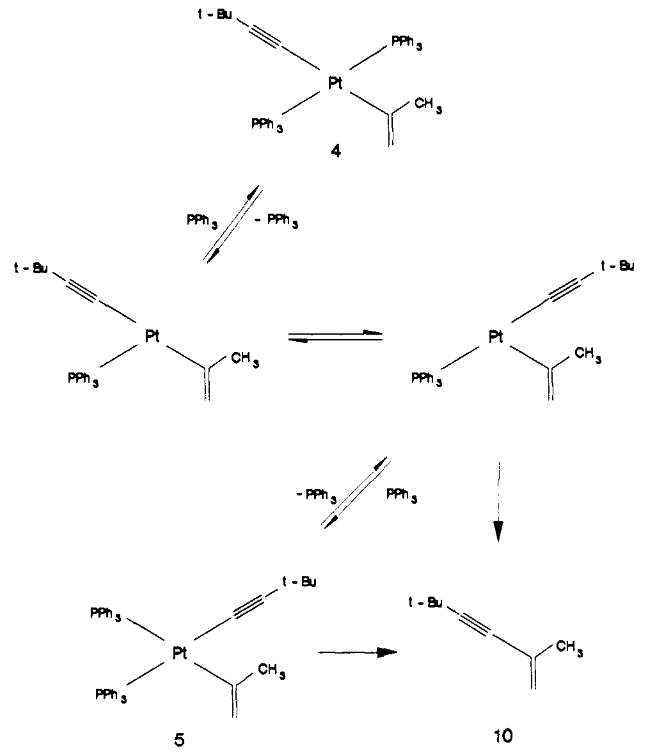


Figure 5. Top: plot of ln [**5**] and ln ([**10**]$_\infty$ − [**10**]$_t$) vs time with added Ph_3P. Bottom: arrayed ^{1}H NMR spectra.

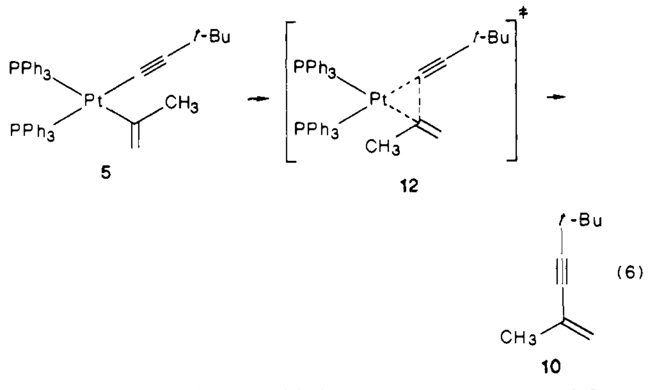
upon addition of PPh_3 is a strong indication that the rate-determining step of the coupling reaction is dissociation of PPh_3 from **4** that can provide an intermediate capable of reductive elimination (Scheme I).

Scheme I. Proposed Mode of Reductive Elimination of Trans Complex **4**



Initial experiments following the decomposition of the cis isomer **5** confirmed the idea that cis orientation of the σ organic groups would give **10** at lower temperatures. Although reproducibility was again a problem,[17] **5** decomposed to yield **10** with rates convenient to follow at 50 °C–70 °C in contrast to the temperatures required for **4** at greater than 100 °C. Lack of reproducibility could only be traced to the concentration of **5**. Therefore, a stock solution of **5** was made (9.0×10^{-3} M), and the rates were followed by ^{1}H NMR. Inspection of the arrayed spectra shows the reaction is not as clean as in the decomposition of the trans isomer **4**: a number of intermediate peaks are observed as the reaction proceeds. One identified resonance at 0.67 ppm is the trans complex **4**, the isomerization product (Figure 4). The other peaks are likely to be π olefin or π acetylene products, a result of complexation of **10** to $Pt(PPh_3)_2$. Heating the final product mixture above 100 °C causes these resonances to disappear with clean formation of more **10**.

