nm, where the molecular extinction coefficient, ϵ, was calibrated to be 3204.5 M^{-1} cm^{-1} at pH 6.5. The following example illustrates the detailed procedure.

To a 1-mL disposable cuvette was added 950 μL of the NaOAc-PIPES buffer solution, 20 μL of the inhibitor solution, and 20 μL of the *p*-nitrophenyl β-D-glucoside solution (100 mM in PIPES-NaOAc buffer, pH 6.5). The solution was well mixed, and 20 μL of the β-D-glucosidase solution was injected into the cuvette to start the reaction. The reaction was monitored at 400 nm on a Beckman DU-70 photospectrometer for 45 s, and the initial hydrolysis rate was calculated. The same procedure was repeated with five other substrate concentrations. After all the initial rates were accumulated, the corresponding Lineweaver-Burk plot at that inhibitor concentration was constructed.

PIPES-NaOAc buffer was used for all the enzymes except β-D-acetyl-D-glucosaminedase, for which PIPES buffer was used.

Structure Optimization, Calculation and Modeling. The structures of inhibitors were optimized with molecular mechanics (MM2) and then with PM3 in MOPAC,[28] all equipped in a Tetronix CAChe system operated on a Macintosh IIX with an 88K acceleration board. The same parameter settings, which include keywords BFGS, RHF, and PRECISE, were employed throughout the calculation. The final structures were visualized as high-resolution graphics, and partial charge distributions were presented in both graphics and numeric formats.

Supplementary Material Available: Inhibition analysis of compounds **1**, **10**, **13**, **14a**, **17-20**, **23**, and **25-31** (7 pages). Ordering information is given on any current masthead page.

(28) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

Novel Synthesis of (η^3-Allyl)platinum(II) Complexes from Enol Triflates and Simple Olefins and Their Regiospecific Deprotonation†

Zhandong Zhong, Robert J. Hinkle, Atta M. Arif, and Peter J. Stang*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.
Received January 10, 1991

Abstract: Reaction of bis(triphenylphosphine)(ethylene)platinum(0) (**1**) with alkylvinyl triflates **2a-c** in ethylene-saturated solutions, exclusively yields the stable cationic (η^3-allyl)platinum(II) complexes **5a-c**. Solution chemistry establishes that the reaction proceeds through the intermediacy of σ-vinyl complexes **3a-c** followed by rate-limiting ethylene migratory insertion. The interaction of **3a** with propylene regiospecifically produces η^3-allyl complex **6**. The σ-vinyl adducts **3b,c** were not isolable, but were characterized in situ by NMR spectroscopy. A single-crystal molecular structure determination is reported for **5b**. Heating **6** and **5b** in the presence of triethylamine at as low as 50 °C in THF cleanly affords 2,3-dimethylbutadiene (**16**) and 2-methyl-1,3-pentadiene (**17**), respectively.

Introduction

The palladium-catalyzed olefination of vinyl electrophiles such as halides[1-3] with alkenes is an excellent method of carbon-carbon bond formation between two unsaturated carbon units. Recently, enol triflates have been utilized and prove to be superb substrates for this important transformation.[4-7] Their high selectivity and tolerance toward various functional groups have allowed for the efficient synthesis of a wide variety of functionalized conjugated dienes. However, such a 1,3-diene synthesis has been limited to "activated" alkenes having ester, amide, carbonyl, nitrile, aryl, or other electron-withdrawing substituents. The olefination with "nonactivated" simple alkenes generally results in mixtures of dienes.[3a,8]

η^3-Allyl intermediates have been proposed for the olefination as well as other transition-metal-mediated reactions.[3c,9-11] Therefore, a considerable number of η^3-allyl complexes have been synthesized in an effort to elucidate the mechanism of the catalytic reactions and develop stoichiometric processes.[12-16] Typical preparations of the group 10 metal complexes include allylic hydrogen abstraction of monoolefins, oxidative addition of allylic electrophiles, and nucleophilic addition to dienes. Direct synthesis via C-C bond formation between two unsaturated carbon units has rarely been reported. The only examples are the preparations of (η^3-allyl)palladium(II) chloride dimers from Li_2PdCl_4, alkenes, and vinylmercurials.[17] Such a synthesis for monomeric (η^3-allyl)platinum(II) complexes is hitherto unknown.

Of the three group 10 metals, only (η^3-allyl)palladium(II) compounds have been extensively studied.[13a,16] Trost and coworkers examined the formation of the palladium complexes from olefins and their nucleophilic addition reactions.[16] The chemistry of (η^3-allyl)platinum(II) complexes is not well-documented.[12] The

† Dedicated to Professor Michael Hanack on the occasion of his 60th birthday.

(1) Sato, Y.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1989**, *54*, 4738.
(2) O'Connor, B.; Zhang, Y.; Negishi, E.; Luo, F.-T.; Cheng, J.-W. *Tetrahedron Lett.* **1988**, *29*, 3903.
(3) (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (b) Heck, R. F. *Pure Appl. Chem.* **1981**, *53*, 2323. (c) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.
(4) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1502.
(5) Scott, W. J.; McMurray, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.
(6) (a) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1987**, *28*, 3039. (b) Harnisch, W.; Morera, E.; Ortar, G. *J. Org. Chem.* **1985**, *50*, 1990. (c) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271.
(7) Scott, W. J.; Pena, M. R.; Sward, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302.
(8) Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898.
(9) Kurosawa, H. *J. Organomet. Chem.* **1987**, *334*, 243.
(10) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(11) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.
(12) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6.
(13) (a) Kurosawa, H.; Ohnishi, H.; Emoto, M.; Chatani, N.; Kawasaki, Y.; Murai, S.; Ikeda, I. *Organometallics* **1990**, *9*, 3038. (b) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813.
(14) Halterman, R. L.; Nimmons, H. L. *Organometallics* **1990**, *9*, 273.
(15) Brown, D. G.; Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 1231.
(16) (a) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 3435. (b) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3426, 3416. (c) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.
(17) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 6718.

0002-7863/91/1513-6196$02.50/0 © 1991 American Chemical Society

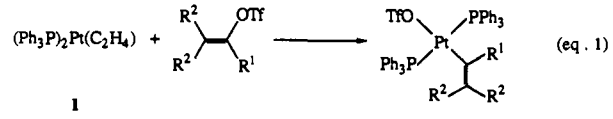
Table I. Summary of Crystallographic Data for **5b**

molecular formula	$C_{43}H_{41}O_3F_3P_2SPt$
molecular weight	951.90
crystal system	orthorhombic
space group	*PCA*21
space group no.	29
cell dimensions	
a, Å	21.734 (2)
b, Å	14.741 (2)
c, Å	25.402 (5)
α, deg	90.00
β, deg	90.00
γ, deg	90.00
V, Å^3	8138.1
Z	8.0
d_{calcd}, g/cm^3	1.554
crystal dimensions, mm	0.25 × 0.22 × 0.18
abs coeff, cm^{-1}	81.710
radiation; γ, Å	Cu; 1.5418
no. of rflns measd	7579
2θ range, deg	4.00–65.00
scan technique	$\theta/2\theta$
scan width	0.8000 + 0.1400 tan θ
data collection position	bisecting, $\omega = 0$
decay correction	anisotropic
min abs correction	39.2409
max abs correction	99.5213
ignorance factor, *P*	0.06
no. of observations, $I > 3.00\sigma(I)$	5367
no. of variables	804
data:param	6.675
shift:error	0.017
R factor	0.0520
R_w factor	0.0589
highest peak in final diff Fourier	0.867 e/Å^3
max ρ in final diff fourier	4432.050 e/Å^3
error in observation of unit weight	1.0008

current study describes the novel formation of cationic (η^3-allyl)platinum(II) complexes via sp^2 C–H bond activation of the precoordinated simple olefins, and their stereo- and regiospecific deprotonation to yield substituted butadienes.

