Articles

Mechanism of the Metal-Mediated Carbalkoxylation of Vinyl Electrophiles. 1. Preparation, Molecular Structure, and Alcoholysis of Vinylic Acyl Platinum(II) Complexes†

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The two key steps of the nickel triad metal-mediated carbalkoxylation of vinyl electrophiles were investigated using platinum complexes: (a) carbonyl insertion of σ-vinyl Pt(II) halides and (b) alcoholysis of vinylic acyl Pt(II) complexes. NMR spectral studies suggest that the carbonyl insertion into the alkenyl C—Pt bond proceeds via the formation of a σ-vinyl Pt(II) carbonyl species, followed by phosphine dissociation and migratory insertion. While the resulting vinylic acyl Pt(II) halides are unreactive toward alcohols, the corresponding cationic triflate complexes readily undergo alcoholysis in the absence of base. Kinetic and NMR spectral studies establish that the alcoholysis of vinylic acyl Pt(II) triflate complexes occurs via a preequilibration to form a reactive, trigonal-planar intermediate, followed by the rate-determining trans–cis isomerization and nucleophilic attack of alcohols prior to the facile reductive elimination to the α,β-unsaturated carboxylic esters. Both the covalent and cationic vinylic acyl Pt(II) complexes were isolated and fully characterized. A single-crystal molecular structure determination is reported for *trans*-$(CH_3)_2C{=}CCOPt(PPh_3)_2I$ (**9b**). Complex **9b** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.924 (5) Å, b = 20.354 (10) Å, c = 15.606 (7) Å, β = 105.93 (3)°, and Z = 4. The structure was solved and refined to R = 0.036 and R_w = 0.045 by using 3245 observed independent reflections. Comparison with the vinyl precursor clearly indicates the stronger trans influence for the acyl moiety than for the vinyl ligand.

Introduction

The carbonyl group has long been known as one of the most versatile functionalities available to synthetic chemists, because of its ability to undergo reactions leading to C–C bond formation.[1] Carbonylation with transition-metal complexes have become an efficient method for the direct introduction of the carbonyl moiety into organic molecules.[2,3] There have been a number of reports on the transition-metal-mediated carbonylation of electrophilic substrates. These include the syntheses of aldehydes,[4] ketones,[5,6] carboxylic acids[7-10] and derivatives[6,7b,8d,11-20] via single carbonylation, and keto esters[21,22] and keto amides[23,24] via double carbonylation.

Particular attention has been given to the carbalkoxylation of vinyl electrophiles to yield α,β-unsaturated carboxylic esters. The reaction requires a stoichiometric quantity of base and mostly employs group 10 metal (Ni, Pd, Pt) complexes as catalysts.[2] Much of the research in catalytic carbalkoxylation uses halides as substrates.[7b,8d,12-14a,15,16a,17-20] However, triflates have recently emerged and proven to be excellent precursors for this important transformation.[25-28]

Most of the existing mechanistic insight into the carbalkoxylation process is the result of investigations with aryl halides.[21a,29,30] In principle, there are two main pathways; each involving the oxidative addition of electrophilic substrates to zerovalent nickel triad metals as the first step. The second step involves CO insertion into the M–C bond to form an acylmetal species, which upon base-assisted

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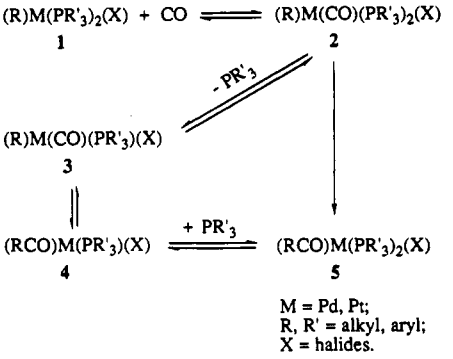
alcoholysis affords the carboxylic ester. Alternatively, an alkoxycarbonyl intermediate is generated, either by CO insertion into the M–O bond of a transition-metal alkoxide or by the nucleophilic addition of the alkoxide anion to the CO ligand of a transition-metal carbonyl. The carboxylic ester is then obtained by reductive elimination.

Considerable effort has been devoted to the understanding of the first pathway.[21a,29,30] Many studies have shown that the function of the base is to deprotonate the alcohol to give the alkoxide anion which is a stronger nucleophile than the alcohol itself.[21a,29] However, the available data do not enable one to discern whether the nucleophilic attack occurs at the carbonyl carbon or at the metal center. Although the acyl carbonyl group has generally been assumed to be the site of nucleophilic addition, evidence for such a reaction route has rarely been found. In contrast, direct attack at metal centers by nucleophiles is ubiquitous,[31,32] which would lead to the formation of σ-acyl σ-alkoxy M(II) species. It has been reported that σ-acetyl σ-aryloxy M(II) (M = Ni, Pd) complexes, prepared by the carbonyl insertion into the M–C of the alkyl M(II) aryloxides, readily undergo reductive elimination of aryl acetate.[33] Unfortunately, there are no unambiguous data for the analogous acyl alkoxy complexes. While most studies with aryl halide substrates have focused on the facility of the acyl species, there is no pertinent information regarding the intermediacy of the alkoxycarbonyl complexes. Milstein reported the preparation of the methoxycarbonyl benzyl Pd(II) complex by the transmetalation of benzyl Pd(II) chloride with methoxycarbonyl Hg(II) chloride.[30a,b] However, the product showed no tendency to undergo reductive coupling.

Scheme I. Mechanism of Carbonyl Insertion for Alkyl and Aryl Substrates[35]



In spite of the above studies, the details of the carbalkoxylation mechanism remain unclear, with virtually no information at all on the reaction with vinyl halides and triflates. Most of the proposed intermediates have not been well characterized. Hence, our aim in elucidating this reaction mechanism is to isolate and characterize the platinum isostructural analogues of the key intermediates in vinylic systems, and to examine their formation and subsequent alcoholysis or reductive coupling reactions. Therefore, all reactions were performed stoichiometrically with platinum. In this paper, we will focus on the preparation and thermal alcoholysis of the vinylic acyl Pt(II) complexes. In the accompanying paper, we report on the synthesis and coupling reactions of σ-alkoxycarbonyl σ-vinyl Pt(II) complexes.

Results and Discussion

Preparation and Characterization of Covalent Vinylic Acyl Pt(II) Complexes. One of the key steps of the carbalkoxylation process is the carbonyl insertion into the M–C bond.[2,32] The carbonylation mechanism of group 10 metal complexes has been the subject of several experimental[34-36] and theoretical[37] publications. Studies with various aryl and alkyl M(II) (M = Ni, Pd, Pt) halides have suggested that the reaction proceeds via CO coordination to generate a covalent pentacoordinate carbonyl species such as **2** (Scheme I).[35] Although such a carbonyl intermediate has been isolated from the reaction of aryl Pt(II) halide complexes, its precise geometry is not clear.[35b] It has also been shown that complex **2** (M = Pt, R = phenyl), formed in nonpolar solvents, dissociates in polar media to give the cationic, square-planar carbonyl complex **6** (eq 1).[36b] Notably absent, however, are studies on the carbonyl insertion into an alkenyl C–M bond. Our recent systematic

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$$[(Ph)Pt(PR'_3)_2(CO)(X)] \underset{\text{non-polar solvents}}{\overset{\text{polar solvents}}{\rightleftharpoons}} \mathbf{6} \quad (1)$$

R' = alkyl, aryl;
X = halides.

synthesis of the σ-alkylvinyl Pt(II) halides[38] provides the opportunity to accomplish this goal.

Thus, complex **7a** was allowed to react with CO under atmospheric pressure in CH_2Cl_2 to give the vinylic acyl iodide complex **9a** in 77% yield (eq 2). Although both ^1H and ^{31}P NMR spectra revealed that the reaction of **7b** with CO quantitatively produced the corresponding acyl complex **9b**, the product slowly decarbonylated, upon isolation from the solution, reverting to the starting **9b**. Similarly, the interaction of the σ-vinyl Pt(II) bromides **8** with CO under 4 atm of pressure resulted in the acyl Pt(II) bromides **10** in 60–65% isolated yield (eq 2).

$$\xrightarrow[CH_2Cl_2]{CO\ (1\text{-}4\ atm)} \quad (2)$$

7a: $R^1 = CH_3$, $R^2 = H$, X = I;
7b: $R^1 = H$, $R^2 = CH_3$, X = I;
8a: $R^1 = CH_3$, $R^2 = H$, X = Br;
8b: $R^1 = H$, $R^2 = CH_3$, X = Br.