The Arrhenius plot obtained from the rates of disappearance of **5** gave activation parameters of E_a = 21 kcal/mol and $\Delta S^\ddagger$ = −6.5 eu. The negative entropy value may indicate an ordered transition state, as described by eq 6.



PPh_3 (0.5 equiv) was added to the stock solution of **5**. In contrast to the reaction with added PPh_3 and **4**, this mixture did react at 70.7 °C albeit somewhat slower. The reaction of *cis*-**5**

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(19) (a) Akermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1979**, *182*, 59. (b) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (c) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

with added Ph_3P was remarkably "clean", and there was no cis/trans isomerization detected (Figure 5). Hence, added PPh_3 effectively stops the isomerization reaction where PPh_3 dissociation must be the first step (Scheme I). Therefore the thermal coupling reaction of the cis isomer **5** involves competitive concerted reductive elimination from activated complex **12** and simultaneous isomerization of **5** to **4** via dissociation of PPh_3.

The competing cis/trans isomerization of **5** without added PPh_3 again gave a strong indication that the trans isomer **4** was indeed the thermodynamic product. Further evidence for this was found after the addition of 50 μL of CD_3SOCD_3 to the stock solution of **5** and following the reaction progress at 70.7 °C. The enhanced solvent polarity facilitated the cis/trans isomerization as a much more significant amount of **4** (close to 50% of products) formed.

Hence, it is clear that the trans complex **4** decomposes with a rate-determining dissociation of PPh_3. The elevated temperatures required for this dissociation are a result of the reluctance of the PPh_3 trans to another PPh_3 to dissociate. By comparison, the PPh_3 dissociation required in the isomerization of *cis*-**5** to *trans*-**4**, where the two PPh_3 ligands are trans to σ-donor ligands, occurs at much lower temperatures. It is therefore the trans effect (or lack of it) of the σ-organo ligands that dictates the relative ease of PPh_3 dissociation. In the case of the trans isomer **4**, the complex must first isomerize to an intermediate capable of reductive elimination. Whereas the cis complex **5** does not have to isomerize in order to undergo reductive elimination.

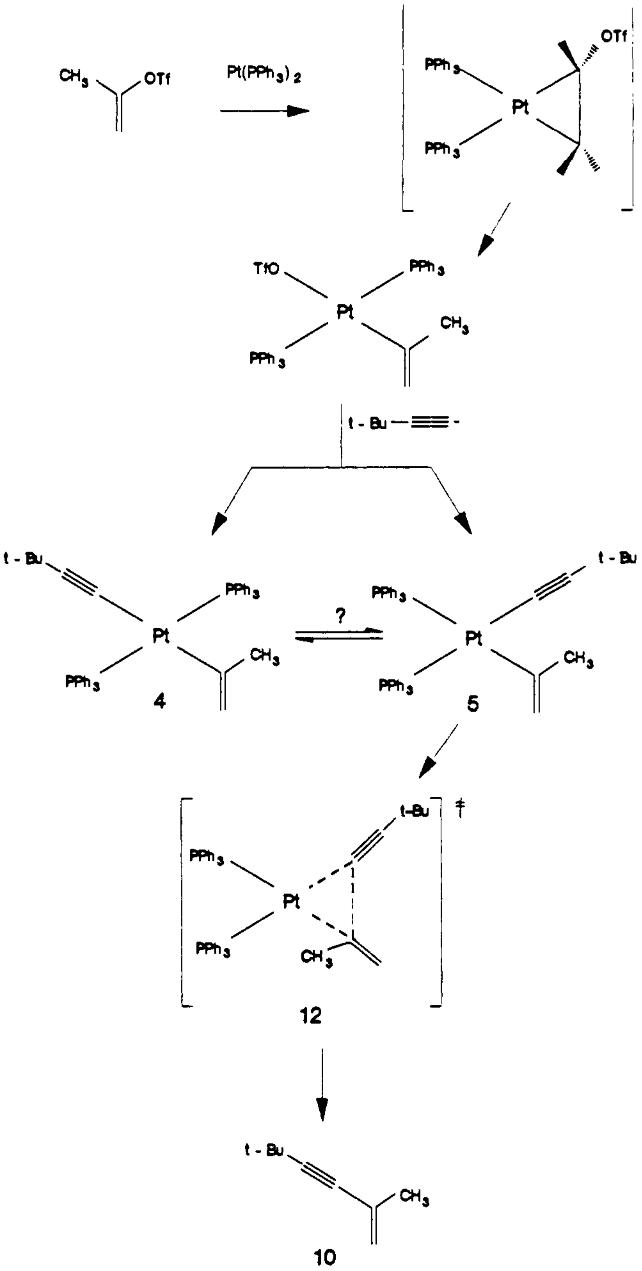
Conclusion. To the best of our knowledge this is the first example of an extensive investigation of the reductive elimination of *both* the cis and trans isomers of a mixed σ-organo group VIII metal species with *unsaturated* organic groups (sp^2 and sp-hybridized). Transmetalation reactions of the labile Pt(II) complexes as demonstrated with lithium acetylides readily give σ-alkynyl, σ-vinyl complexes. Structural data and solution chemistry results indicate that **5** (cis) is the kinetic and **4** (trans) the thermodynamic isomer. The reductive elimination of enyne from the trans complex **4** occurs via rate-determining dissociation of PPh_3 from the starting material. In contrast the rate-determining coupling of the cis complex **5** probably occurs via a concerted transition state (Scheme II) as implied from the highly strained nature of the molecular structure and indicated by activation parameters. The thermal coupling chemistry of **5** is complicated at the observed temperatures by a significant amount of isomerization to the thermodynamic isomer **4** and a lack of reproducibility of rates at varying concentrations.[17]