Results and Discussion

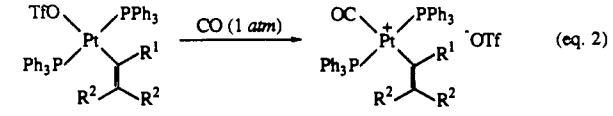
σ-Vinyl Complex Formation. The first step in olefination and other palladium-catalyzed cross-coupling reactions is the oxidative addition of the electrophilic substrates to to give a σ-complex.[10,18-21] Because of their high reactivity, however, (σ-vinyl)palladium(II) triflate species have never been isolated and characterized. Recently, the greater stability of the platinum system has allowed for the efficient synthesis of the covalent (σ-2-propenyl)platinum(II) triflate (**3a**) by the reaction of triflate **2a** with **1** in toluene (eq 1).[19] Argon degassing during the course of the reaction expelled the ethylene of the platinum precursor to give the product



1

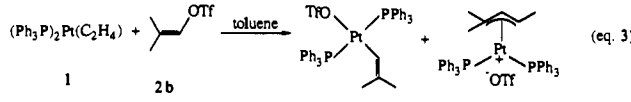
2a: $R^1 = CH_3$, $R^2 = H$; **3a**: $R^1 = CH_3$, $R^2 = H$;
b: $R^1 = H$, $R^2 = CH_3$; **b**: $R^1 = H$, $R^2 = CH_3$;
c: $R^1 = tert$-Bu, $R^2 = H$. **c**: $R^1 = tert$-Bu, $R^2 = H$.

in 80–90% yield. NMR observation of the reaction of triflates **2b,c** in C_6D_6 revealed that the analogous σ-vinyl complexes **3b,c** were quantitatively formed under the same conditions. Unfortunately, repeated attempts to isolate and purify each of these complexes were fruitless due to their instability in polar solvents. The in situ ^{31}P NMR spectrum of complex **3b** displays a singlet at 27.0 ppm with ^{195}Pt satellites ($^1J_{PtP}$ = 3223 Hz). Moreover, the ^1H NMR spectrum shows resonances at 0.99 (methyl), 1.24 (methyl), and 5.34 (vinyl) ppm. However, the low solubility of the product prevented the acquisition of a ^{13}C NMR spectrum. Similarly, the ^{31}P spectrum of **3c** shows a singlet at 26.5 ppm with ^{195}Pt satellites ($^1J_{PtP}$ = 3482 Hz). The key σ-vinyl resonances (^1H NMR) appear at 0.99 (*tert*-butyl), 4.38 (*cis*-H, $^3J_{PtH}$ = 80.0 Hz), and 4.99 (*trans*-H, $^3J_{PtH}$ = 171.6 Hz) ppm. Although the *tert*-butyl resonance is not coupled to ^{195}Pt, the pseudotriplets of the vinyl resonances clearly indicate that the ligand is σ-bonded. Fortunately, the complex was soluble enough to obtain a $^{13}C\{^1H\}$ spectrum, which showed the key signals at 142.6 (α) and 115.9 (β) ppm for the vinylic carbons. These (σ-vinyl)platinum(II) compounds were further verified by reaction with carbon monoxide to give the cationic (σ-vinyl)platinum carbonyls **4a–c**, the details of which have been reported elsewhere (eq 2).[22]

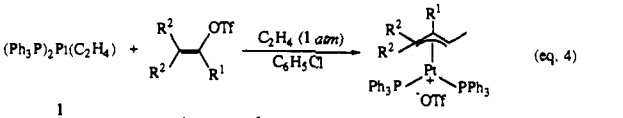


3a: $R^1 = CH_3$, $R^2 = H$; **4a**: $R^1 = CH_3$, $R^2 = H$;
b: $R^1 = H$, $R^2 = CH_3$; **b**: $R^1 = H$, $R^2 = CH_3$;
c: $R^1 = tert$-Bu, $R^2 = H$. **c**: $R^1 = tert$-Bu, $R^2 = H$.

η^3-Allyl Complex Formation. The interaction of triflates **2a–c** with **1** without continual argon degassing yielded very different results. Reaction of triflate **2b** with **1** resulted in a small amount of white precipitate, which was collected by filtration and recrystallized in CH_2Cl_2/toluene/hexane (complex **5b**, 11% yield); in addition, the mother liquor contained σ-vinyl complex **3b** (eq 3), which was converted to the carbonyl complex **4b** (eq 2).[22a] NMR observation of these reactions under various conditions then revealed that adding **1** to ethylene-saturated C_6H_5Cl solutions of the corresponding triflates **2a–c** produced complexes **5a–c** cleanly (eq 4). Each of these η^3-allyl complexes was isolated and fully characterized by IR, MS (FAB), multinuclear NMR, and elemental analysis.



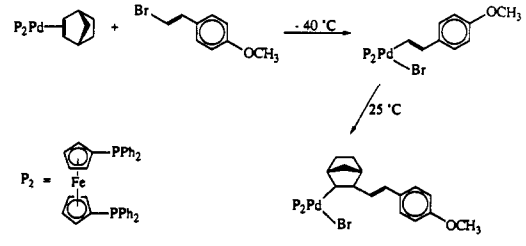
1 **2b** **3b** **5b**



1

2a: $R^1 = CH_3$, $R^2 = H$; **5a**: $R^1 = CH_3$, $R^2 = H$;
b: $R^1 = H$, $R^2 = CH_3$; **b**: $R^1 = H$, $R^2 = CH_3$;
c: $R^1 = tert$-Bu, $R^2 = H$. **c**: $R^1 = tert$-Bu, $R^2 = H$.

(18) (a) Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353. (b) Brown, J. M.; Cooley, N. A.; Price, D. W. *J. Chem. Soc., Chem. Commun.* **1989**, 458. It was reported that the oxidative addition styryl bromide to palladium(0) norbornene complex, followed by the norbornene insertion yielded a (σ-alkyl)palladium(II) bromide:



(19) (a) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, 3347. (b) Kowalski, M. H.; Arif, A. M.; Stang, P. J. *Organometallics* **1988**, *7*, 1227.

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

(21) (a) Stille, J. K.; Scott, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (b) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.

(22) Preparations and spectral properties of **8a,b**: (a) Stang, P. J.; Zhong, Z.; Kowalski, M. H. *Organometallics* **1990**, *9*, 833. (b) Zhong, Z.; Stang, P. J.; Arif, A. M. *Organometallics* **1990**, *9*, 1703. Preparation, spectral properties, and crystal structure of **8c**: Stang, P. J.; Hinkle, R. J.; Zhong, Z. Unpublished results.

Table II. Selected Bond Distances (Å) for **5b**[a]

Pt–P1	2.280 (5)	C4–C5	1.57 (3)
Pt–P2	2.317 (5)	C4–C6	1.60 (4)
Pt–C2	2.23 (2)	P1–C7	1.84 (2)
Pt–C3	2.21 (2)	P1–C13	1.82 (2)
Pt–C4	2.25 (2)	P1–C19	1.82 (2)
C1–C2	1.47 (3)	P2–C25	1.79 (2)
C2–C3	1.33 (4)	P2–C31	1.81 (2)
C3–C4	1.38 (3)	P2–C37	1.88 (2)

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

Table III. Selected Bond Angles (deg) for **5b**[a]

P1–Pt–P2	98.6 (2)	C1–C2–C3	126. (2)
P1–Pt–C2	167.1 (6)	Pt–C3–C2	73. (1)
P1–Pt–C3	134.6 (8)	Pt–C3–C4	74. (1)
P1–Pt–C4	101.7 (6)	C2–C3–C4	128. (2)
P2–Pt–C2	93.6 (5)	Pt–C4–C3	70. (1)
P2–Pt–C3	125.6 (6)	Pt–C4–C5	109. (1)
P2–Pt–C4	159.2 (6)	Pt–C4–C6	122. (2)
C2–Pt–C4	65.9 (8)	C3–C4–C5	131. (3)
Pt–C2–C1	133. (2)	C3–C4–C6	114. (2)
Pt–C2–C3	72. (2)	C5–C4–C6	107. (2)

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

The IR spectra unambiguously identify them as cationic due to the presence of strong absorptions at ca. 635 and 1270 cm^{-1}, which are assigned to the S=O stretch of the anionic triflates.[23] The ^{19}F NMR shows a singlet resonance at −79.2 ppm in CD_2Cl_2.