9a: $R^1 = CH_3$, $R^2 = H$, X = I;
9b: $R^1 = H$, $R^2 = CH_3$, X = I;
10a: $R^1 = CH_3$, $R^2 = H$, X = Br;
10b: $R^1 = H$, $R^2 = CH_3$, X = Br.

The analogous acyl chloride complexes **11** were obtained by oxidative addition of the corresponding acyl chlorides **12** to tetrakis(triphenylphosphine)platinum(0) (**13**), a well-established procedure (eq 3).[39-41]

$$Pt(PPh_3)_4 + \quad \xrightarrow{\text{toluene}} \quad (3)$$

13 **12**

11a: $R^1 = CH_3$, $R^2 = H$;
11b: $R^1 = H$, $R^2 = CH_3$.

These covalent acyl Pt(II) complexes except for **9b** were isolated as stable yellow microcrystals. They have been characterized by IR, multinuclear NMR, and mass (FAB) spectroscopy and elemental analysis. The IR spectra exhibit strong absorptions at 1605–1640 cm^{-1} due to the C=O stretching of the conjugated vinylic acyl moieties. The presence of the acyl carbonyl group is further corroborated by the triplet ^{13}C resonances at about 210 ppm. The downfield shifts of the vinylic proton resonances also indicate the introduction of the electron-withdrawing carbonyl group.

The acyl structure was also confirmed by X-ray diffraction analysis of **9b**. A suitable single crystal of **9b** was obtained by pentane diffusion into the reaction solution of **7b** with CO in $CDCl_3$. The solid-state structure is illustrated in Figure 1. Crystallographic data, selected bond distances, and selected bond angles are presented in Tables I–III, respectively. Although there are no previously known molecular structures for any acyl complexes comparable to **9b**, the complex exhibits structural features similar to other Pt(II) compounds bearing an RCO moiety[42,43] as well as Pt(II) complexes containing Pt–C (sp^2) bonds.[38,44-47]

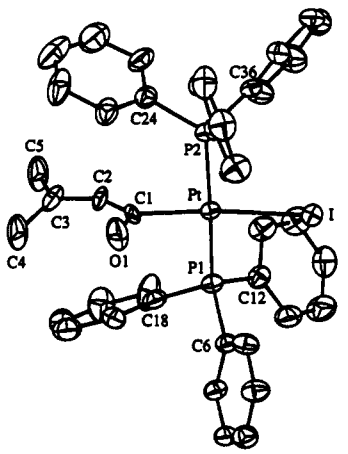

Figure 1. Solid-state structure and atom numbering of vinylic acyl Pt(II) iodide **9b**.

Table I. Summary of Crystallographic Data for Vinylic Acyl Pt(II) Complex 9b

mol formula	$C_{41}H_{37}OP_2PtI$
mol wt	926.69
space group	$P2_1/n$
space group no.	14
cryst syst	monoclinic
cell dimens	
a, Å	11.924 (5)
b, Å	20.354 (10)
c, Å	15.606 (7)
β, deg	105.93 (3)
V, Å^3	3641.9
Z	4
d_{calcd}, g/cm^3	1.695
cryst dimens, mm	0.25 × 0.23 × 0.18
abs coeff, cm^{-1}	48.47
radiation; λ, Å	Mo; 0.710 73
no. of reflns measd	5563
no. of unique reflns	5201
2θ range, deg	3.00–46.00
scan technique	θ/2θ
scan speed, deg/min	3.0–8.0
scan range	$K_{\alpha 1}$ − 1.0 to $K_{\alpha 2}$ + 1.0
total bkgd time/scan time	0.5
no. of reflns between std.	98
no. of obsns, $I > 3.0\sigma(I)$	3245
no. of variables	432
$R(F)$	0.036
$R_w(F)$	0.045

highest peak in final Fourier map, 1.200 e/Å^3 about 0.930 Å from Pt atom

Table II. Selected Bond Distances (Å) for Vinylic Acyl Pt(II) Complex 9b[a]

Pt–I	2.7236 (8)	O1–C1	1.18 (4)
Pt–P1	2.311 (2)	P1–C6	1.82 (4)
Pt–P2	2.299 (2)	P1–C12	1.82 (2)
Pt–C1	2.08 (2)	P1–C18	1.82 (3)
C1–C2	1.27 (4)	P2–C24	1.84 (2)
C2–C3	1.28 (3)	P2–C30	1.81 (3)
C3–C4	1.51 (4)	P2–C36	1.81 (3)
C3–C5	1.41 (4)		

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

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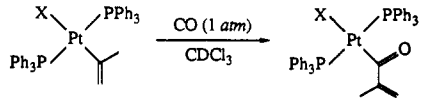
Table III. Selected Bond Angles (deg) for Vinylic Acyl Pt(II) Complex 9b[a]

I-Pt-P1	91.91 (7)	Pt-C1-C2	130. (2)
I-Pt-P2	91.51 (7)	O1-C1-C2	118. (2)
I-Pt-C1	167.5 (8)	C1-C2-C3	139. (2)
P1-Pt-P2	171.24 (9)	C2-C3-C4	123. (2)
P1-Pt-C1	90.0 (6)	C2-C3-C5	113. (2)
P2-Pt-C1	88.4 (6)	C4-C3-C5	123. (3)
Pt-C1-O1	113. (2)		

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

As we have recently reported the X-ray structure of the precursor **7b**,[38] comparison of complex **9b** with **7b** in the solid state is possible. Both complexes have very similar geometries, and the bond angles around the Pt-bonded carbons are significantly distorted from the ideal trigonal carbons (133.3 (7)° for **7b** and 130 (2)° for **9b**). However, the differing trans influence of the vinyl versus vinylic acyl ligands is at least semiquantitatively observed. The Pt-I bond distance is elongated upon CO insertion (from 2.7088 (4) to 2.7236 (8) Å), suggesting the stronger trans influence of the acyl group. The Pt-C1 (sp^2) bond length in complex **9b** is slightly longer than in **7b**.

NMR Studies on the Carbonyl Insertion Reaction of Vinyl Pt(II) Halides. The reactions of the σ-vinyl Pt(II) halides with CO were examined by ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectra of the reaction mixture revealed that complex **7a** was cleanly converted to the vinylic acyl complex **9a**, after passing CO through the $CDCl_3$ solution for 30 min. However, the conversions of the vinyl Pt(II) bromide (**8a**) and chloride (**14**) derivatives were not complete (eq 4). Only 55% of **8a** and 19% of

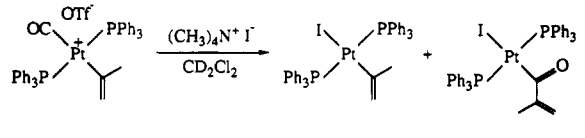


(4)

	Yield (% mole)
7a: X = I;	100
8a: X = Br;	55
14: X = Cl.	19

14, respectively, reacted to give the acyl products, even after prolonged CO delivery. The reaction apparently depends on the nature of the platinum–halide bonds. No intermediate was observed by NMR spectroscopy in these carbonylations even at lower temperature (from −78 to 0 °C).

In an attempt to observe the vinyl analogues of **2** (R = vinyl, R′ = phenyl), the interaction of the σ-vinyl Pt(II) carbonyl triflate **15**[36] with tetramethylammonium iodide was examined (eq 5). The reaction course was followed



(5)

15 **7a** **9a**

by ^{31}P NMR spectroscopy in CD_2Cl_2 at ambient temperature. A ^{31}P NMR spectral array and a plot of molarity

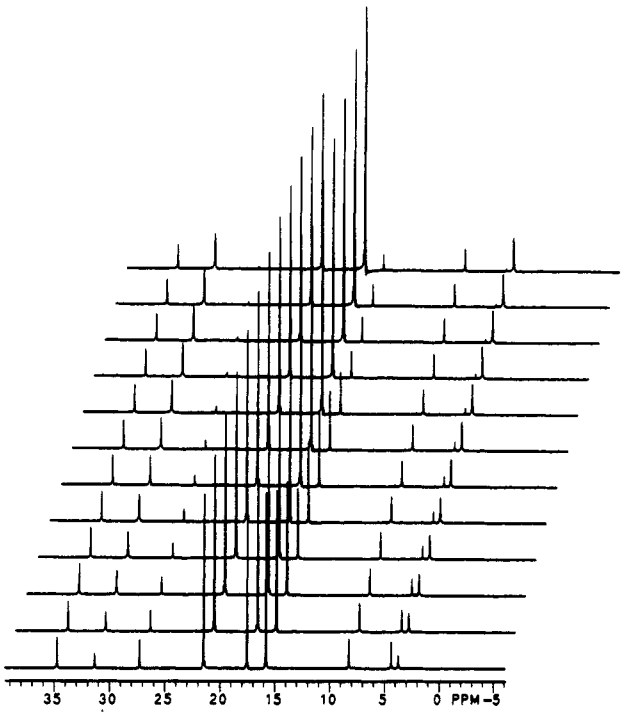


Figure 2. Arrayed ^{31}P NMR spectra of the reaction of **15** with tetramethylammonium iodide. Signals at 15.8, 17.5, and 21.5 ppm are the resonances of **15**, **9a**, and **7a**, respectively, along with their corresponding ^{195}Pt satellites.