The mechanism of the Nickel triad metal catalyzed vinyl cross coupling reactions in general and the platinum-mediated coupling of vinyl triflates in particular can be described as in Scheme II with most of the key intermediates isolated and fully characterized. The oxidative addition of vinyl triflates yields σ-vinyl complexes such as **2** via the rate-determining formation of a π complex intermediate. This labile complex undergoes transmetalation with organometallic reagents such as $t\text{-BuC}{\equiv}\text{C}^-$ to yield both thermodynamic (**4**) and kinetic (**5**) σ-alkynyl σ-vinyl products. Reductive elimination of conjugated enyne (**10**) occurs from both isomers. Evidence has been presented showing that PPh_3 dissociation is the rate-determining step in the thermal decomposition of the trans isomer **4** to **10**. Although the data are not as straightforward, the reductive coupling of the cis isomer **5** does not seem to require dissociation of PPh_3 and occurs at much lower temperatures most likely via a concerted process. These conclusions are in accord with current ab initio and related theoretical studies.[19]

Experimental Section

General Data. All melting points are uncorrected and were measured on a Mel-Temp capillary apparatus. Infrared spectra were recorded on a Perkin-Elmer 298 and are reported in wavenumbers (cm^{-1}). ^1H NMR spectra were recorded on a Varian XL-300 spectrometer, and all chemical shifts were reported in ppm relative to internal tetramethylsilane (Me_4Si) or the proton resonance resulting from undeuteration of the NMR solvent. ^{13}C NMR spectra were obtained on a Varian XL-300 at 75 MHz and reported in ppm relative to the carbon of the deuterated NMR solvent. All ^{31}P NMR spectra were recorded on the Varian XL-300 at 121 MHz with broadband ^1H decoupling with the magnet locked on the deuterated solvent and chemical shift reported relative to external 85% H_3PO_4 at 0.00 ppm.

Scheme II. Proposed Mechanism for Pt Mediated Vinylic Cross Coupling Reaction of Vinyl Triflates



Materials. In general, solvents were either reagent grade or were purified according to known procedures.[20] 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, benzene, 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_2Cl_2) or CaH_2 (C_6D_6, C_7D_8), then freeze-pump-thawed three times, and vacuum transferred.