The ^{31}P NMR spectra display a characteristic AB splitting pattern, along with ^{195}Pt satellites, resulting from the presence of two inequivalent phosphorus ligands. The ^{13}C NMR spectra are complex due to the inequivalent phosphorus nuclei, but all of the alkyl and allyl carbon resonances (except for the central allylic carbon of **5a**, which is obscured by the aromatic resonances) are resolved. The ^{1}H NMR spectra displayed more complex multiplets for each of the protons on the allyl moiety with a wide range of mixed coupling observed. Assignment of the syn and anti protons was based on homonuclear ^{1}H decoupling experiments and comparison to known compounds.[24]

Confirmation of the η^3-allyl structure was made by X-ray diffraction analysis of a single crystal of **5b** grown from CH_2Cl_2/Et_2O. An ORTEP of the cationic portion of complex **5b** is shown in Figure 1. A summary of the crystallographic data and selected bond distances and bond angles is shown in Tables I–III, respectively. The structure is significantly distorted from the ideal square-planar geometry. Steric repulsion between the two bulky phosphine ligands results in a P(1)–Pt–P(2) bond angle of 98° rather than 90°. All methyl substituents are coplanar with the η^3-allyl carbons except C(5), which lies 0.78 (3) Å out of the allyl plane and away from the platinum center. Also, the plane formed by the three carbons of the allyl moiety intersects the plane formed by the two phosphines and the platinum center (P–Pt–P) at a 114.6° angle instead of 90°; this is within the typical range of (η^3-allyl)platinum(II) structures and maximizes the bonding interactions between the allyl moiety and the metal d orbitals.[12] The bond distances in the allyl ligand are as follows: C(2)–C(3) = 1.33 (4) Å, and C(3)–C(4) = 1.38 (3) Å. The allyl carbon–Pt bond distances, C(2)–Pt, C(3)–Pt, and C(4)–Pt of 2.23 (2) Å, 2.21 (2) Å, and 2.25 (2) Å, respectively, are similar to others in analogous (η^3-allyl)platinum(II) complexes.[25,26]

Mechanistic Consideration: Reactions. We have recently reported the likely mechanism for the oxidative addition of vinyl triflates to the platinum ethylene complex.[19] The current η^3-allyl complex formation deserves further consideration, however. The NMR observation of reactions of triflates **2a–c** with **1** under

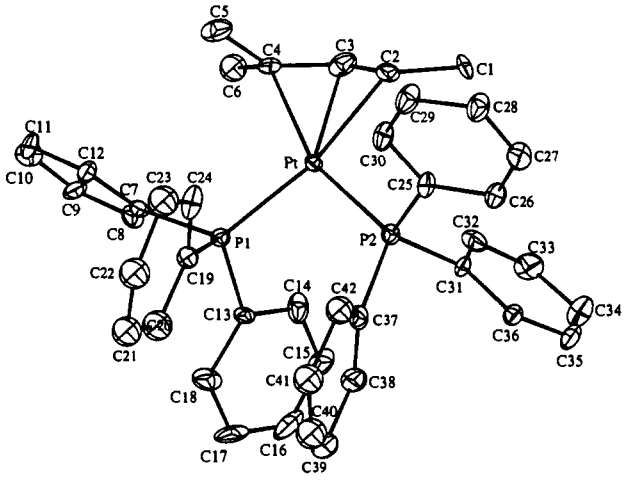
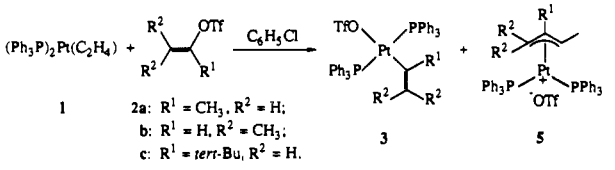


Figure 1. ORTEP of (η^3-allyl)platinum(II) complex **5b**. The triflate anion is omitted for clarity.

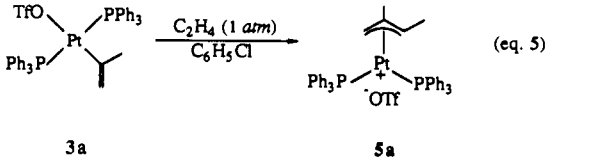
Table IV. Products Formed from the Reactions of **1** and **2**



R^1	R^2	σ-vinyl:η^3-allyl (3:5)
CH_3	H	73:27
H	CH_3	43:57
tert-Bu	H	0:100

[a] All reactions were monitored by ^{31}P NMR (unlocked) at room temperature. Product ratios were determined by integration of the corresponding resonances.

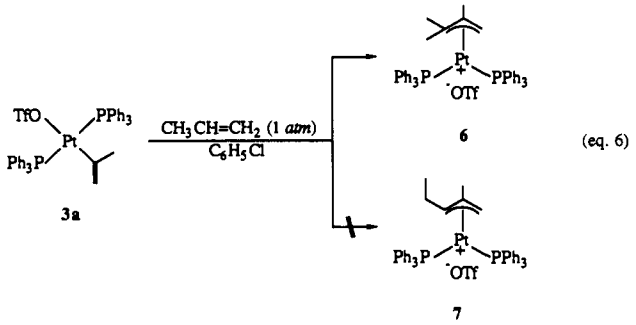
different conditions revealed that the σ-vinyl and η^3-allyl complexes can be selectively produced. As indicated above, continuous argon degassing leads exclusively to the σ-vinyl complexes. However, reaction of triflate **2a** in chlorobenzene with no argon degassing yielded a 73:27 mixture of **3a**/**5a** as shown by integration of ^{31}P NMR resonances (Table IV). Under similar conditions, triflate **2b** afforded a 43:57 ratio of **3b**/**5b**. The most sterically demanding triflate, **2c**, provided the allyl complex exclusively at room temperature, suggesting that, at least for this triflate, the η^3-allyl complex is the thermodynamic product, and this is likely due to the lower steric repulsion between the bulky *tert*-butyl ligand and the phosphines in the allyl product vs the σ-vinyl product. Passing ethylene (only 15 min) through the solutions containing the σ-vinyl and η^3-allyl complexes (vide supra), the 73:27 mixture **3a**/**5a** was changed to a 31:69 ratio, whereas the 43:57 mixture of **3b**/**5b** gave **5b** as the sole product. The above experiments indicate that the σ-vinyl complex is likely an intermediate. This hypothesis was verified by reacting the solution of previously isolated pure **3a** with ethylene; complete conversion to **5a** was realized (eq 5). Further



(eq. 5)

support was provided by the regiospecific synthesis of another η^3-allyl complex **6**; this was accomplished by reaction of **3a** with propylene under atmospheric pressure (eq 6). It should be noted that the other possible regioisomer **7** was never observed. This result is in direct contrast to those obtained with palladium. Heck and co-workers found that with α-substituted vinyl bromides, the dienes produced were the result of carbon–carbon bond formation between the vinyl bromides and the least substituted carbon of

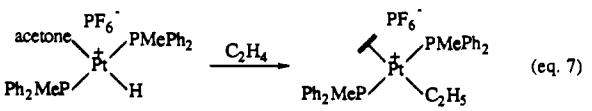
(23) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17.
(24) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 357.
(25) Smith, J. D.; Oliver, J. D. *Inorg. Chem.* **1978**, *17*, 2585.
(26) Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 142.



the unactivated alkenes.[3,8] This implies that for palladium, the η^3-allyl intermediates leading to the diene products would be analogous to **7**, not **6** which we observe.

Kinetics. Because triflate **2c** gave the allyl complex **5c** exclusively without the presence of excess ethylene, the course of this particular reaction was followed by both ^{1}H and ^{31}P NMR at room temperature in C_6D_6 solution (0.025 M) until 75% completion. The plot of [ethylene] vs time and the arrayed proton spectrum are shown in Figures 2 and 3, respectively. Several observations have been made that provide considerable insight into the nature of this unique reaction. The data clearly indicate that the reaction proceeds through a two-stage process. In the first stage, essentially complete ethylene replacement occurs upon the addition of triflate **2c**; within 15 min the free-ethylene (5.24 ppm) concentration quickly reaches its maximum (0.023 M). It is generally assumed that a low concentration of "$Pt(Ph_3P)_2$" exists in solutions of $(Ph_3P)_2Pt(C_2H_4)$ (**1**).[27] Indeed, a trace amount of free ethylene is present in C_6D_6 solutions of **1**. The addition of triflate **2c** prevents the "recoordination" of the free ethylene to the platinum center, causing the ethylene concentration to increase dramatically. In addition, the ^{31}P NMR spectral array shows that the σ-vinyl complex **3c** was concomitantly formed as the predominant species. Other than a trace amount of the η^3-allyl complex **5c**, no other intermediate was observed. In the second stage, the ethylene concentration slowly decreases with concurrent decrease in the σ-complex, and increases in the η^3-allyl proton resonances (3–4 ppm). The above data demonstrate that ethylene replacement is facile, whereas the ethylene incorporation into the σ-vinyl complex appears to be the rate-limiting process.