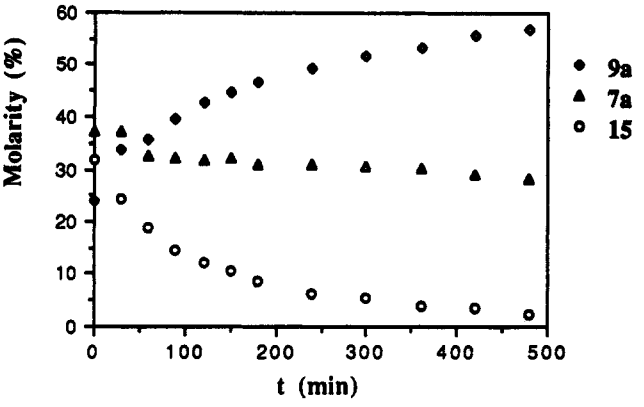


Figure 3. Plot of the molarity of **7a**, **9a**, and **15** versus time.

versus time are shown in Figures 2 and 3, respectively. The data clearly indicate the immediate CO loss upon the addition of the iodide source with the concurrent formation of two products **7a** and **9a**. While the concentration of **15** (at 15.8 ppm) gradually decreases with the concomitant increase in **9a** (at 17.5 ppm), the concentration of **7a** (at 21.5 ppm) remains unchanged throughout the reaction course. Clearly, both **7a** and **9a** are thermodynamically more stable than the cationic platinum carbonyl **15** in the presence of halide anions. Since no other additional species was observed according to ^{31}P NMR spectroscopy even at lower temperature (from −78 °C to ambient temperature), the presumed pentacoordinate carbonyl species may exist only as a short-lived intermediate in solvents such as CH_2Cl_2.

Upon the formation of the platinum carbonyl intermediate, the subsequent migratory insertion could occur directly within the coordination sphere of **2** or proceed via phosphine dissociation (Scheme I, R = vinyl, R′ = phenyl). When **7a** was allowed to react with CO at low temperature in the presence of excess elemental sulfur, a large amount of $Ph_3P{=}S$ was formed, together with other unidentified

(44) (a) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356. (b) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, 3347. (c) Kowalski, M. H.; Arif, A. M.; Stang, P. J. *Organometallics* **1988**, *7*, 1227.

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

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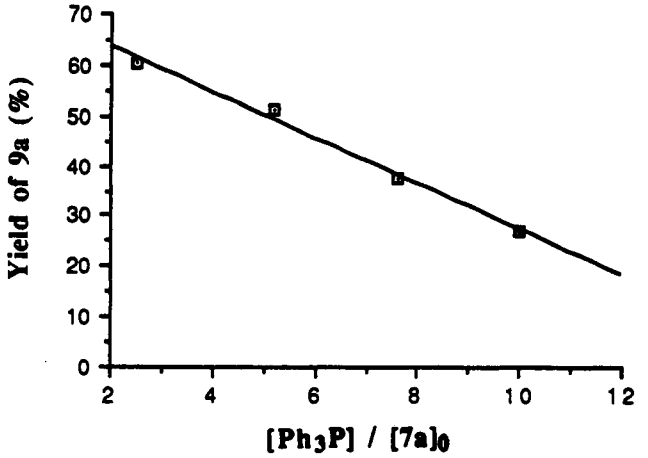
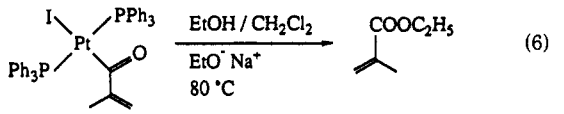


Figure 4. Plot of the yield of **9a** (percent) versus $[PPh_3]/[\mathbf{7a}]_0$.

components, suggesting the dissociative route. To further test this dissociative hypothesis, the effect of added Ph_3P on carbonyl insertion was examined. The reaction of **7a** with CO was essentially inhibited by the addition of excess Ph_3P. A plot of the acyl product yield versus $[Ph_3P]/[\mathbf{7a}]_0$ is shown in Figure 4, where $[Ph_3P]/[\mathbf{7a}]_0$ is the ratio of the phosphine concentration and the initial concentration of **7a**. The data show that the formation of acyl complex **9a** is inversely proportional to the amount of excess Ph_3P. The phosphine inhibition experiments provide further support for the dissociative route for the carbonyl insertion into an alkenyl C–M bond. However, the possibility of direct migratory insertion in **2** cannot be completely ruled out.

Preparation and Alcoholysis of Cationic Vinylic Acyl Pt(II) Complexes. These covalent vinylic acyl Pt(II) halide complexes are very reluctant to undergo thermal alcoholysis. For example, when **9a** was subjected to ethanolysis in CH_2Cl_2/THF in the presence of excess sodium ethoxide, high temperature (>80 °C) and long reaction time (>5 h) were necessary to observe any product (eq 6). A similar observation was made using triethyl-



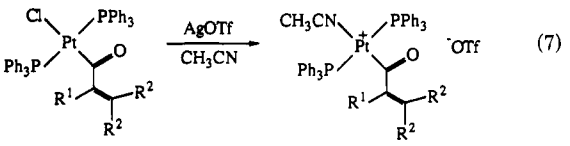
(6)

9a **16**

amine as the base. Hence, this reaction (eq 6) is not amenable for detailed mechanistic investigation. Therefore, in order to enhance the reactivity of these vinylic acyl Pt(II) halides and prepare the σ-acyl σ-alkoxy Pt(II) complexes, attention was directed toward the synthesis of the acyl Pt(II) triflates.

Initially, **11a** was treated with silver triflate in CH_2Cl_2 or toluene; however, immediate decomposition took place, leading to numerous unidentified products. Fortunately, when either **9a** or **11a** was allowed to react with silver triflate in CD_3CN, a clean reaction occurred, both giving the same product **17a** according to ^1H and ^{31}P NMR spectroscopy. Thus, addition of equimolar amounts of silver triflate to a suspension of **11** in CH_3CN resulted in **17** as colorless feathery microcrystals in 89–94% isolated yield (eq 7).

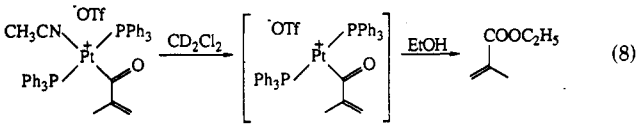
Complexes **17** are extremely labile in solution due to the strong trans effect of the acyl ligand. This problem can be sufficiently circumvented in the presence of excess CH_3CN, and hence only CD_3CN was suitable for NMR spectral characterization. The nature of such a high reactivity is demonstrated by the reaction of **17a** with eth-



(7)

11a: $R^1 = CH_3$, $R^2 = H$; **11b**: $R^1 = H$, $R^2 = CH_3$. **17a**: $R^1 = CH_3$, $R^2 = H$; **17b**: $R^1 = H$, $R^2 = CH_3$.

