

Mechanism of the Metal-Mediated Carbalkoxylation of Vinyl Electrophiles. 2. Preparation, Molecular Structure, and Reductive Couplings of σ -Alkoxy carbonyl σ -Vinyl Platinum(II) Complexes[†]

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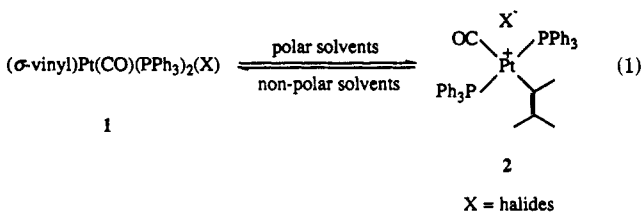
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The nucleophilic substitution reaction of the covalent σ -vinyl Pt(II) triflates 8 with carbon monoxide results in the cationic σ -vinyl Pt(II) carbonyls 12, which react with sodium alkoxides in the corresponding alcohols to afford the σ -alkoxycarbonyl σ -vinyl Pt(II) complexes 13. The interaction of triflate complex 8a with sodium ethoxide produces σ -vinyl Pt(II) hydride 10, rather than the expected ethoxide complex. Both compounds 12 and 13 were isolated and fully characterized. A single-crystal molecular structure determination is reported for *trans*-CH₂=C(CH₃)Pt(PPh₃)₂(COOC₂H₅) (13a). Complex 13a crystallizes in the triclinic space group P $\bar{1}$ with *a* = 9.696 (2) Å, *b* = 11.410 (3) Å, *c* = 16.069 (3) Å, α = 94.83 (2)°, β = 100.03 (2)°, γ = 91.64 (2)°, and *Z* = 2. The structure was solved and refined to *R* = 0.040 and *R*_w = 0.054 by using 4634 observed independent reflections. Kinetic studies on the coupling reactions of these alkoxy carbonyl Pt(II) complexes (13) were conducted with variable-temperature ¹H NMR spectroscopy. The reactions are greatly dependent on the substitution pattern of the vinyl ligands but little on the alkoxy carbonyl moieties. Phosphine inhibition and activation parameters strongly suggest that the reductive elimination of α,β -unsaturated carboxylic esters occurs via a pre-equilibration involving phosphine dissociation, followed by a rate-determining *trans*-*cis* isomerization.

Introduction

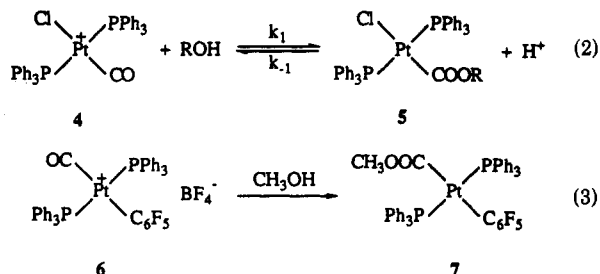
The two major pathways for the carbalkoxylation of organic electrophiles involve the reductive elimination reactions of two distinct species: (a) σ -acyl σ -alkoxy M(II) complexes; and (b) σ -alkoxycarbonyl σ -organo M(II) complexes.¹ In the preceding paper,² with emphasis on the reactions of vinyl halides, we have demonstrated the feasibility of carbonyl insertion into the alkenyl C-M bond to form the vinylic acyl complexes. The initial step of the insertion reaction proceeds via the precoordination of carbon monoxide to form a σ -vinyl Pt(II) carbonyl adduct 1. Ionization of 1 in polar solvents would lead to the formation of the cationic square-planar metal carbonyl 2 (eq 1). This observation raises the possibility of a



markedly different route in which the nucleophilic addition of alkoxide anions to the carbonyl ligand results in the formation of the σ -alkoxycarbonyl σ -vinyl M(II) complexes. Early studies on the carbalkoxylation of aryl halides have reported the isolations of *trans*-(CH₃OOC)Pd(PPh₃)₂X (X = halides) (3) from the catalytic system³ or under conditions similar to those employed in the carbalkoxylation process.⁴