The exact mode of ethylene incorporation unfortunately remains unclear. Olefin insertion into the M-C bond of palladium(II) and platinum(II) complexes is well-established and generally proceeds through olefin precoordination.[10,28-30] Moreover, both palladium(II) and platinum(II) are known to be able to coordinate a number of olefins, particularly cationic (π-olefin)(σ-organo)-platinum(II).[31] Clark and Kurosawa studied the olefin insertion into Pt–H bonds and reported the formation of *trans*-$[Pt(C_2H_5)(PPh_2Me)_2(C_2H_4)]^+PF_6^-$ (eq 7).[32] In the case of covalent



vinyl platinum(II) triflate, the exceptional lability of the triflate ligand provides a ready vacant site for olefin coordination to form a *trans*-(σ-vinyl)(π-olefin)platinum(II) species, such as **9** (Scheme I). In order for olefin migratory insertion to occur, an isomerization step would have to be invoked via phosphine dissociation so that the two combining ligands (π-olefin and σ-vinyl) are cis to each other.[10] In the presence of excess elemental sulfur, the interaction of the isolated σ-complex **3a** with ethylene at low

(27) Birk, J. P.; Halpern, J.; Pickard, A. L. *J. Am. Chem. Soc.* **1968**, *90*, 4491.
(28) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735 and references therein.
(29) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076.
(30) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.
(31) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269 and references therein.
(32) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1972**, *11*, 1275.

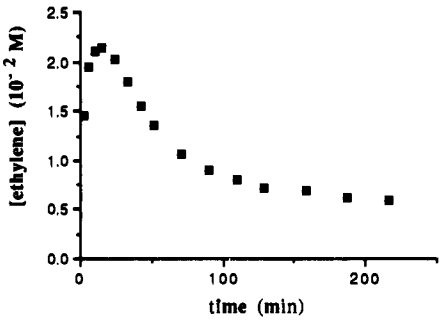


Figure 2. Plot of ethylene concentration (M) vs time (min) after addition of 3,3-dimethyl-1-butenyl triflate (**2c**) to $(Ph_3P)_2Pt(C_2H_4)$ (**1**).

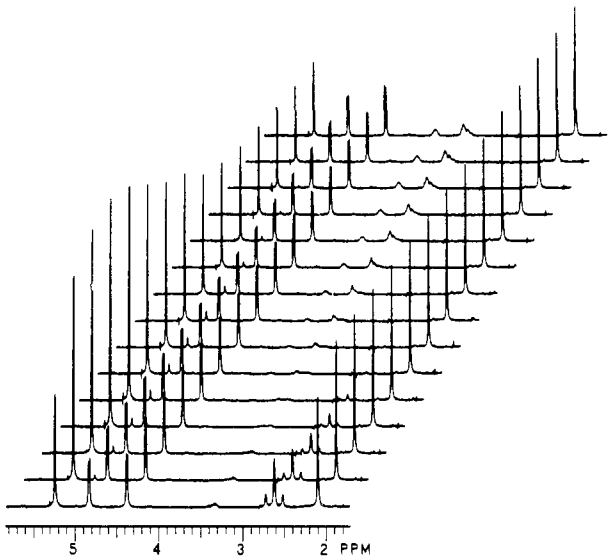
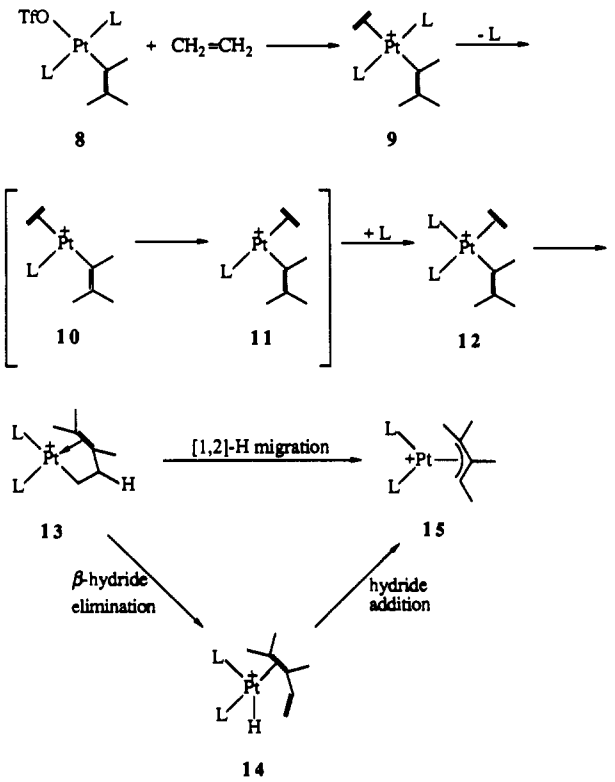


Figure 3. ^{1}H spectral array of reaction between 3,3-dimethyl-1-butenyl triflate (**2c**) and $(Ph_3P)_2Pt(C_2H_4)$ (**1**) at room temperature. See Experimental Section for more details.

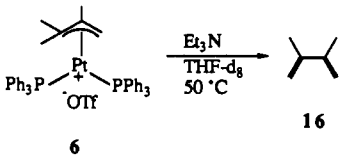
Scheme I. Likely Mechanism of (η^3-Allyl)platinum(II) Complex Formation



temperature indeed produces $Ph_3P{=}S$ (43.1 ppm in ^{31}P spectrum); neither **3a** nor **5a** reacts with sulfur at room temperature.

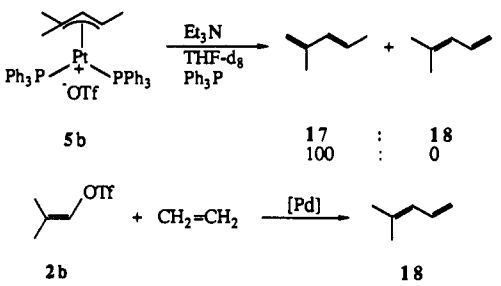
The formation of the η^3-allyl moiety also involves a 1,2-H shift. Metal hydrides and β-hydride elimination are well precedented in the literature.[10] Complex **13** could rearrange to the η^3-allyl complex either via direct 1,2-hydrogen migration or through a platinum hydride intermediate, such as **14**. Although all attempts to observe a hydride intermediate by ^1H NMR at low temperature were unsuccessful (spectral window −25 to +15 ppm), its presence as a short-lived intermediate cannot be ruled out. It is worth noting that a recent report by Brown and Cooley showed that olefin insertion took place upon the oxidative addition of styryl bromide to palladium(0) norbornene complex without further 1,2-H shift to form the η^3-allyl complex.[18]

Formation of Substituted Butadienes. Having demonstrated the novel carbon–hydrogen bond activation of unactivated olefins to afford monomeric (η^3-allyl)platinum(II) complexes, we directed our attention toward their deprotonation to yield substituted butadienes. First, complex **6** was deprotonated with 2 equiv of Et_3N in THF-d_8. Heating at 50 °C for 6 h led to 2,3-dimethyl-1,3-butadiene (**16**) cleanly (eq 8).



(eq. 8)

Because only a single diene could result from the deprotonation of **6**, **5b** was subjected to similar conditions. Reaction of **5b** with 1.1 equiv of Et_3N in THF-d_8 at 50 °C for 4 h provided 2-methyl-1,3-pentadiene (**17**) and trace unidentified impurities. The addition of 1 equiv of Ph_3P resulted in a clean reaction, but still only produced **17**, while the "normal" olefination product **18** (eq 9), which would result from the palladium-catalyzed reaction, was not observed (eq 10).[3,8]



(eq. 9)

(eq. 10)

There are two possible means of producing diene **17**: (a) the direct deprotonation of the methyl groups at the disubstituted end of the η^3-allyl moiety; or (b) deprotonation of the monosubstituted end to give **18** followed by isomerization to **17**. Control experiments in which pure **17** was heated at 50 °C in the presence of Ph_3P and Et_3N showed no tendency to isomerize, nor did a mixture of **17** and **18** (75/25) under the same conditions undergo any changes. The pure diene **17** and the mixture of **18** and **17** were also stable in the presence of added platinum ethylene complex **1**. Thus, diene **17** must be generated by the direct deprotonation of **5b**.