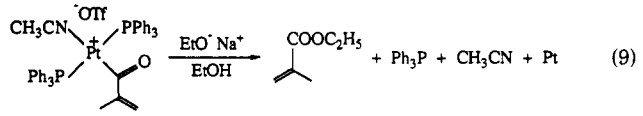
anol. Dissolving **17a** in a solution of ethanol (2.5 equiv) in CD_2Cl_2 at room temperature led to the immediate formation of ethyl methacrylate **16**, according to the ^1H NMR spectrum and comparison with authentic material (eq 8). Unlike the alcoholysis of the covalent precursor



(8)

17a *trans*-**18** **16**

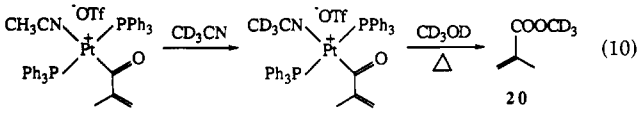
9a, bases are not required to facilitate this reaction. This exceptional reactivity could be attributed to the ready dissociation of the CH_3CN ligand and the formation of the coordinatively unsaturated species *trans*-**18** in the polar solvent CD_2Cl_2. Addition of **17a** to a suspension of sodium ethoxide (5 equiv) in ethanol led to the formation of **16**, together with Ph_3P, CH_3CN, and metallic platinum black (eq 9). The organic products were identified by TLC, GC, and GC–MS analysis and comparisons with authentic material.



(9)

17a **16**

Fortunately, methanolysis in CD_3CN/CD_3OD allowed for more detailed investigations under controlled conditions (eq 10). It should be noted that upon dissolving **17a** in excess CD_3CN solvent, essentially complete ligand ex-



(10)

17a **19**

change takes place and the actual reactant is **19**. The vinylic proton resonances for complex **17a** (6.5 ppm) and ester **20** (6.0 ppm) are well separated for quantitative studies.

When a 0.03 M solution of **17a** in CD_3CN was allowed to react at 70 °C with CD_3OD, the clean formation of **20** was observed with no spectral evidence for any other intermediates. However, substantial product loss (50%) resulted presumably due to acrylate polymerization. Indeed, authentic methyl methacrylate readily undergoes polymerization under similar conditions. However, treatment of the data by plotting ln [**17a**] versus time gives the pseudo-first-order rates k_1' in 1.37, 1.09, and 0.821 M CD_3OD (Table IV, runs 1–3). The plot of the reaction rate versus the methanol concentration then provided the second-order rate constant

$$-d[Pt]/dt = k_2[Pt][CD_3OD]$$

where $k_2 = 4.0 \times 10^{-2}$ M^{-1} min^{-1} and [Pt] and $[CD_3OD]$ are the concentrations of **17a** and deuterated methanol, respectively.

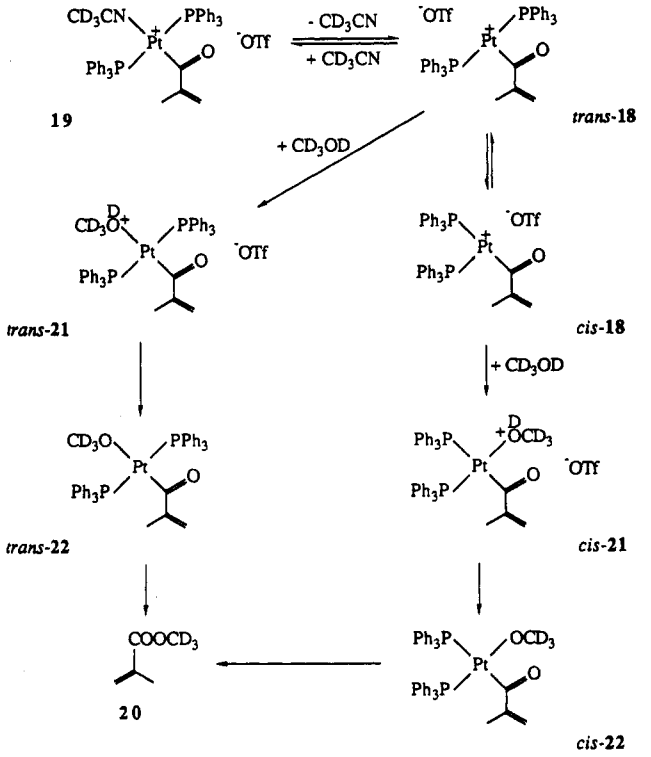
A likely mechanism for this reaction is outlined in Scheme II. As mentioned previously, the highly reactive

Table IV. Rate Constants and Activation Parameters for the Thermal Alcoholysis of 17a

rung	$[CD_3OD]$, M	temp, °C	k_1', min^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	0.82	69.9	0.017		
2	1.09	69.9	0.028		
3	1.37	69.9	0.039	20	−7
4	1.37	65.3	0.021		
5	1.37	60.1	0.021		
6	1.37	50.2	0.0059		

[a] Temperature controlled to ±0.5 °C.

Scheme II. Likely Mechanism of Thermal Alcoholysis of Cationic Vinyl Acyl Pt(II) Complexes



nature of the cationic acyl complexes is due to the ready dissociation of the acetonitrile ligand. By using CD_3CN as solvent, however, the unsaturated tricoordinate species *trans*-**18** may exist only in an undetectable small amount via preequilibration. In support of this hypothesis is the ^{31}P NMR spectrum of **17a** in CD_2Cl_2 (Figure 5). Besides the expected resonance of **17a** at 20.6 ppm ($^1J_{PtP}$ = 3334 Hz), an additional singlet at 29.0 ppm ($^1J_{PtP}$ = 2904 Hz) was observed, which could be assigned to the dissociation product *trans*-**18** (Table V). The existence of *trans*-**18** is further corroborated by ^1H NMR spectroscopy (Figure 5). Specifically, the ^1H resonances at 5.63 and 6.16 ppm are due to the vinylic protons of *trans*-**18** (Table V). The signal at 1.93 ppm is that of free CH_3CN liberated from **17a**. Addition of ethanol to this solution of **17a** immediately causes the clean production of ethyl methacrylate **16**.

Theoretical calculations indicate that reductive elimination from d^8 complexes must proceed via a cis or a trigonal-planar orientation.[48] The reductive elimination reaction of *trans*-**22** (from *trans*-**21**) is symmetry-prohibited and is expected to be a slow process. This is not compatible with the observation that the reaction of **17a** with ethanol in CD_2Cl_2 is facile. Therefore, the reaction route involving the formation of *trans*-**21** is less likely. Indeed, there are two additional small doublets (13.1 ppm, 29.3 ppm, $^2J_{PP}$ = 13.7 Hz) in the ^{31}P NMR spectrum of **17a** in CD_2Cl_2 without the addition of alcohols (Figure 5). These signals are an indication of the formation of the

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Table V. ^1H and ^{31}P NMR Data of 17a and *trans*-18 in CD_2Cl_2

compd	^1H NMR[a]	^{31}P NMR[b]
17a	0.89 (s, CH_3) 1.36 (br s, CH_3CN) 5.69 (t, $^5J_{PH}$ = 1.3 Hz, (*E*)-CH=) 6.49 (br s, (*Z*)-CH=)	20.6 (s, $^1J_{PtP}$ = 3334 Hz)
trans-**18**	1.51 (br s, CH_3) 5.63 (t, $^5J_{PH}$ = 1.6 Hz, (*E*)-CH=) 6.16 (br s, (*Z*)-CH=)	29.0 (s, $^1J_{PtP}$ = 2904 Hz)
CH_3CN	1.93	

[a] At 300 MHz in CD_2Cl_2 referenced to $CHDCl_2$ at 5.32 ppm. [b] At 121 MHz in CD_2Cl_2 referenced to external H_3PO_4 (85%) at 0.0 ppm.