The addition of nucleophiles to the carbonyl ligand has been recognized in the related catalytic carbonylation of aryl halides to give amides,⁵ α -keto amides,^{5,6} and α -keto esters.⁷ Many transition-metal carbonyls are known to react with alcohols to yield the corresponding alkoxy-carbonyl compounds.⁸ Kinetic studies on the reaction of

platinum carbonyl chloride 4 with various alcohols suggested that nucleophilic addition of the alkoxide anions occurred on the carbon atom of the CO ligand (eq 2).⁹ Moreover, the reaction of the cationic perfluorophenyl Pt(II) carbonyl 6 with methanol has been reported to give the perfluorophenyl methoxycarbonyl Pt(II) complex 7 (eq 3).¹⁰



Alternatively, the electropositive metal center, generated from the oxidative addition step, is also susceptible to the attack by a Lewis base. Many late-transition-metal complexes are known to react with alkoxide anions to give the

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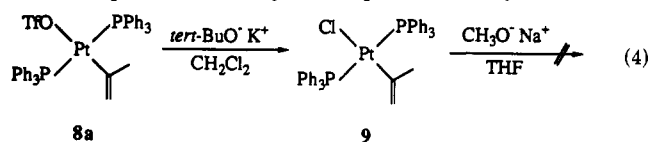
[†] Abstracted in part from: Zhong, Z. Ph.D. Dissertation, University of Utah, 1991. Dedicated to Professor George A. Olah on the occasion of his 65th birthday.

alkoxy compounds,¹¹ particularly those of group 10 metals containing σ -organo ligands.¹²⁻¹⁴ The subsequent carbonyl insertion into the M-O bond then produces the alkoxy-carbonyl complexes.^{13a,15-17} Just as in the carbonylation of σ -vinyl Pt(II) halides, carbonyl insertion into the M-O bond must proceed via a metal carbonyl intermediate; ionization of the carbonyl adduct in polar solvents would give an ion pair such as $[L_2M(CO)(R)]^+R'O^-$. Addition of the alkoxide counterion to the CO ligand then affords the alkoxy carbonyl complexes.^{18,19}

There are a number of alkoxy carbonyl organo M(II) (M = Ni, Pd, Pt) complexes known, some containing alkyl groups,^{12a,15,17} and others bearing electron-withdrawing σ -ligands.^{10,13a} However, few alkoxy carbonyl complexes with nonstabilized, unsaturated moieties have been reported,^{1,16,20} and the reductive elimination reactions of alkoxy carbonyl organo M(II) complexes remain unexplored.¹ Furthermore, triflate is a much better leaving group than halides and is expected to exhibit different reactivities.²¹ Because of the superior leaving group ability of the triflate ligand,²² the formation of the alkoxy carbonyl intermediate is very likely in the reaction with triflate substrates. However, there is no mechanistic information of any kind on the carbalkoxylation of organic triflates. Finally, the generation and controlled decomposition of the alkoxy carbonyl species, M-CO₂R, have also been considered as the key steps in many other carbonylation reactions.^{1,23} Hence, in this study, attention was directed toward the synthesis and coupling reactions of σ -alkoxy carbonyl σ -vinyl Pt(II) complexes, with reference to the metal-mediated carbalkoxylation of enol triflates.

Results and Discussion

Reaction of σ -Vinyl Pt(II) Triflate 8a with Sodium Ethoxide. A few perchlorovinyl Pt(II) halides are known to react with sodium alkoxides to yield Pt(II) alkoxy compounds.¹⁴ However, the nonactivated alkylvinyl Pt(II) halides are completely unreactive toward alkoxide nucleophiles. Thus, the interaction of triflate complex 8a with excess potassium *tert*-butoxide (5 equiv) in CH₂Cl₂ led to the exclusive formation of σ -vinyl Pt(II) chloride 9. Complex 9 is also unreactive toward sodium methoxide in THF (eq 4). Recently, we reported the synthesis and



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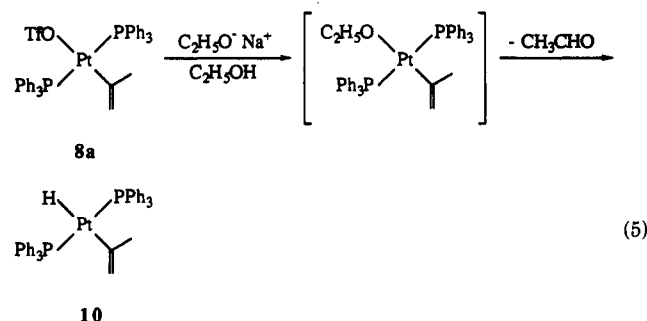
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characterization of several covalent σ -vinyl Pt(II) triflates.²⁴ The exceptional lability of these Pt(II) triflate complexes has allowed the syntheses of a wide variety of new σ -vinyl Pt(II) complexes, particularly those of unsaturated bis-(organo) Pt(II) compounds, by reactions with various nucleophiles.^{24b,25} Therefore, it was anticipated that σ -alkoxy σ -vinyl Pt(II) complexes may be prepared by the reaction of the covalent triflate complex 8a with alkoxide anions.