If based solely on statistics, the allyl ligand would lead to a 67:33 mixture of **17**/**18**. However, we only observed the formation of **17**. This surprising result could be attributed to the structural features of complex **5b**. The solid-state structure indicates that C5 of the allyl moiety lies out of the plane formed by C1–C2–C3–C4–C6 and away from the Pt center (vide supra). It is therefore more accessible to the base. As shown in Scheme II, there are two major resonance structures for the η^3-allyl moiety. The most stable structure is A with tertiary carbon C4 bearing the positive charge, and thus more capable of stabilizing the negative charge developed during the deprotonation at C5.

Conclusions. We have demonstrated that covalent (σ-vinyl)platinum(II) and cationic (η^3-allyl)platinum(II) complexes can be selectively produced in the reaction of alkylvinyl triflates with $(PPh_3)_2Pt(C_2H_4)$ (**1**), depending upon the substrate structure and reaction conditions. While removing liberated ethylene affords the labile σ-vinyl complexes, a higher ethylene concentration leads to the stable η^3-allyl complexes exclusively. Although isolation of the (σ-vinyl)platinum(II) for further characterization was not successful, it can be prepared in situ for other reactions, such as olefin insertion and ligand substitution of the labile triflate group. These reactions provide a novel synthesis of η^3-allyl complexes—with likely regiospecificity with unsymmetrical olefins—via the C–C bond formation between two unsaturated carbon units. Solution chemistry studies established that oxidative addition of vinyl triflates yields the σ-vinyl complexes via facile replacement of the precoordinated olefin ligands. The subsequent rate-limiting olefin insertion and 1,2-H shift then afford the (η^3-allyl)platinum(II) complexes. These η^3-allyl complexes readily undergo thermal decomposition to yield 1,3-dienes under mild conditions. This study demonstrates the first examples of olefination of vinyl substrates with "nonactivated" olefins, in which the "isomerized" substituted butadienes are regiospecifically obtained.

Scheme II. Resonance Structures of η^3-Allyl Moiety of **5b**

Experimental Section

General Data. All melting points are uncorrected and were measured on a Mel-Temp capillary apparatus. Infrared spectra were obtained from KBr pellets on a Mattson Polaris FT-IR spectrometer and measured in wavenumbers (cm^{-1}). All NMR spectra were recorded on a Varian XL-300 NMR spectrometer. The ^1H NMR spectra were obtained at 300 MHz, and all chemical shifts are reported in ppm relative to external tetramethylsilane (Me_4Si) at 0.00 ppm or the proton resonance resulting from residual hydrogens of the NMR solvents: $CDCl_3$ (7.24 ppm), CD_2Cl_2 (5.32 ppm), and THF-d_8 (3.58 and 1.73 ppm). The ^{13}C NMR spectra were obtained at 75 MHz and resonances are reported in ppm relative to the carbon of the deuterated NMR solvents: $CDCl_3$ (77.0 ppm), CD_2Cl_2 (53.8 ppm), and C_6D_6 (128.0 ppm). The ^{31}P NMR spectra were obtained at 121 MHz with broad band ^1H decoupling with the magnet locked on the deuterated solvent and chemical shift reported relative to external 85% H_3PO_4 at 0.0 ppm. The ^{19}F NMR spectra were obtained at 282 MHz, and resonances are reported relative to external $CFCl_3$ at 0.0 ppm.

Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Fast-atom-bombardment mass spectra were obtained with a VG Analytical 7050-E mass spectrometer. The X-ray crystal structure was obtained with a CAD4 diffractometer at ambient temperature (16 ± 1 °C).

Materials. In general, solvents were either reagent grade or were purified according to known procedures.[33] Hydrocarbon solvents (hexanes, benzene, and toluene) were stirred over H_2SO_4 and distilled from CaH_2. Chlorobenzene and triethylamine were dried over t.h.e. desiccant (EM) for at least 2 days.

Deuterated NMR solvents (Aldrich or Cambridge) were purified by drying over CaH_2 ($CDCl_3$) and then vacuum transfered, or directly used as packaged without purification (C_6D_6, THF-d_8, CD_2Cl_2).

Trifluoromethanesulfonic acid (3 M) was converted to the anhydride (Tf_2O), by the method of Anderson.[34] *N,N*-Diisobutyl-2,4-dimethyl-3-pentylamine, was purchased from Fluka or recovered from the triflic acid salt and then distilled in vacuo. Ph_3P was recrystallized from hexanes and dried in vacuo. Vinyl triflates were prepared according to known procedures.[35] Propylene and ethylene (Matheson) were directly used without purification.

K_2PtCl_4 (Johnson-Matthey) was used as shipped without purification. $(Ph_3P)_2Pt(C_2H_4)$ was prepared according to a standard literature procedure.[36]

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

(34) Anderson, A. G. Ph.D. Dissertation, The University of Utah, Salt Lake City, UT, 1977.

(35) Stang, P. J.; Hanack, M. C.; Subramanian, L. R. *Synthesis* **1982**, 85. Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.

Preparation of Covalent σ-(2-Methyl-1-propenyl)platinum(II) Triflate (3b). The toluene (15 mL) solution of 2-methyl-1-propenyl triflate (**2b**) (58 mg, 0.28 mmol) in a 25-mL three-neck round-bottom flask was degassed by bubbling argon for 15 min, and charged with $(Ph_3P)_2Pt(C_2H_4)$ (**1**) (107 mg, 0.143 mmol). The solution was stirred for 1.5 h with bubbling argon, during which time it remained clear and colorless. After filtration, dry hexanes were slowly added to afford the white microcrystalline solid **3b**. The product was filtered, washed with hexanes, and dried in high vacuo. The yield was 90 mg (68%). The ^1H NMR spectrum indicated immediate decomposition in polar solvents such as CD_3NO_2, $CDCl_3$, CD_2Cl_2, and acetone: mp 184–185 °C dec, FAB MS 774 ([M − CF_3SO_3]$^+$, 45, 719 ([M − CF_3SO_3 − C_4H_7]$^+$, 74), 457 ([M − CF_3SO_3 − C_4H_7 − Ph_3P]$^+$, 63); IR 3054 (w), 2914 (w), 2896 (w), 2844 (w), 1614 (w), 1573 (m), 1435 (s), 1292 (s), 1243 (s), 1164 (s), 1098 (s), 1032 (s), 999 (m), 744 (s), 693 (s), 636 (s).

NMR Observation of the Reaction between 2-Methyl-1-propenyl Triflate (2b) and $(Ph_3P)_2Pt(C_2H_4)$ (1). A slow stream of argon was blown through a 5-mm NMR tube containing complex **1** (30.2 mg, 4.04 × 10^{-2} mmol). The C_6D_6 (0.5 mL) solution of **2b** (7.1 μL, *d* 1.28 g/mL, 4.4 × 10^{-2} mmol) was added via a syringe. Bubbling argon through the solution for 15 min resulted in a small amount of a white solid. ^1H and ^{31}P NMR were taken of the mixture: ^1H NMR (C_6D_6) δ 0.99 (br s, 3 H, CH_3), 1.24 (br s, 3 H, CH_3), 5.34 (br s, $^2J_{PtH}$ = 141.1 Hz, 1 H, CH=); ^{31}P NMR (C_6D_6) δ 27.0 (s, $^1J_{PtP}$ = 3223 Hz).