Table VI. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	B,[a] Å^2
Pt	0.02646 (3)	0.09218 (2)	0.22949 (2)	3.928 (7)
I	−0.01959 (6)	0.21235 (4)	0.28875 (5)	6.04 (2)
P1	−0.1633 (2)	0.0576 (1)	0.2113 (2)	4.35 (6)
P2	0.2228 (2)	0.1148 (1)	0.2646 (2)	4.08 (6)
O1	0.044 (2)	0.023 (1)	0.082 (1)	9.3 (6)
C1	0.057 (1)	0.0111 (7)	0.1581 (8)	3.6 (3)
C2	0.084 (1)	−0.0472 (6)	0.184 (1)	6.5 (3)
C3	0.103 (1)	−0.1026 (8)	0.152 (1)	5.6 (4)
C4	0.065 (4)	−0.117 (2)	0.054 (3)	3.9 (9)
C5	0.134 (3)	−0.152 (1)	0.218 (2)	9 (1)
C6	−0.2776 (7)	0.0967 (5)	0.1248 (6)	4.2 (2)
C7	−0.3881 (8)	0.0654 (6)	0.0974 (7)	5.3 (3)
C8	−0.4743 (8)	0.0960 (6)	0.0292 (7)	5.8 (3)
C9	−0.4536 (9)	0.1535 (6)	−0.0123 (6)	5.6 (3)
C10	−0.3441 (9)	0.1825 (6)	0.0143 (7)	6.0 (3)
C11	−0.2564 (8)	0.1541 (6)	0.0826 (6)	5.3 (3)
C12	−0.2034 (8)	0.0691 (5)	0.3148 (6)	4.8 (2)
C13	−0.3131 (9)	0.0859 (7)	0.3192 (8)	7.6 (4)
C14	−0.337 (1)	0.0908 (8)	0.4004 (8)	8.5 (4)
C15	−0.253 (1)	0.0771 (6)	0.4776 (7)	6.7 (3)
C16	−0.140 (1)	0.0608 (7)	0.4764 (7)	7.4 (3)
C17	−0.114 (1)	0.0559 (6)	0.3937 (6)	6.3 (3)
C18	−0.1923 (8)	−0.0288 (5)	0.1853 (7)	5.3 (3)
C19	−0.1943 (9)	−0.0499 (6)	0.0997 (7)	5.9 (3)
C20	−0.213 (1)	−0.1186 (7)	0.0780 (9)	7.8 (4)
C21	−0.229 (1)	−0.1621 (7)	0.1398 (8)	7.6 (4)
C22	−0.228 (1)	−0.1417 (7)	0.2223 (9)	9.1 (4)
C23	−0.207 (1)	−0.0735 (6)	0.2471 (8)	8.0 (3)
C24	0.3183 (8)	0.0446 (5)	0.2602 (7)	4.9 (2)
C25	0.3255 (9)	0.0257 (6)	0.1776 (7)	6.4 (3)
C26	0.394 (1)	−0.0324 (7)	0.1740 (9)	9.2 (3)
C27	0.445 (1)	−0.0664 (7)	0.248 (1)	10.4 (5)
C28	0.439 (1)	−0.0456 (8)	0.332 (1)	9.9 (5)
C29	0.375 (1)	0.0106 (6)	0.3377 (8)	7.0 (3)
C30	0.2692 (8)	0.1748 (5)	0.1963 (6)	4.7 (2)
C31	0.3893 (8)	0.1800 (5)	0.1994 (7)	5.5 (3)
C32	0.422 (1)	0.2251 (6)	0.1427 (8)	7.6 (3)
C33	0.341 (1)	0.2633 (6)	0.0848 (8)	7.5 (3)
C34	0.224 (1)	0.2580 (7)	0.0809 (8)	7.5 (3)
C35	0.1869 (9)	0.2133 (5)	0.1372 (7)	5.4 (3)
C36	0.2752 (8)	0.1410 (5)	0.3796 (6)	4.6 (2)
C37	0.3573 (9)	0.1917 (6)	0.4054 (7)	6.0 (3)
C38	0.399 (1)	0.2076 (7)	0.4982 (8)	8.3 (4)
C39	0.354 (1)	0.1760 (7)	0.5602 (8)	8.7 (4)
C40	0.273 (1)	0.1279 (7)	0.5308 (8)	8.5 (4)
C41	0.233 (1)	0.1098 (7)	0.4432 (7)	7.0 (3)

[a] Anisotripically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

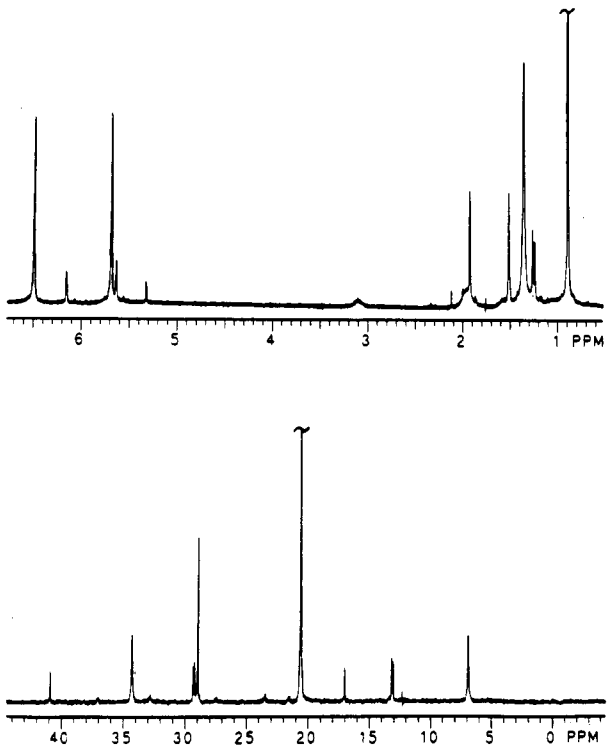


Figure 5. ^1H (top) and ^{31}P (bottom) NMR spectra of **17a** in CD_2Cl_2.

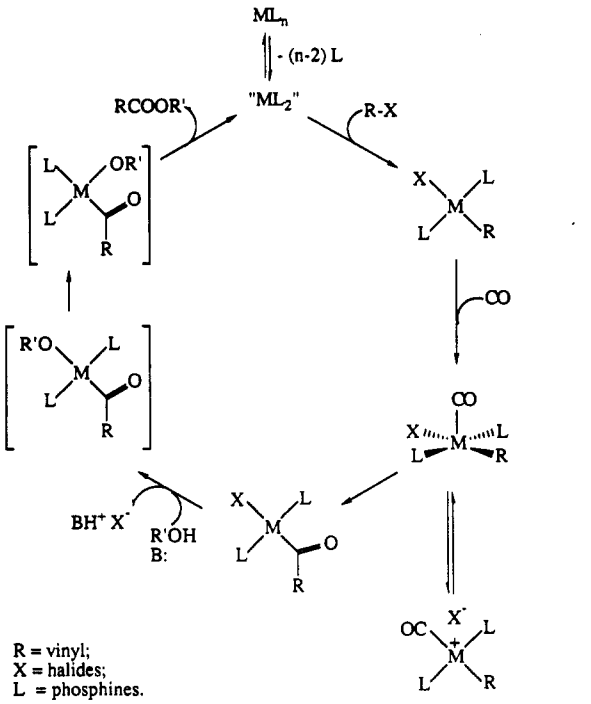
rearranged trigonal-planar species *cis*-18. The nucleophilic addition of alcohols would afford the cis σ-acyl σ-alkoxy Pt(II) complexes. Moreover, the negative entropies of activation derived under pseudo-first-order conditions suggest that the reaction proceeds via an associative rate-determining step (Table IV, runs 3–6). Therefore, the thermal alcoholysis is likely to proceed via the rate-determining formation of the cis σ-acyl σ-alkoxy Pt(II) complex, which then reductively eliminates methyl methacrylate.

Conclusions

The mechanism of the carbalkoxylation of vinylic halides may be summarized as outlined in Scheme III. The oxidative addition of vinyl electrophiles to zerovalent nickel metals is well established.[44b] Solution chemistry indicates that the carbonyl insertion into the alkenyl C–M bond proceeds via a pentacoordinate carbonyl species, which exists as a cationic square-planar metal carbonyl in polar media. Phosphine inhibitions demonstrate that phosphine dissociation occurs prior to migratory insertion. The X-ray structural determination of **9b** clearly illustrates the structural transformation of the carbonyl insertion with σ-vinyl Pt(II) halides. The vinylic acyl moiety has a stronger trans influence than the vinyl ligand, weakening the bond in the trans position.

While the covalent vinylic acyl Pt(II) halides themselves are relatively unreactive toward alcoholysis, the corresponding cationic acyl triflate complexes react with alcohols to yield α,β-unsaturated carboxylic esters under extremely mild conditions. Such an exceptional reactivity could be attributed to the ready dissociation of the CH_3CN ligand to generate the reactive trigonal-planar intermediate, *trans*-18. Complex *trans*-18 can be characterized in situ by ^1H and ^{31}P NMR spectroscopy in CD_2Cl_2. The trans–cis isomerization of 18 in CD_2Cl_2 was also observed by ^{31}P NMR spectroscopy. Nucleophilic attack of alcohols in *cis*-18 would result in the formation of cis σ-acyl σ-alkoxy Pt(II) complexes. Kinetic data suggest that the alcoholysis

Scheme III. Mechanism of the Carbalkoxylation of Vinyl Halides



of the cationic acyl complex occurs via the rate-determining formation of cis σ-acyl σ-alkoxy Pt(II) complex, followed by the facile reductive elimination of acrylic esters.