Alkyllithium and borohydride reagents were used as packaged: CH_3Li (Aldrich, 1.5 M, Et_2O, LiBr complex) and *n*-BuLi (Aldrich, 2.5 M, hexane). *trans*-2-Propenyl$(PPh_3)_2$PtOTf (**2**) was prepared as described in the preceeding paper.[3]

***cis*-2-Propenyl$(PPh_3)_2$Pt(*tert*-butylacetylide) (5).** To a solution of $t\text{-BuC}{\equiv}\text{CH}$ (148 mg, 1.80 mmol) in 50 mL of dry THF at −78 °C was added *n*-BuLi (480 μL, 1.20 mmol). The reaction was stirred for 35 min,

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

and the temperature was maintained. Complex **2** (956 mg, 1.00 mmol) was added all at once at −78 °C to give a suspension. The solution was slowly warmed over a period of 1 h to −30 °C to give a pink homogeneous solution. The cold solution was added to 150 mL of dry hexanes, and the solution was filtered through a plug of florisil to give a pale yellow solution, which was evaporated to dryness. Hexanes were added, the solid was broken up, and the solvent was again evaporated to dryness. Approximately 5 mL of dry acetone was added, and the solution was stored overnight in the freezer. The insoluble white solid was collected, then dissolved in a minimum of Et_2O, and filtered. Hexanes were added, and the solution was evaporated to near dryness. More hexanes were added, and the process was repeated twice more. The suspension was stored in the freezer, and the powdery white solid was collected yielding 114 mg (14%) of **5**: mp 138–140 °C dec; IR (KBr) 3048 w, 2960 w, 2917 w, 2112 w, 1587 m, 1478 m, 1430 s, 1351 m, 2151 m, 1182 m, 1174 m, 1090 s, 1025 m, 996 m, 842 m, 738 s, 692 s; ^{1}H NMR (CD_2Cl_2) δ 0.67 (s, 9 H), 1.80 (dm, $^{4}J_{PH} = 5.7$ Hz, $^{3}J_{PtH} = 47$ Hz, 3 H), 4.51 (dm, $^{4}J_{PH} = 8.3$ Hz, $^{3}J_{PtH} = 61$ Hz, 1 H), 5.25 (dm, $^{4}J_{PH} = 19.5$ Hz, $^{3}J_{PtH} = 119$ Hz, 1 H), 7.08–7.59 (aromatics, 30 H); ^{31}P NMR ($CDCl_3$) δ 13.8 (d, $^{1}J_{PtP} = 1385$ Hz), $^{2}J_{PP} = 15$ Hz), 22.5 (d, $^{1}J_{PtP} = 2758$ Hz); ^{13}C NMR δ 28.7 (br s), 31.3 (d, $^{3}J_{PC} = 4.2$ Hz, $^{2}J_{PtC} = 75$ Hz), 31.6 (s), 94.5 (dd, $^{2}J_{PC} = 143$ Hz, $^{2}J_{PC} = 20$ Hz), 112.7 (dd, $^{3}J_{PC} = 5.4$ Hz, $^{3}J_{PC} = 3.0$ Hz, $^{2}J_{PtC} = 47$ Hz), 117.1 (d, $^{3}J_{PC} = 31$ Hz), 127.3 (d, $^{3}J_{PC} = 9.5$ Hz), 127.4 (d, $^{3}J_{PC} = 10$ Hz), 129.0 (s), 129.7 (s), 132.5 (d, $^{1}J_{PC} = 51$ Hz), 133.7 (d, $^{1}J_{PC} = 43$ Hz), 134.8 (d, $^{2}J_{PC} = 11$ Hz), 134.9 (d, $^{2}J_{PC} = 11$ Hz), 161.5 (dd, $^{2}J_{PC} = 105$ Hz, $^{2}J_{PC} = 11$ Hz). Anal. Calcd for $C_{45}H_{44}P_2Pt$: C, 64.20; H, 5.28; P, 7.36. Found: C, 64.05; H, 5.40; P, 7.22. X-ray quality single crystals were obtained by slowly evaporating a solution of **5** in acetone in an open air container.