NMR Observation of the Reaction between 3,3-Dimethyl-2-butenyl Triflate (2c) and $(Ph_3P)_2Pt(C_2H_4)$ (1). The reaction was carried out as above with **2c** (8.8 μL, *d* 1.257 g/mL, 4.8 × 10^{-2} mmol) and **1** (32.4 mg, 4.33 × 10^{-2} mmol) in C_6D_6 (0.5 mL). A clear yellow solution was obtained. ^1H, ^{31}P, ^{13}C NMR spectra were taken of the solution: ^1H NMR (C_6D_6) δ 0.89 (s, 9 H, *t*-Bu), 4.38 (br s, $^3J_{PtH}$ = 80.0 Hz, 1 H, (*Z*)-CH_2=), 4.99 (br s, $^3J_{PtH}$ = 171.6 Hz, 1 H, (*E*)-CH_2=), 7.1 (m, 18 H, aromatics), 7.9 (m, 12 H, aromatics); ^{31}P NMR (C_6D_6) δ 26.5 (s, $^1J_{PtP}$ = 3482 Hz); ^{13}C NMR (C_6D_6) δ 33.0 (s, CH_3), 115.9 (t, $^3J_{PC}$ = 4.8 Hz, CH_2=), 142.6 (t, $^2J_{PtC}$ = 8.4 Hz, *t*-BuC=).

General Procedure for the Preparation of (η^3-Allyl)platinum(II) Complexes: (η^3-$(CH_3)CHC(CH_3)CH_2)Pt(Ph_3P)_2(OTf)$ (5a). The solution of 2-propenyl triflate (**2a**) (52 mg, 0.27 mmol) in dry chlorobenzene (5 mL) was degassed through three freeze–pump–thaw cycles, and was saturated with ethylene by bubbling for 15 min. Complex **1** (100 mg, 0.134 mmol) was added all at once. The solution was stirred for 2 h while the slow flow of ethylene was maintained. The reaction was quenched by hexanes (10 mL). The recovered solid was recrystallized in CH_2Cl_2/toluene/hexanes to give 86 mg (65%) of feathery microcrystalline product **5a**, which contains 1/2 CH_2Cl_2 solvate according to ^1H NMR: mp 177–178 °C dec; IR 3062 (w), 1481 (m), 1434 (s), 1268 (vs), 1222 (m), 1149 (s), 1096 (s), 1031 (s), 998 (w), 747 (m), 695 (s), 636 (s); ^1H NMR (CD_2Cl_2) δ 1.07 (m, 3 H, CH_3), 1.99 (br s, J_{PtH} = 63.9 Hz, 3 H, CH_3), 2.71 (dd, J_{PH} = 3.0 Hz, J_{PH} = 8.4 Hz, J_{PtH} = 35.8 Hz, 1 H, *anti*-CH), 3.60 (m, 1 H, *syn*-CH), 3.90 (m, 1 H, $(CH_3)CH$), 7.0–7.5 (m, 30 H, aromatics); ^{31}P NMR (C_6H_5Cl) δ 15.1 (d, $^2J_{PP}$ = 8.6 Hz, $^1J_{PtP}$ = 3656 Hz, 1 P), 17.2 (d, $^2J_{PP}$ = 8.6 Hz, $^1J_{PtP}$ = 3954 Hz, 1 P); ^{13}C NMR (CD_2Cl_2) δ 16.3 (s, J_{PtC} = 34.4 Hz, CH_3), 25.6 (s, J_{PtC} = 34.9 Hz, CH_3), 62.1 (d, J_{PC} = 30.5 Hz, J_{PtC} = 98.1 Hz, CH_2), 87.0 (d, J_{PC} = 29.3 Hz, J_{PtC} = 99.4 Hz, $(CH_3)CH$), 121.4 (q, $^1J_{FC}$ = 321.2 Hz, CF_3), 129.1 (d, overlapping, *meta*-C), 129.2 (d, overlapping, *meta*-C), 130.3 (d, $^1J_{PC}$ = 2.8 Hz, $^2J_{PtC}$ = 32.1 Hz, *ipso*-C), 131.1 (d, $^1J_{PC}$ = 3.4 Hz, $^2J_{PtC}$ = 33.9 Hz, *ipso*-C), 131.8 (s, *para*-C), 131.9 (s, *para*-C), 133.8 (m); FAB MS 788 (M$^+$, 100), 719 ([M − C_5H_9]$^+$, 56), 526 ([M − Ph_3P]$^+$, 15), 457 ([M − C_5H_9 − Ph_3P]$^+$, 55). Anal. Calcd for $C_{42.5}H_{40}O_3F_3ClP_2SPt$: C, 52.07; H, 4.11. Found: C, 52.35; H, 4.14.

(η^3-$(CH_3)CHC(t\text{-}Bu)CH_2)Pt(Ph_3P)_2(OTf)$ (5c): Method A. This compound was prepared according to the general procedure from $(Ph_3P)_2Pt(C_2H_4)$ (**1**) (100 mg, 0.12 mmol) and 3,3-dimethyl-1-butenyl-2-triflate (**2c**) (62 mg, 0.27 mmol) in toluene (5 mL) to yield 82 mg (63%) of product: mp 215–216 °C dec; IR 3055 (w), 2967 (w), 1597 (w), 1553 (w), 1434 (w), 1414 (m), 1274 (vs), 1150 (m), 1098 (m), 1032 (s), 758 (m), 744 (m), 695 (s), 637 (s); ^1H NMR (CD_2Cl_2) δ 0.88 (s, 9 H, *t*-Bu H), 1.3 (m, 3 H, CH_3), 2.9 (dm, 1 H, *anti*-CH=), 3.6 (m, 1 H, *syn*-CH=), 4.1 (m, 1 H, $(CH_3)CH$), 7.2–7.5 (m, 30 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 15.9 (d, $^2J_{PP}$ = 9.1 Hz, $^1J_{PtP}$ = 3634 Hz, 1 P), 17.9 (d, $^2J_{PP}$ = 9.1 Hz, $^1J_{PtP}$ = 3923 Hz, 1 P); ^{13}C NMR ($CDCl_3$) δ 17.7 (d, J_{PC} = 4.4 Hz, J_{PtC} = 38.0 Hz, CH_3), 29.4 (s, J_{PtC} = 27.5 Hz, *t*-Bu), 36.3 (s, J_{PtC} = 23.7 Hz, *t*-Bu C), 57.7 (d, J_{PC} = 30.0 Hz, J_{PtC} = 92.0 Hz), 81.4 (d, J_{PC} = 28 Hz, J_{PtC} = 97.0 Hz), 121.4 (q, $^1J_{FC}$ = 320.0 Hz), 128–129 (m. *meta*-C), 129.7 (s, $^2J_{PtC}$ = 32.0 Hz, *ipso*-C), 130.4 (s, $^2J_{PC}$ = 32.0 Hz), 131.4 (d, $^2J_{PC}$ = 20.0 Hz, *meta*-C), 133–134 (m, *ortho*-C), 142.0 (s, J_{PtC} = 29.0 Hz); FAB MS 830 (M$^+$, 100), 719 ([M − C_8H_{15}]$^+$, 24), 568 ([M − Ph_3P]$^+$, 17), 457 ([M − C_8H_{15} − Ph_3P]$^+$, 45). Anal. Calcd for $C_{45}H_{45}O_3F_3P_2SPt$: C, 55.16; H, 4.63. Found: C, 55.05; H, 4.61.

Method B. $(Ph_3P)_2Pt(C_2H_4)$ (**1**) (100 mg, 0.134 mmol) was placed in a 5.0-mL conical vial equipped with a spin vane and charged with 1.5 mL of toluene. Triflate **2c** (62 mg, 0.27 mmol) was added via syringe at room temperature. After 5 min a precipitate formed, which then quickly dissolved. The mixture was stirred for 6 h at room temperature; a small amount of a light yellow precipitate was present. The mixture was transferred to a 25-mL round-bottom flask and the solvent removed in vacuo. The solid was then passed through a plug of unactivated Florisil with CH_2Cl_2 and the solvent removed in vacuo. This was repeated once more, yielding 66 mg (52%) of a light yellow powder. The spectral properties of this compound are identical with those obtained in Method A.