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 Perkin-Elmer 298 spectrometer or a Mattson Polaris FT-IR spectrometer and measured in wavenumbers (cm^{-1}). All NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H NMR spectra were acquired at 300 MHz, and all chemical shifts are reported in ppm relative to the residual proton resonance of the NMR solvents: CD_3CN (1.93 ppm), $CDCl_3$ (7.24 ppm), CD_2Cl_2 (5.32 ppm). ^{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), CD_3CN (CN at 1.3 ppm). ^{31}P NMR spectra were recorded at 121 MHz with broad-band ^1H decoupling with the magnet locked on the deuterated solvents, and chemical shifts are reported in ppm relative to external 85% H_3PO_4 at 0.0 ppm. ^{19}F NMR spectra were acquired at 282 MHz, and resonances are reported in ppm relative to external $CFCl_3$ at 0.0 ppm.

Fast atom bombardment mass spectra were obtained with a VG Analytical 7050-E mass spectrometer. The X-ray crystal structure was determined on a Syntex P1 bar diffractometer at ambient temperature (16 ± 1 °C). Analytical GC analysis was performed on a Hewlett-Packard 5711 GC instrument equipped with a flame ionization detector and a Hewlett-Packard 3380 integrator, using a 0.125 in. × 6 ft. UCW-98 on 80/100 Chromosorb W analytical column or on a Hewlett-Packard 5890 Series II GC instrument equipped with a flame ionization detector and a Hewlett-Packard 3396A integrator, using a 25 m × 0.32 mm × 0.3 mm film thickness Carbowax 20M (HP-20M) capillary column.

Materials. In general, solvents were either reagent grade or were purified according to known procedures.[49] Specifically, acetonitrile was predried over anhydrous $MgSO_4$ and then over anhydrous K_2CO_3 and finally distilled from CaH_2. Hydrocarbon solvents (hexanes, pentane, benzene, and toluene) were stirred over concentrated H_2SO_4 and distilled from CaH_2. Methylene chloride was distilled from CaH_2.

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

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 (CD_2Cl_2, CD_3CN, CD_3OD).

Triphenylphosphine and fluorene were recrystallized from hexanes and vacuum-dried. Triethylamine was purchased from Aldrich and dried over t.h.e. desiccant (EM) for at least 2 days. Carbon monoxide (Matheson) was directly used without purification.

K_2PtCl_4 (Johnson-Matthey) was used as shipped without purification. Silver triflate was purchased from Aldrich and directly used without purification. Tetrakis(triphenylphosphine)platinum(0) (**13**) was prepared according to standard literature procedure.[50] The σ-vinyl Pt(II) halides **7**, **8**, and **14** were synthesized according to known methods.[38]

General Procedure for the Preparation of Vinylic Acyl Pt(II) Iodides and Bromides: *trans*-CH_2=$C(CH_3)COPt(PPh_3)_2I$ (9a). Complex **7a** (174 mg, 0.196 mmol) was placed in a 25-mL three-necked round-bottom flask and charged with 15 mL of CH_2Cl_2. CO was bubbled through the solution for 2 h with stirring. The solution turned light yellow. Column chromatography using silica gel and CH_2Cl_2 as eluent, followed by recrystallization from CH_2Cl_2/hexane, afforded a yellow microcrystalline solid. The product was filtered out, washed with hexane, and dried in high vacuo to give 139 mg of **9a** (77%): mp 215–216 °C dec; IR 3050 (w), 1607 (s), 1479 (m), 1431 (s), 1091 (s), 868 (w), 739 (m), 690 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 0.67 (s, 3 H, CH_3), 5.73 (br s, 1 H, (*E*)-CH=), 6.88 (s, 1 H, (*Z*)-CH=), 7.4 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 17.4 (s, $^1J_{PtP}$ = 3335 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3 (s, CH_3), 127.9 (t, $^3J_{PC}$ = 5.4 Hz, *m*-C), 130.3 (s, *p*-C), 131.1 (t, $^1J_{PC}$ = 28.4 Hz, $^2J_{PtC}$ = 29.3 Hz, ipso-C), 135.2 (t, $^2J_{PC}$ = 6.0 Hz, *o*-C), 153.7 (t, $^3J_{PC}$ = 4.8 Hz, $C(CH_3)$=), 215.5 (t, $^2J_{PC}$ = 5.4 Hz, CO); FAB MS 846 (6%), 788 (20%), 760 (100%), 720 (54%), 718 (89%), 457 (73%). Anal. Calcd for $C_{40}H_{35}OP_2IPt$: C, 52.47; H, 3.85. Found: C, 52.48; H, 3.80.

***trans*-CH_2=$C(CH_3)COPt(PPh_3)_2Br$ (10a).** Complex **8a** (107 mg, 0.127 mmol) was placed in a pressure reactor. The reactor was charged with 20 mL of CH_2Cl_2 and 62 psi of CO. Stirring overnight at room temperature resulted in a light yellow solution. Some decomposition to Pt black was also observed. After depressurization, TLC showed that the starting complex had completely reacted. Workup as above gave a yellow microcrystalline solid. The solid was filtered out, washed with hexane, and dried in high vacuo for 5 h to give 66 mg of **10a** (60%): mp 206–207 °C dec; IR 3048 (w), 1608 (s), 1476 (m), 1428 (s), 1180 (w), 1088 (s), 1010 (w), 992 (w), 945 (w), 918 (w), 870 (w), 739 (s), 690 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 0.67 (s, 3 H, CH_3), 5.65 (t, $^5J_{PH}$ = 1.6 Hz, 1 H, (*E*)-CH=), 6.83 (br s, 1 H, (*Z*)-CH=), 7.4 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 20.0 (s, $^1J_{PtP}$ = 3380 Hz); ^{13}C NMR ($CDCl_3$) δ 16.1 (s, CH_3), 128.0 (t, $^3J_{PC}$ = 5.2 Hz, *m*-C), 130.3 (s, *p*-C), 130.6 (overlapping t, $^1J_{PC}$ = 28.4 Hz, ipso-C), 135.0 (t, $^2J_{PC}$ = 6.2 Hz, *o*-C), 153.8 (t, $^3J_{PC}$ = 4.5 Hz, $C(CH_3)$=), 213.1 (t, $^2J_{PC}$ = 5.8 Hz, CO).

***trans*-$(CH_3)_2C$=$CHCOPt(PPh_3)_2Br$ (10b).** The reaction was carried out as above with **8b** (125 mg, 0.146 mmol) to afford 88 mg of yellow microcrystalline **10b** (68%): mp 217–218 °C dec; IR 3050 (w), 1635 (s), 1595 (m), 1480 (m), 1432 (s), 1091 (s), 994 (m), 835 (m), 781 (m), 750 (s), 691 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.04 (d, $^4J_{HH}$ = 1.0 Hz, 3 H, (*Z*)-CH_3), 1.14 (d, $^4J_{HH}$ = 0.9 Hz, 3 H, (*E*)-CH_3), 5.73 (br t, $^3J_{PH}$ = 1.2 Hz, 1 H, CH=), 7.3 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 20.8 (s, $^1J_{PtP}$ = 3557 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7 (s, (*E*)-CH_3), 26.7 (s, (*Z*)-CH_3), 127.9 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 130.3 (s, *p*-C), 130.7 (overlapping t, $^1J_{PC}$ = 28.0 Hz, ipso-C), 135.0 (t, $^2J_{PC}$ = 6.2 Hz, *o*-C), 136.2 (t, $^3J_{PC}$ = 6.8 Hz, CH=), 144.3 (s, $C(CH_3)_2$=), 209.9 (t, $^2J_{PC}$ = 5.0 Hz, CO); FAB MS 801 (11%), 774 (15%), 719 (100%), 457 (63%).