***trans*-2-Propenyl(PPh_3)$_2$Pt(*tert*-butylacetylide) (4).** $LiNH_2$ (27.4 mg, 1.19 mmol) was weighed into a dry round-bottomed flask in a drybox, and 100 mL of dry THF was added. *t*-BuC≡CH (147 mg, 1.80 mmol) was added at room temperature, and the reaction was stirred for 3 h. The cloudy solution was pumped on the high vacuum to remove any ammonia. Complex **2** (285 mg, 0.30 mmol) was added all at once, and the reaction was stirred overnight at room temperature. The homogeneous solution was added to 200 mL of dry hexane, and the solution was filtered through a plug of florisil. The THF/hexanes solution was concentrated to dryness under reduced pressure. The crude solid was then recrystallized from warm hexanes to yield 151 mg (60%) of pure **4** as colorless translucent crystals: mp 167–170 °C dec; IR (KBr) 3050 w, 2960 w, 2112 vw, 1572 w, 1480 m, 1431 s, 1248 m, 1093 s, 858 m, 739 s, 691 s; ^{1}H NMR δ 0.41 (s, 9 H), 0.97 (s, $^{3}J_{PtH} = 26$ Hz, 3 H), 4.43 (m, $^{3}J_{PtH} = 34$ Hz, 1 H), 5.24 (m, $^{3}J_{PtH} = 64$ Hz, 1 H), 7.28–7.45 (aromatics, 18 H), 7.70–7.90 (aromatics, 12 H); ^{31}P NMR δ 22.5 (s, $^{1}J_{PtP} = 3088$ Hz); ^{13}C NMR δ 29.0 (s), 31.4 (s), 95.6 (t, $^{2}J_{PC} = 17$ Hz), 116.9 (t, $^{3}J_{PC} = 3.5$ Hz), 124.5 (s, $^{2}J_{PtC} = 196$ Hz), 127.7 (t, $^{3}J_{PC} = 4.8$ Hz), 130.1 (s), 132.6 (t, $^{1}J_{PC} = 28$ Hz), 135.6 (t, $^{2}J_{PC} = 6.0$ Hz), 164.8 (t, $^{2}J_{PC} = 10$ Hz). Anal. Calcd for $C_{45}H_{44}P_2Pt$: C, 64.20; H, 5.28; P, 7.36. Found: C, 63.91; H, 5.37; P, 6.93.

***trans*-2-Propenyl(PPh_3)$_2$Pt(phenylacetylide) (8).** This complex was prepared similarly to **4**. Complex **2** (160 mg, 0.168 mmol) was added to the acetylide solution (19.1 mg, 0.83 mmol NH_2Li; 127 mg, 1.24 mmol PhC≡CH; in 30 mL of THF) and stirred overnight at room temperature. The pale yellow solution was diluted with 30 mL of hexanes and filtered through a plug of florisil. The solvent mixture was evaporated, and the complex was purified using silica gel column chromatography (toluene eluent). The column fractions were concentrated to about 1 mL, 15 mL of hexanes were added, and the solution was allowed to crystallize. Pale yellow crystals of **8** (98 mg, 68%) were collected: mp 169–170 °C dec; IR (KBr) 3048 w, 2917 w, 2102 m, 1590 m, 1574 w, 1479 m, 1431 s, 1180 w, 1082 s, 858 m, 739 s, 690 s; ^{1}H NMR δ 0.96 (s, $^{3}J_{PtH} = 25$ Hz, 3 H), 4.49 (m, $^{3}J_{PtH} = 33$ Hz, 1 H), 5.31 (m, $^{3}J_{PtH} = 64$ Hz, 1 H), 6.17 (m, 2 H), 6.83 (m, 3 H), 7.30–7.50 (aromatics, 18 H), 7.75–7.86 (aromatics, 12 H); ^{31}P NMR δ 19.9 (s, $^{1}J_{PtP} = 3065$ Hz); ^{13}C NMR δ 31.0 (s, $J_{PtC} = 27$ Hz), 115.4 (s), 116.9 (t, $^{2}J_{PC} = 17$ Hz), 117.5 (br s), 124.4 (s), 127.6 (s), 128.8 (t, $^{3}J_{PC} = 5.2$ Hz), 129.5 (br s, $^{3}J_{PtC} = 9.0$ Hz), 130.4 (s), 130.7 (s), 132.2 (t, $^{1}J_{PC} = 28$ Hz), 135.5 (t, $^{2}J_{PC} = 6.0$ Hz), 163.2 (t, $^{2}J_{P}C = 10$ Hz). Anal. Calcd. for $C_{47}H_{40}P_2Pt$: C, 65.49; H, 4.69; P, 7.19. Found: C, 65.08; H, 4.74; P, 7.18.