Preparation of (η^3-$(CH_3)_2CC(CH_3)CH_2)Pt(Ph_3P)_2(OTf)$ (6). The suspension of σ-vinyl triflate platinum(II) complex **3a** (96 mg, 0.11 mmol) in dry chlorobenzene (5 mL) was degassed through three freeze–pump–thaw cycles. Propylene was slowly bubbled through the mixture for 0.5 h, resulting in a clear solution. The flask was sealed with a rubber septum and stirred for 24 h. Addition of dry hexanes (10 mL) produced a yellow oil. The oil was recrystallized from CH_2Cl_2/toluene/hexanes to yield 67 mg (65%) of white microcrystalline complex **6**, which contains 1/4 CH_2Cl_2 solvate according to ^1H NMR: mp 200–201 °C dec; IR 3074 (w), 3058 (w), 1481 (m), 1434 (s), 1371 (w), 1271 (vs), 1223 (m), 1148 (s), 1096 (s), 1065 (w), 1030 (s), 998 (w), 744 (m), 694 (s), 637 (s); ^1H NMR (CD_2Cl_2) δ 1.02 (dd, J_{PH} = 3.4 Hz, J_{PH} = 7.5 Hz, 3 H, CH_3), 1.27 (br d, J_{PH} = 3.5 Hz, 3 H, CH_3), 1.98 (br s, J_{PtH} = 61.0 Hz, 3 H, CH_3), 2.72 (ddd, J_{PH} = $^2J_{HH}$ = 1.6 Hz, J_{PH} = 9.5 Hz, J_{PtH} = 34.8 Hz, 1 H, *anti*-H), 3.3 (m, 1 H, *syn*-H), 7.1–7.5 (m, 30 H, aromatics); ^{31}P NMR (CD_2Cl_2) δ 16.9 (d, $^2J_{PP}$ = 8.5 Hz, $^1J_{PtP}$ = 3766 Hz, 1 P), 21.0 (d, $^2J_{PP}$ = 8.5 Hz, $^1J_{PtP}$ = 3948 Hz, 1 P); ^{13}C NMR (CD_2Cl_2) δ 21.1 (br s, CH_3), 22.3 (s, J_{PtC} = 33.8 Hz, CH_3), 23.9 (d, J_{PC} = 5.1 Hz, J_{PtC} = 37.6 Hz, CH_3), 63.9 (d, J_{PC} = 30.0 Hz, J_{PtC} = 116.7 Hz, CH_2), 95.2 (dd, J_{PC} = 36.0 Hz, J_{PC} = 64.4 Hz, $C(CH_3)_2$), 121.4 (q, $^1J_{FC}$ = 321.3 Hz, CF_3), 123.9 (t, J_{PC} = 3.0 Hz, J_{PtC} = 27.8 Hz, $C(CH_3)$), 129.0 (s, *para*-C), 129.2 (s, *para*-C), 129.7 (d, $^1J_{PC}$ = 54.5 Hz, $^1J_{PtC}$ = 30.2 Hz, *ipso*-C), 130.8 (d, $^1J_{PC}$ = 55.3 Hz, $^2J_{PtC}$ = 34.5 Hz, *ipso*-C), 131.7 (d, $^1J_{PC}$ = 2.5 Hz, *meta*-C), 131.8 (d, $^1J_{PC}$ = 2.3 Hz, *meta*-C), 133.8 (dd, $^2J_{PC}$ = 10.9 Hz, $^2J_{PC}$ = 22.2 Hz, *ortho*-C), 134.2 (dd, $^2J_{PC}$ = 11.0 Hz, $^2J_{PC}$ = 22.8 Hz, *ortho*-C); FAB MS 802 (M$^+$, 100), 719 ([M − C_6H_{11}]$^+$, 80), 540 ([M − Ph_3P]$^+$, 34), 457 ([M − C_6H_{11} − Ph_3P]$^+$, 39). Anal. Calcd for $C_{43.3}H_{42}O_3F_3ClP_2SPt$: C, 53.38; H, 4.30. Found: C, 53.03; H, 4.29.

Interaction of *trans*-(2-Propenyl)$Pt(Ph_3P)_2(OTf)$ (3a) with Ethylene in the Presence of Sulfur. *trans*-(2-Propenyl)$Pt(Ph_3P)_2(OTf)$ (**3a**) (18.0 mg, 1.98 × 10^{-2} mmol) was placed in a thin-wall 5-mm NMR tube and charged with 0.5 mL of C_6D_5Cl. Sulfur (13.5 mg, 0.421 mmol) was then added. No reaction was observed according ^{31}P NMR spectrum. The solution was cooled to −40 °C while C_2H_4 was bubbled through the solution for 15 min. The NMR tube was then sealed with a rubber septum and warmed up to room temperature. The ^{31}P NMR spectrum showed the formation of triphenylphosphine sulfide (Ph_3P=S) at 43.1 ppm, as well as the η^3-allyl complex **5a** and some other unidentified products.

Reaction of 2-Methyl-1-propenyl Triflate (2b) with $(Ph_3P)_2Pt(C_2H_4)$ (1). Complex **1** (486 mg, 0.650 mmol) was weighed into a three-neck round-bottom flask in a dry box. Toluene (10 mL) was degassed through three freeze–pump–thaw cycles and transferred to the flask. The solution was light brown. A degassed solution of 2-methyl-1-propenyl triflate (**2b**) (250 mg, 1.25 mmol) in toluene (5 mL) was slowly added. The mixture was stirred overnight. The resulting brown solid was separated from the solution by filtration and washed with dry hexanes. Recrystallization from CH_2Cl_2/toluene/hexanes gave 70 mg (11%) of compound **5b** as white microcrystals: mp 179–180 °C dec; IR 3076 (m), 2895 (w), 1481 (m), 1436 (s), 1268 (vs), 1223 (m), 1149 (s), 1096 (m), 1068 (w), 1031 (s), 999 (w), 753 (m), 637 (s), 695 (s); ^1H NMR (CD_2Cl_2) δ 1.11 (dd, J_{PH} = 4.1 Hz, J_{PH} = 7.9 Hz, 3 H, CH_3), 1.24 (m, 3 H, CH_3), 1.33 (dd, J_{PH} = 2.5 Hz, J_{PH} = 4.8 Hz, 3 H, CH_3), 3.23 (m, 1 H, $(CH_3)CH$), 4.86 (d, $^3J_{HH}$ = 12.5 Hz, J_{PtH} = 53.4 Hz, 1 H, CH), 7.1–7.5 (m, 30 H, aromatics); ^{31}P NMR (CD_2Cl_2) δ 19.0 (d, $^2J_{PP}$ = 6.9 Hz, $^1J_{PtP}$ = 4001 Hz, 1 P), 20.0 (d, $^2J_{PP}$ = 6.9 Hz, $^1J_{PtP}$ = 4078 Hz, 1 P); ^{13}C NMR (CD_2Cl_2) δ 16.5 (d, J_{PC} = 3.2 Hz, CH_3), 22.6 (d, J_{PC} = 4.9 Hz, J_{PtC} = 34.9 Hz, CH_3), 24.2 (d, J_{PC} = 2.6 Hz, CH_3), 76.8 (d, J_{PC} = 29.5 Hz, J_{PtC} = 91.8 Hz, $(CH_3)C$), 96.7 (d, J_{PC} = 26.6 Hz, J_{PtC} = 82.9 Hz, $(CH_3)_2C$), 111.9 (t, J_{PC} = 3.5 Hz, J_{PtC} = 20.9 Hz, CH), 121.4 (q, $^1J_{FC}$ = 320.8 Hz, CF_3), 128.9 (d, $^3J_{PC}$ = 3.3 Hz, *meta*-C), 129.0 (d, $^3J_{PC}$ = 3.2 Hz, *meta*-C), 129.3 (d, $^1J_{PC}$ = 20.2 Hz, *ipso*-C), 130.0 (dd, $^3J_{PC}$ = 18.0 Hz, $^1J_{PC}$ = 36.6 Hz, *ipso*-C), 131.58 (s, *para*-C), 131.61 (s, *para*-C), 134.0 (d, $^2J_{PC}$ = 2.5 Hz, $^3J_{PtC}$ = 23.7 Hz, *ortho*-C), 134.1 (d, $^2J_{PC}$ = 2.4 Hz, $^3J_{PtC}$ = 22.6 Hz, *ortho*-C); FAB MS 802 (M$^+$, 40), 719 ([M −

(36) Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1968**, *18*, 121.

$C_6H_{11}]^+$, 100), 457 ([M − C_6H_{11} − $Ph_3P]^+$, 39). Anal. Calcd for $C_{43}H_{41}O_3F_3P_2SPt$: C, 54.26; H, 4.34. Found: C, 54.40; H, 4.36.

Carbon monoxide was bubbled through the mother liquors for 2 h, leading to a white precipitate. Workup as above afforded 313 mg (50%) of carbonyl product **4b** as white microcrystals.