NMR Observation of the Reaction of *trans*-$(CH_3)_2C$=$CHPt(PPh_3)_2I$ (7b) with CO. Complex **7b** (30.0 mg, 3.33×10^{-2} mmol) was placed in a 5-mm thin-wall NMR tube and charged with 0.5 mL of $CDCl_3$. CO was slowly bubbled through the solution for 1 h, leading to a light yellow clear solution. The NMR tube was sealed with a rubber septum. ^1H, ^{31}P, and ^{13}C NMR spectra were taken of the solution. Recrystallization by diffusion of pentane to the solution afforded **9b** as a yellow microcrystalline solid. Decarbonylation of **9b** occurred to give a small amount of starting **7b**, according to ^1H and ^{31}P NMR spectroscopy: mp 231–233 °C dec; IR 3025 (w), 1638 (s), 1478 (m), 1431 (s), 1092 (s), 994 (w), 740 (m), 690 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 5.74 (br s, 1 H, CH=), 7.3 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 18.5 (s, $^1J_{PtP}$ = 3515 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7 (s, (*E*)-CH_3), 26.8 (s, (*Z*)-CH_3), 127.8 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 130.2 (s, *p*-C), 131.2 (t, $^1J_{PC}$ = 28.2 Hz, ipso-C), 135.2 (t, $^2J_{PC}$ = 6.1 Hz, *o*-C), 144.9 (s, $C(CH_3)_2$=), 212.6 (t, $^2J_{PC}$ = 5.0 Hz, CO).

Single-Crystal X-ray Diffraction Analysis of 9b. The reaction of **7b** with CO in $CDCl_3$, followed by diffusion recrystallization with pentane, provided the light yellow single crystals of **9b**. The crystal was glued onto a glass fiber and mounted for data collection on a Syntex $P\bar{1}$ automated diffractometer. Cell constants (Table I) were obtained from 25 reflections with $20.0 < 2\theta < 30.0$. The space group was determined from systematic absences ($h0lh + l = 2n$, $0k0 = 2n$) and subsequent least-squares refinement. Standard reflections showed about 7.0% decay during data collection, therefore anisotropic decay correction was applied.

Lorentz and polarization corrections and an empirical absorption correction based upon a series of ψ scans were applied to the data. Intensities of equivalent reflections were averaged with R (averaging) on F_o about 0.017. The structure was solved by the standard heavy-atom techniques with the SDP/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were calculated and added to the structure factor calculations but were not refined. Scattering factors and $\delta f'$ and $\delta f''$ values were taken from the literature.[51]

General Procedure for the Preparation of Vinylic Acyl Pt(II) Chlorides: *trans*-CH_2=$C(CH_3)COPt(PPh_3)_2Cl$ (11a). Complex **13** (503 mg, 0.404 mmol) was weighed in a dry box, and placed in a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer bar. The flask was charged with 10 mL of degassed toluene. A solution of methacryloyl chloride (48.6 mg, 0.47 mmol) in 1 mL of toluene was added with syringe, resulting in a light yellow clear solution. Stirring overnight led to a white precipitate. Hexanes (10 mL) were added to complete the precipitation. The solid was filtered and washed with dried hexanes. Recrystallization from CH_2Cl_2/toluene/hexanes gave 211 mg of **11a** as yellow microcrystals (63%). The product contained $^1/_{10}CH_2Cl_2$ solvate according to the ^1H NMR spectrum: mp 203–204 °C dec; IR 3052 (w), 1606 (s), 1480 (m), 1432 (s), 1093 (s), 1011 (w), 740 (m), 691 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 0.68 (s, CH_3), 5.60 (br s, CH=), 6.78 (br s, CH=), 7.4 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 20.8 (s, $^1J_{PtP}$ = 3340 Hz); ^{13}C NMR ($CDCl_3$) δ 16.0 (s, CH_3), 128.0 (t, $^3J_{PC}$ = 5.4 Hz, *m*-C), 130.4 (overlapping s, *p*-C), 134.9 (t, $^2J_{PC}$ = 6.2 Hz, *o*-C), 154.0 (t, $^3J_{PC}$ = 4.1 Hz, $C(CH_3)$=), 212.6 (t, $^2J_{PC}$ = 5.9 Hz, CO); FAB MS 825 (2%), 760 (39%), 719 (100%), 457 (58%). Anal. Calcd for $C_{40.1}H_{35.2}OP_2Cl_{1.2}Pt$: C, 57.84; H, 4.26. Found: C, 57.75; H, 4.29.

***trans*-$(CH_3)_2C$=$CHCOPt(PPh_3)_2Cl$ (11b).** This compound was prepared according to the above procedure with **13** (206 mg, 0.165 mmol) and 3,3-dimethylacryloyl chloride (22 mg, 0.185 mmol) in about 15 mL of toluene, giving 112 mg (81%) of **11b** as yellow microcrystals: mp 211–212 °C dec; IR 3054 (w), 1637 (s), 1594 (m), 1480 (m), 1431 (s), 1185 (w), 1093 (s), 994 (m), 784 (w), 750 (m), 691 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.03 (s, CH_3), 1.16 (s, CH_3), 5.70 (br s, CH=), 7.3 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ^{31}P NMR ($CDCl_3$) δ 21.4 (s, $^1J_{PtP}$ = 3580 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7 (s, CH_3), 26.6 (s, CH_3), 128.0 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 130.3 (overlapping s, *p*-C), 130.5 (t, $^1J_{PC}$ = 27.8 Hz, ipso-C), 135.0 (t, $^2J_{PC}$ = 6.3 Hz, *o*-C), 143.8 (s, $C(CH_3)_2$=), 209.4 (t, $^2J_{PC}$ = 5.3 Hz, CO); FAB MS 802 (4%), 774 (16%), 719 (100%), 457 (44%).

NMR Observation of the Carbonyl Insertion Reactions of σ-Vinyl Pt(II) Halides. Complex **7a** (14.5 mg, 1.63×10^{-2} mmol) was placed in a thin-wall 5-mm NMR tube and dissolved

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

(51) Cromer, D. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

with 0.6 mL of $CDCl_3$. Carbon monoxide was slowly bubbled through the solution for 30 min. The tube was sealed with a rubber septum. The solution turned bright yellow. Complete conversion of **7a** to **9a** was observed by ^1H and ^{31}P NMR spectroscopy. Similarly, complex **8a** ($^1/_4CH_2Cl_2$ solvate, 15.0 mg, 1.74 × 10^{-2} mmol) was allowed to react with CO in 0.6 mL of $CDCl_3$ for 30 min. The yield of **10a** was determined to be 55% (mole) by integration of the ^{31}P NMR signals. The reaction with vinyl Pt(II) chloride **14** ($^1/_8CH_2Cl_2$ solvate, 15.5 mg, 1.92 × 10^{-2} mmol) gave 19% (mole) of **11a**, according to the ^{31}P NMR spectrum.

NMR Observation of the Interaction of 7a with CO in the Presence of Sulfur. Complex **7a** (14.0 mg, 1.58 × 10^{-2} mmol) was placed in a thin-wall 5-mm NMR tube and charged with 0.5 mL of CD_2Cl_2. Sulfur (5.5 mg, 0.17 mmol) was then added. No reaction was observed by ^{31}P NMR spectroscopy. The solution was cooled to −78 °C while CO 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 a large amount of phosphine sulfide ($Ph_3P{=}S$) at 43.1 ppm, as well as the acyl complex **9a** and other, unidentified components.

NMR Observation of the Interaction of *trans*-[$CH_2{=}C(CH_3)Pt(PPh_3)_2(CO)]^+TfO^-$ (15) with $(CH_3)_4N^+I^-$. Complex **15** (15.3 mg, 1.63 × 10^{-2} mmol) and $(CH_3)_4N^+I^-$ (6.6 mg, 3.28 × 10^{-2} mmol) were placed in a thin-wall 5-mm NMR tube and charged with 0.470 mL of CD_2Cl_2. The tube was then sealed with a rubber septum. The reaction was monitored by ^{31}P NMR spectroscopy at ambient temperature (30 ± 1 °C). A ^{31}P spectral array was obtained with a preacquisition delay (PAD (1) = 0, 900, 900, 900, 900, 900, 900, 2700, 2700, 2700, 2700, 2700, 2700), and the first spectrum was acquired 20 min after mixing. Both **7a** and **9a** were formed. The molarity of each compound (**7a**, **9a**, and **15**) was calculated by the integration of the corresponding ^{31}P NMR signals and then plotted versus time.