***trans*-2-Propenyl(PPh_3)$_2$Pt(methoxymethylacetylide) (9).** This complex was prepared on the same scale as **4** from NH_2Li (19.8 mg, 0.861 mmol), $CH_3OCH_2C{\equiv}CH$ (90 mg, 1.29 mmol), and **2** (160 mg, 0.168 mmol). This procedure gave 53 mg (38%) of **9** as a colorless crystalline solid after silica gel column chromatography (CH_2Cl_2 eluent) and crystallization from CH_2Cl eluent) and crystallization from CH_2Cl_2/hexanes: mp 166–168 °C dec; IR (KBr) 3055 w, 2920 w, 2108 m, 1572 m, 1479 m, 1431 s, 1352 m, 1183 m, 1092 s, 997 w, 745 s, 691 s; ^{1}H NMR δ 0.90 (s, $^{3}J_{PtH} = 25$ Hz, 3 H), 2.53 (s, 3H), 3.35 (t, $^{5}J_{HP} = 1.5$ Hz, $^{4}J_{PtH} = 11$ Hz, 2 H), 4.45 (m, $^{3}JP_{tH} = 34$ Hz, 1 H), 5.26 (br s, $^{3}J_{PtH} = 64$ Hz, 1 H), 7.30–7.48 (aromatics, 18 H), 7.70–7.83 (aromatics, 12 H); ^{31}P NMR δ 23.8 (s, $^{1}J_{PtP} = 3078$ Hz); ^{13}C NMR δ 30.9 (s, $^{2}J_{PtC} = 28$ Hz), 55.6 (s), 61.7 (br s, $^{3}J_{PtC} = 16$ Hz), 110.1 (br s), 117.4 (br t, $^{3}J_{PC} = 4.3$ Hz), 127.9 (t, $^{3}J_{PC} = 5.4$ Hz), 130.4 (s), 132.2 (t, $^{1}J_{PC} = 28$ Hz), 135.5 (t, $^{2}J_{PC} = 6.0$ Hz), 163.1 (t, $^{2}J_{PC} = 10$ Hz). Anal. Calcd for $C_{43}H_{40}P_2OPt$: C, 62.23; H, 4.87; P, 7.46. Found: C, 61.67; H, 4.88, P, 7.10.

5,5-Dimethyl-2-methyl-1-hexen-3-yne (10). CH_3Li (16 mL, 24 mmol, 1.5 M in Et_2O) was slowly added to 2.46 g (30.0 mmol) of *t*-BuC≡CH in 20 mL of Et_2O at −78 °C. The reaction was stirred for 20 min. Acetone (1.57 g, 24 mmol) was added to 5 mL of Et_2O, and this solution was added over 10 min to the reaction mixture. The solution was warmed to room temperature and added to 1 g of NH_4Cl in 10 mL of water in a separatory funnel. The layers were separated, and the aqueous layer was extracted twice with Et_2O. The combined organic layer was distilled until a pot temperature of 90 °C was obtained. The pot was then pumped for 10 min at 15 Torr (aspirator), and the volatile alcohol was vacuum transferred at high vacuum to yield 2.0 g (60%) of ynol **11**: IR (neat, cm^{-1}) 3360 s, 2970 s, 2865 m, 2225 w, 1458 m, 1360 s, 1273 s, 1202 s, 1161 s, 987 m, 939 m, 939 s, 854 s; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9 H), 1.43 (s, 6 H), 2.07 (s, 1 H); ^{13}C NMR δ 27.1, 31.0, 31.8, 65.1, 83.4, 90.6.