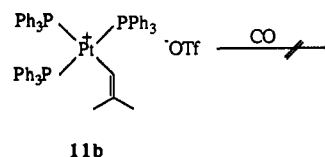
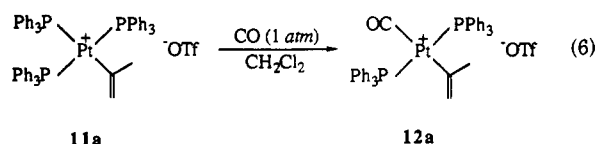
Unexpectedly, the reaction of 8a with excess sodium ethoxide in absolute ethanol led to the formation of the σ -vinyl Pt(II) hydride 10 in 39% isolated yield, rather than the corresponding ethoxy Pt(II) compound (eq 5). The



Pt-H bonding is clearly indicated by the broad IR band at 1996 cm⁻¹. Further support for the metal-hydride structure is provided by the upfield proton resonance at -5.43 ppm (²J_{PH} = 19.3 Hz, ¹J_{PtH} = 595.9 Hz). The singlet ³¹P resonance at 31.7 ppm (¹J_{PtP} = 3190 Hz) establishes the trans geometry of the product. The vinylic carbon resonances are similar to those of other trans σ -vinyl Pt(II) complexes.²⁴⁻²⁷

Although no mechanistic information was obtained, the formation of platinum hydride seems to involve the β -hydride elimination of the alkoxy ligand, which is well recognized in late-transition-metal alkoxy complexes.^{11,16b} Therefore, the σ -alkoxy σ -vinyl Pt(II) complexes are not suitable for the current study, and substitution with carbon monoxide was examined.

Preparation of Cationic σ -Vinyl Pt(II) Carbonyls. We recently reported the substitution reaction of cationic vinyl Pt(II) triflate 11a with carbon monoxide to give 12a by the displacement of the trans Ph₃P ligand (eq 6).²⁶



However, no reaction was observed with the analogous triflate salt 11b even under forcing conditions. Therefore, a general procedure for the preparation of these cationic σ -vinyl Pt(II) carbonyls was desirable.²⁷ This was accomplished by allowing the solutions of the covalent σ -vinyl Pt(II) triflates 8 to react with carbon monoxide under

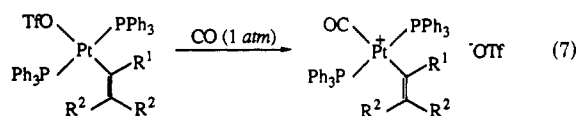
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atmospheric pressure. Recrystallization from CH_2Cl_2 /toluene afforded the carbonyl complexes **12** in 50–65% isolated yield (eq 7).



8a: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$;

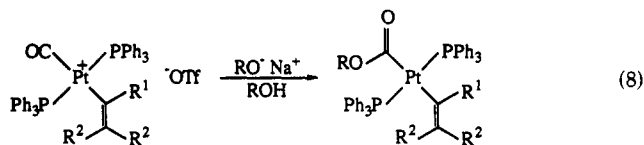
8b: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$.

12a: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$;

12b: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$.

Carbonyl complexes **12** were obtained as colorless microcrystals and have been fully characterized by IR, multinuclear NMR, mass (FAB) spectroscopy, and elemental analysis. The terminal CO ligand is evident from the strong IR absorption at about 2090 cm^{-1} ; the intense absorptions at about 1270 and 630 cm^{-1} are due to the triflate counterion, indicating the cationic nature of the complexes.²² In the ^{13}C NMR spectra the carbonyl carbon resonances appear at 176 – 180 ppm as triplets due to the coupling with two equivalent phosphorus groups. The presence of two equivalent Ph_3P groups was also supported by the singlet ^{31}P resonances, along with ^{195}Pt satellites. The ^1H NMR spectra display all the expected vinyl proton resonances similar to the other trans σ -vinyl Pt(II) complexes.^{24–26}

Preparation of σ -Alkoxy carbonyl σ -Vinyl Pt(II) Complexes. The synthesis of the alkoxy carbonyl complexes **13** involves a straightforward metathetical reaction between σ -vinyl Pt(II) carbonyls **12** and sodium alkoxides (eq 8). Addition of excess sodium ethoxide to the sus-



12a: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$;

12b: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$.