Phosphine Inhibition Experiments on the Carbonyl Insertion Reaction of 7a. A stock solution of **7a** in $CDCl_3$ was made (49.2 mg, 2.4 mL, 2.31 × 10^{-2} M). NMR tubes were charged with 0.6 mL of the stock solution and triphenylphosphine: 36.2 mg (0.138 mmol), 27.8 mg (0.106 mmol), 18.6 mg (7.09 × 10^{-2} mmol), and 9.1 mg (3.5 × 10^{-2} mmol). Carbon monoxide was slowly bubbled through the four samples each for 1 h. The NMR tubes were then sealed with rubber septums and ^{31}P NMR spectra were obtained. Relative mole percent of acyl product **9a** was calculated from the integrals of **7a** and **9a**: $I_{9a}/(I_{7a} + I_{9a}) \times 100\%$, where I_{7a} and I_{9a} are the integrals of **7a** and **9a**, respectively. The relative mole percent of **9a** was then plotted versus the ratio of triphenylphosphine and the initial concentration of **7a**.

General Procedure for the Preparation of Vinylic Acyl Pt(II) Triflates: [*trans*-$CH_2{=}C(CH_3)COPt(PPh_3)_2(CH_3CN)](OTf)$ (17a). To a suspension of **11a** (75 mg, 9.1 × 10^{-2} mmol) in 2 mL of CH_3CN was added silver triflate (24 mg, 9.3 × 10^{-2} mmol), immediately resulting in a white precipitate (AgCl). The mixture was stirred for 20 min. The solution was reduced to about 1 mL by evaporation on a rotovap, and CH_2Cl_2 (1 mL) was added. Silver chloride was filtered with a pipet filled with micro glass fiber and filter paper, and the solution was collected in a 100-mL round-bottom flask containing a mixture of 25 mL of toluene and 40 mL of hexanes. The flask was kept in a refrigerator for 2 h. The resulting microcrystals were filtered and dried in high vacuo to give 60 mg (89%) of **17a** as feathery microcrystals: mp 138–139 °C dec; IR 2991 (m), 2927 (m), 2279 (w), 1633 (s), 1482 (m), 1436 (s), 1272 (s), 1225 (m), 1150 (s), 1099 (s), 1031 (s), 998 (m), 951 (m), 921 (w), 879 (m), 753 cm^{-1} (s); ^1H NMR (CD_3CN) δ 0.86 (s, 3 H, CH_3), 1.96 (s, 3 H, CH_3CN), 5.66 (t, $^5J_{PH}$ = 1.3 Hz, 1 H, (*E*)-CH=), 6.53 (s, 1 H, (*Z*)-CH=), 7.4–7.7 (m, 30 H, aromatics); ^{31}P NMR (CD_3CN) δ 21.3 (s, $^1J_{PtP}$ = 3339 Hz); ^{13}C NMR (CD_3CN) δ 16.6 (s, CH_3), 128.7 (t, $^1J_{PC}$ = 28.7 Hz, ipso-C), 129.8 (t, $^3J_{PC}$ = 5.5 Hz, *m*-C), 132.5 (s, *p*-C), 132.9 (br s, CH_2=), 135.0 (t, $^2J_{PC}$ = 6.4 Hz, *o*-C), 204.7 (t, $^2J_{PC}$ = 6.3 Hz, CO); FAB MS 788 (13%), 760 (49%), 719 (69%), 178 (100%), 457 (16%). Anal. Calcd for $C_{43}H_{38}O_4NP_2F_3SPt$: C, 52.76; H, 3.91. Found: C, 52.16; H, 3.92.

[*trans*-$(CH_3)_2C{=}CHCOPt(PPh_3)_2(CH_3CN)](OTf)$ (17b). The reaction was accomplished with **11b** (92 mg, 0.11 mmol) and silver triflate (28 mg, 0.11 mmol) according to the above procedure to give 102 mg (89%) of complex **17b** as $^1/_2C_6H_5CH_3$ solvate, according to the ^1H NMR spectrum: mp 127–128 °C dec; IR 3056 (w), 2931 (w), 2284 (w), 1644 (s), 1602 (m), 1482 (m), 1436 (s), 1373 (m), 1269 (s), 1224 (m), 1150 (s), 1099 (s), 1032 (s), 998 (m), 838 (m), 787 (m), 751 (m), 694 (s), 637 cm^{-1} (s); ^1H NMR (CD_3CN) δ 1.03 (d, $^4J_{HH}$ = 1.1 Hz, 3 H, (*E*)-CH_3), 1.19 (d, $^4J_{HH}$ = 1.0 Hz, 3 H, (*Z*)-CH_3), 1.95 (s, 3 H, CH_3CN), 5.74 (br t, $^4J_{PH}$ = 1.2 Hz, 1 H, CH=), 7.4–7.7 (m, 30 H, aromatics); ^{31}P NMR (CD_3CN) δ 22.0 (s, $^1J_{PtP}$ = 3544 Hz); ^{13}C NMR (CD_3CN) δ 21.0 (s, CH_3), 26.8 (s, CH_3), 126.2 (s, $C(CH_3)_2$=), 129.1 (t, $^1J_{PC}$ = 28.3 Hz, ipso-C), 129.9 (t, $^3J_{PC}$ = 5.5 Hz, *m*-C), 132.7 (s, *p*-C), 135.3 (t, $^2J_{PC}$ = 6.3 Hz, *o*-C), 148.5 (s, CH=), 200.7 (t, $^2J_{PC}$ = 5.5 Hz, CO); FAB MS 802 (6%), 774 (24%), 719 (23%), 457 (7%), 154 (100%). Anal. Calcd for $C_{47.5}H_{44}O_4NP_2F_3SPt$: C, 54.91; H, 4.27. Found: C, 54.78; H, 4.28.

NMR Observation and Kinetic Studies of the Thermal Alcoholysis of 17a. A stock solution of **17a** was made (0.03 M) with the addition of internal standard (fluorene). NMR tubes were charged with 0.45 mL of the stock solution and sealed with rubber septums. Deuterated methol (25.0, 20.0, and 15.0 μL) was then injected with a microliter syringe. The rubber septums were wrapped with parafilm. The NMR probe was thermostated at 70 °C using the variable-temperature heater and calibrated with the TEMCAL(E) program. The decompositions were followed by monitoring the ^1H NMR resonances at 6.53, 6.02, and 3.90 ppm of the complex **17a**, methyl acrylate (**20**), and fluorene, respectively. Arrayed ^1H NMR spectra were obtained by creating a preacquisition delay array (PAD (1) = 0, 570, 570, 570, 570, 870, 870, 870, 870, 1170, 1170, 1170, 1170, 1770, etc.). The time of each spectrum was calculated by adding the PAD parameter to the acquisition time (30 s). The concentration of each species ([**17a**] and [**20**]) with respect to time was calculated by dividing the integral of the vinylic proton resonance by the integral of the internal standard (fluorene): concentration (M) = 2[fluorene]-$I/I_{fluorene}$, where [fluorene] (M) is the known concentration of the fluorene internal standard and I and $I_{fluorene}$ are the integrals of the compounds (**17a** and **20**) and fluorene, respectively. The concentrations were then plotted versus time to give the reaction profiles. The natural logarithm (ln) of the concentration of **17a** could then be plotted versus time. Linear least-squares analysis provided the pseudo-first-order rate constants ($k_1' = -$(slope)), which was then plotted versus methanol concentration to give the second-order rate constant k_2. Reactions at 65, 60, and 50 °C were performed with addition of 25 μL of deuterated methanol in the same way. Activation parameters were derived from the plot of ln (k_1'/T) versus ($1/T$) (K^{-1}) at 70, 65, 60, and 50 °C, where $\Delta H^\ddagger = -R$(slope) in cal/mol and $\Delta S^\ddagger = R(y$ intercept $-\ln(k/h))$ in eu (R = ideal gas constant; k = Boltzmann constant; h = Planck constant).

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Registry No. **7a**, 125540-89-8; **7b**, 125540-95-6; **8a**, 125540-90-1; **8b**, 125540-96-7; **9a**, 138813-36-2; **9b**, 138813-37-3; **10a**, 138813-38-4; **10b**, 138813-39-5; **11a**, 40192-91-4; **11b**, 138813-40-8; **12a**, 920-46-7; **12b**, 3350-78-5; **13**, 14221-02-4; **14**, 125540-91-2; **15**, 125540-80-9; **16**, 97-63-2; **17a**, 138834-32-9; **17b**, 138813-42-0; **18**, 138813-44-2; **20**, 35777-12-9.

Supplementary Material Available: Tables of crystal data, bond distances and angles, least-squares planes, general displacement parameters, and bond distance and angle calculation for **9b** (10 pages); a listing of structure factors for **9b** (12 pages). Ordering information is given on any current masthead page.