Ynol **11** (1.0 g, 7.1 mmol) was added to $KHSO_4$ (1.0 g, 7.3 mmol) in a thick-walled ampoule. The tube was sealed and heated to 100 °C overnight. The contents of the tube were extracted with pentane. The solution was dried with $MgSO_4$ and filtered, and the pentane was distilled. A few grains of CaH_2 were added, and the volatile product was vacuum transferred to yield **10** (0.34 g, 39%): IR (neat, cm^{-1}) 3097 w, 2965 s, 2215 w, 1678 w, 1615 m, 1461 m, 1351 m, 1304 s, 1201 m, 887 s; ^{1}H NMR (C_6D_6) δ 1.18 (s, 9 H), 1.80 (t, $^{4}J_{HH} = 1.2$ Hz, 3 H), 5.01 (m, 1 H), 5.34 (m, 1 H); ^{13}C NMR (C_6D_6) δ 24.0, 26.6, 31.1, 81.0, 97.6, 120.4, 127.8. The coupled product (**10**) obtained from the decomposition of **4** and **5** was identical in all respects with authentic **10**.

NMR Observation of the Thermal Decomposition of 4. Thick-walled NMR tubes were charged with recrystallized **4** (ca. 6 mg) and internal standard fluorene (ca. 1 mg), evacuated, and then filled with dry O_2 free C_7D_8 to give solutions of **4** and fluorene (ca. 10^{-2} M). The tubes were then flamed sealed. The NMR probe was thermostated using the variable temperature heater and calibrated using the Varian TEMCAL(E) program. NMR observation between −0.5 and 4.5 ppm provided a convenient window in order to follow the decomposition by observing the aliphatic resonances of **4**, **10**, and the fluorene internal standard. Decomposition of **4** with added reagents was performed in the same way. Arrayed ^{1}H NMR spectra were obtained by creating a preacquisition delay array (PAD(1) = 0, 480, 480, etc.). The time of each spectrum was calculated by adding the PAD parameter to the acquisition time (10 transients, AT = 2.00 s, 20 s total time). Concentrations of each species ([**4**] and [**10**]) with respect to time were calculated by dividing the integral of resonance by the integral of the internal standard (fluorene). This data was then plotted against time to give the reaction profiles.

NMR Observation and Kinetics of the Thermal Decomposition of 5. A C_7D_8 stock solution of **5** was made (38 mg, 5.0 mL, 9.0×10^{-3} M). NMR tubes were charged with 0.4 mL of stock solution, and reagents were added when required. The tubes were then flame sealed.

NMR data acquisition was done as with the decomposition reactions of **4**. Normalized integrals were calculated by dividing by the fluorene standard integral. $[\mathbf{5}]_t$ was calculated from the integrals from the expression: $((\mathbf{5})_t - (\mathbf{5})_\infty)/((\mathbf{5})_0 - (\mathbf{5})_\infty)$, where $(\mathbf{5})_0$ is the normalized integral of (**5**) of the first spectrum taken, $(\mathbf{5})_t$ is the normalized integral of (**5**) at the time measured, and $(\mathbf{5})_\infty$ is the integral of (**5**) at 100% reaction. In some cases measurement of $(\mathbf{5})_\infty$ required heating the solution well above the reaction temperature to complete the reaction. $([\mathbf{10}]_\infty - [\mathbf{10}]_t)$ was calculated from the integrals from the following expression: $((\mathbf{10})_\infty - (\mathbf{10})_t)/((\mathbf{10})_\infty - (\mathbf{10})_0)$. The natural log (ln) of the concentrations of $[\mathbf{5}]_t$ and $([\mathbf{10}]_\infty - [\mathbf{10}]_t)$ could then be plotted against time which provided the first-order rate constants (k = −slope) from linear least-squares analysis. Activation parameters were calculated by standard procedures.

Acknowledgment. Financial support by the NSF (CHE 8802622) and the generous loan of K_2PtCl_4 by Johnson Matthey is gratefully acknowledged.