13a: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$, $\text{R} = \text{C}_2\text{H}_5$;

13b: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$, $\text{R} = \text{C}_2\text{H}_5$;

13c: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$, $\text{R} = \text{CH}_3$.

pension of **12a** in absolute ethanol immediately resulted in a homogeneous solution, which then slowly turned heterogeneous with stirring. The remaining sodium ethoxide and the resulting triflate salt were removed by filtration and extraction. Careful recrystallization from CH_2Cl_2 /hexane gave the ethoxycarbonyl product **13a** in 76% yield. Similarly, the suspensions of **12a** and **12b** in methanol were allowed to react with excess sodium methoxide to give methoxycarbonyl complexes **13b** and **13c** in 65–80% isolated yield.

These alkoxy carbonyl complexes **13** are stable, colorless microcrystalline solids and have been fully characterized on the basis of IR, multinuclear NMR, and mass (FAB) spectroscopy, and elemental analysis. The spectral data clearly establish the neutral, tetracoordinate nature of the compounds and the trans stereochemistry around the platinum center. ^{31}P NMR spectra display singlet resonances between 17.8 and 19.1 ppm, along with ^{195}Pt satellites. All ^{13}C NMR spectra show the resonances of the carbonyl carbon of the σ -bonded alkoxy carbonyl moieties at about 206 ppm as triplets, due to coupling with two equivalent phosphorus groups. The strong IR absorptions at $1625 \pm 5 \text{ cm}^{-1}$ are the $\text{C}=\text{O}$ stretching frequencies of the alkoxy carbonyl ligand.

The alkoxy carbonyl structure was confirmed by X-ray crystallographic analysis of **13a**. A single crystal of **13a** was grown from $\text{ClCH}_2\text{CH}_2\text{Cl}$ /pentane solution. An ORTEP diagram is illustrated in Figure 1. Crystallographic data

Table I. Summary of Crystallographic Data for Alkoxy carbonyl Pt(II) Complex **13a**

mol formula	$\text{C}_{22}\text{H}_{40}\text{O}_2\text{P}_2\text{Pt}$
mol weight	833.82
space group	P1
space group no.	2
cryst syst	triclinic
cell dimens	
<i>a</i> , Å	9.696 (2)
<i>b</i> , Å	11.910 (3)
<i>c</i> , Å	16.069 (3)
<i>α</i> , deg	94.83 (2)
<i>β</i> , deg	100.03 (2)
<i>γ</i> , deg	91.64 (2)
<i>V</i> , Å ³	1819.1
<i>Z</i>	2
<i>d</i> _{calcd} , g/cm ³	1.522
cryst dimens, mm	$0.31 \times 0.27 \times 0.21$
abs coeff, cm ⁻¹	40.16
radiation; λ, Å	Mo; 0.71073
no. of reflns measd	6133
no. of unique reflns	5745
2θ range, deg	2.50–48.00
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>I</i> > 3.0σ(<i>I</i>)	4634
no. of variables	424
<i>R</i> (<i>F</i>)	0.040
<i>R</i> _w (<i>F</i>)	0.054

highest peak in final Fourier map, $1.704 \text{ e}/\text{Å}^3$ about 1.1 Å from Pt atom

Table II. Selected Bond Distances (Å) for Alkoxy carbonyl Pt(II) Complex **13a**^a

Pt–P1	2.292 (1)	O2–C5	1.480 (8)
Pt–P2	2.299 (1)	C5–C6	1.49 (1)
Pt–C1	2.071 (6)	P1–C7	1.828 (6)
Pt–C4	2.092 (6)	P1–C13	1.828 (6)
C1–C2	1.306 (9)	P1–C19	1.838 (6)
C1–C3	1.54 (1)	P2–C25	1.837 (5)
O1–C4	1.205 (8)	P2–C31	1.815 (6)
O2–C4	1.378 (8)	P2–C37	1.801 (6)