Single-Crystal X-ray Diffraction Analysis of 5b. Colorless single crystals of **5b** were obtained as thin plates by diffusion crystallization from CH_2Cl_2/Et_2O. X-ray data were collected on a CAD4 automated diffractometer as summarized in Table I. The structure was solved by treating the phenyl rings of the Ph_3P as rigid bodies and by other standard heavy-atom techniques using the UCLA Crystallographic Package.

NMR Observation of η^3-Allyl Complex 5c Formation. Complex **1** (11.3 mg, 1.51 × 10^{-2} mmol) was placed in a thin-wall 5-mm NMR tube equipped with a rubber septum. Previously degassed C_6D_6 (0.6 mL) was added via syringe along with toluene (1.1 mg, 1.2 × 10^{-2} mmol) as an internal standard (δ 2.1 ppm). A ^1H NMR spectrum was obtained at room temperature, and then 3,3-dimethyl-2-butenyl triflate was added via syringe. The tube was inverted five times to mix the reagents, and then the reaction was monitored by ^1H NMR. The arrayed spectra were recorded with preacquisition delays of 0, 212, 212, 212, 512, 512, 512, 512, 1112, 1112, 1112, 1112, 1712, 1712, 1712 s, and the acquisition time for each spectrum was 48 s.

Reaction of 6 with Et_3N. Complex **6** (13.3 mg, 1.40 × 10^{-2} mmol) was placed in a thin-wall 5-mm NMR tube and charged with 0.45 mL of THF-d_8. The tube was sealed with a rubber septum and Et_3N (3.9 μL, *d* 0.726 g/mL, 2.8 × 10^{-2} mmol) was then added via syringe. The mixture was heated in a 65 °C oil bath for 6 h, leading to a yellow heterogeneous solution. The ^1H NMR showed the clean production of 2,3-dimethyl-1,3-butadiene (**16**).

Reaction of 5b with Et_3N in the Absence of Ph_3P. Complex **5b** (12.8 mg, 1.35 × 10^{-2} mmol) was weighed into a thin-wall 5-mm NMR tube and 0.50 mL of THF-d_8 was added via syringe. The tube was sealed with a rubber septum and Et_3N (2.0 μL, *d* 0.726 g/mL, 1.5 × 10^{-2} mmol) was added via syringe. The septum was wrapped with liberal amounts of parafilm, and the mixture was heated at about 50 °C in an oil bath for 4 h. The clear solution turned orange within 5–10 min. At the end of the reaction, a precipitate was present. The ^1H NMR spectrum of the heterogeneous mixture showed the formation of 2-methyl-1,3-pentadiene (**17**) and trace impurities with resonances between 6.5 and 6.8 ppm.

Reaction of 5b with Et_3N in the Presence of Ph_3P. The reaction was performed according to the above procedure with **5b** (13.1 mg, 1.38 × 10^{-2} mmol), Et_3N (2.1 μL, *d* 0.726 g/mL, 1.5 × 10^{-2} mmol), and Ph_3P (4.0 mg, 1.5 × 10^{-2} mmol) in 0.50 mL of THF-d_8. The ^1H NMR spectrum of the heterogeneous mixture revealed the clean formation of **17**.

Isomerization Reaction of 2-Methyl-1,3-pentadiene (17) and 4-Methyl-1,3-pentadiene (18) in the Presence of Et_3N and Ph_3P. Ph_3P (6.3 mg, 2.4 × 10^{-2} mmol) was placed in a thin-wall 5-mm NMR tube. THF-d_8 (0.50 mL) was then added and the tube was sealed with a rubber septum. Et_3N (3.3 μL, *d* 0.726 g/mL, 2.4 × 10^{-2} mmol) was added via syringe followed by the pure diene **17** (2.6 μL, *d* 0.718 g/mL, 2.4 × 10^{-2} mmol). The septum was then wrapped with liberal amounts of parafilm. The solution was placed in a 60 °C oil bath for 24 h. The 75/25 mixture of **17** and **18** was also subjected to the same conditions. No isomerization of the pure diene or the mixture dienes had occurred according to ^1H NMR spectroscopy.

Isomerization Reaction of 2-Methyl-1,3-pentadiene (17) and 4-Methyl-1,3-pentadiene (18) in the Presence of $(Ph_3P)_2Pt(C_2H_4)$ (1), Ph_3P, and Et_3N. Platinum ethylene complex **1** (11.8 mg, 2.4 × 10^{-2} mmol) and Ph_3P (6.3 mg, 2.4 × 10^{-2} mmol) were weighed into a thin-wall 5-mm NMR tube. THF-d_8 (0.50 mL) was added and the tube was sealed with a rubber septum. Et_3N (3.3 μL, *d* 0.726 g/mL, 2.4 × 10^{-2} mmol) was added via syringe followed by the pure diene **17** (2.6 μL, *d* 0.718 g/mL, 2.4 × 10^{-2} mmol). The septum was wrapped with liberal amounts of parafilm. The resulting yellow solution was then heated in a 60 °C oil bath for 24 h. The 75/25 mixture of **17**/**18** was also subjected to the same conditions. The ^1H NMR spectra of both solutions were obtained. No isomerization of dienes was observed.

Acknowledgment. We are grateful to the NSF for financial support (CHE 8802622 and CHE 9101767) and to Johnson-Matthey, Inc., for the generous loan of K_2PtCl_4.

Supplementary Material Available: Details of the single-crystal X-ray structure of **5b** (32 pages); observed and calculated structure factors for **5b** (19 pages). Ordering information is given on any current masthead page.

Thianthrene 5-Oxide as a Mechanistic Probe for Assessing the Electronic Character of Oxygen-Transfer Agents

Waldemar Adam,* Wolfgang Haas,† and Braj B. Lohray‡

Contribution from the Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, Germany. *Received December 11, 1990*

Abstract: Thianthrene 5-oxide (SSO) was employed to assess the electronic nature of oxygen-transfer reagents: Those oxidants that attack preferentially the sulfide "S" site to give the bis(sulfoxide) SOSO are electrophilic in their reactivity; those that predominantly react at the sulfoxide "SO" site to give the sulfone SSO_2 are nucleophilic. The X_{SO} parameter was introduced, defined as the mole fraction of SSO_2 product (SO attack), for which strongly electrophilic oxygen-transfer agents (typically acidified hydroperoxides and hypochlorite) take near-zero values and strongly nucleophilic ones (typically basified hydroperoxides and superoxide) near-unity. On the X_{SO} scale, ozone and peroxy acids are as expected electrophilic oxidants and dioxiranes are significantly more nucleophilic but more electrophilic than carbonyl oxides. The latter exhibit pronounced nucleophilic reactivity toward SSO, which is in agreement with their observed reactivity. Free radicals, e.g., *t*-BuOO•, display very high electrophilicity in their oxygen-transfer propensity by reacting essentially exclusively at the S site. Control experiments have established that such radicals do not act through electron transfer to afford the $SSO^{\bullet+}$ radical cation, although the latter, generated either by photosensitized or chemical oxidation, behaves toward dioxygen strongly electrophilic. While the SSO probe provides a realistic measure of the electronic nature of oxygen-transfer agents, caution should be excercised when preferential complexation of the reagent at the S or SO site of SSO takes place or when electron transfer is involved with SSO to produce the $SSO^{\bullet+}$ or $SSO^{\bullet-}$ radical ions. Also, during the in situ generation of transient oxidants, several species of different electronic character might act simultaneously and the composite X_{SO} value erroneously express the reactivity of the oxidant in question. In such suspicious cases, control experiments are obligatory to acquire meaningful X_{SO} data with SSO.

Oxygen-transfer reactions are of wide interest in peroxide chemistry[1] due to their importance in biological oxidations as well as in industrial applications. For example, in the recent past, model studies have been made to understand the mechanism of oxygen

† Present address: Dr. W. Haas, Consortium für Elektrochemische Industrie, GmbH, Zielstattstraße 20, W-8000 München 70, Germany.

‡ Present address: Dr. B. B. Lohray, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

(1) Kropf, H., Ed. *Organische Peroxo-Verbindungen, Methoden der Organischen Chemie (Houben-Weyl)*; Georg Thieme Verlag: Stuttgart, 1988; Vol. E13, Parts 1 and 2.

0002-7863/91/1513-6202$02.50/0 © 1991 American Chemical Society