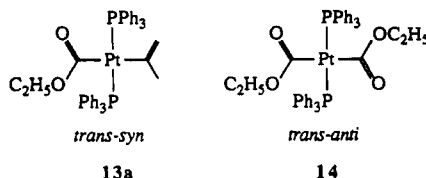
^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Selected Bond Angles (deg) for Alkoxy carbonyl Pt(II) Complex **13a**^a

P1–Pt–P2	174.94 (6)	Pt–C1–C3	118.9 (5)
P1–Pt–C1	89.0 (2)	C2–C1–C3	119.2 (6)
P1–Pt–C4	91.3 (2)	Pt–C4–O1	123.4 (5)
P2–Pt–C1	89.3 (2)	Pt–C4–O2	114.7 (5)
P2–Pt–C4	89.8 (2)	O1–C4–O2	121.9 (6)
C1–Pt–C4	172.9 (3)	C4–O2–C5	116.3 (5)
Pt–C1–C2	121.9 (6)	O2–C5–C6	111.3 (7)

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

and selected bond distances and bond angles are presented in Tables I–III, respectively. The geometry of complex **13a** is very close to square planar. The ethoxycarbonyl and vinyl groups are essentially coplanar but nearly perpendicular to the coordination plane of Pt–P1–P2–C1–C4 with a mean dihedral angle of $86.5 (3)^\circ$. Interestingly, the trans-anti configuration reported for complex **14**²⁶ is not



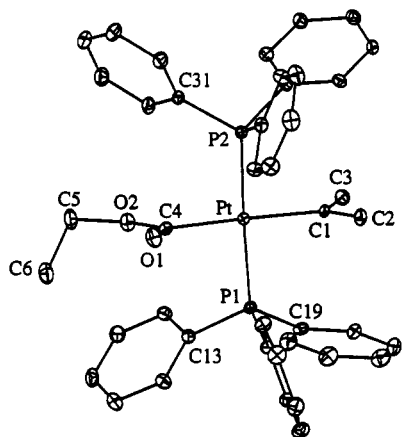
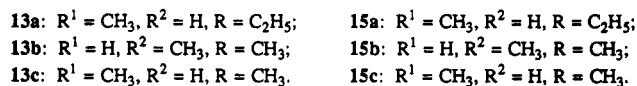
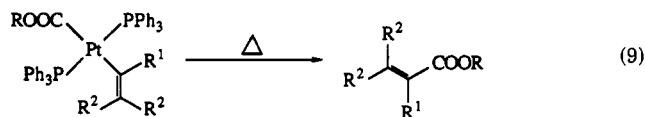


Figure 1. Solid-state structure and atom numbering of alkoxy carbonyl Pt(II) complex 13a.

observed here; the molecule of 13a possesses a trans-syn configuration. The C4–Pt bond distance of 2.092 (6) Å is slightly longer than all known cis alkoxy carbonyl carbon–platinum bonds in the literature.^{7b,29,30} The carbonyl C4–O1 bond distance of 1.205 (8) Å lies within the range of C=O double bonds (1.19–1.23 Å) of other coordinated alkoxy carbonyl moieties.^{7b,28–30} The vinyl C–Pt bond appears to be normal.^{24a,b,25,26,31–33}

Kinetic Studies on the Reductive Elimination Reactions of σ -Alkoxy carbonyl σ -Vinyl Pt(II) Complexes. Although a few alkoxy carbonyl M(II) (Pd, Pt) complexes have been reported,^{1,10,13a,15–17,20} there is no pertinent information on the reductive elimination to carboxylic esters. The best Pd(II) analogue to complexes 13, *trans*-(benzyl)Pd(PMe₃)₂(methoxycarbonyl), has no tendency to undergo thermal decomposition to give methyl benzoate.¹ The reaction is apparently retarded by the strong complexation of the small, basic trimethylphosphine ligands. Having synthesized these new σ -alkoxy carbonyl σ -vinyl Pt(II) complexes, we examined their reductive elimination couplings to yield α,β -unsaturated carboxylic esters.

Initially, complex 13a was subjected to thermal decomposition by heating a C₆D₅CD₃ solution in a sealed NMR tube. Complex 13a is only slightly soluble in C₆D₅CD₃ at room temperature. Heating the mixture at 45 °C slowly resulted in a light yellow homogeneous solution. However, no reaction was observed by ¹H and ³¹P NMR spectroscopy, but further heating at 60 °C overnight led to the clean formation of ethyl methacrylate 15a (eq 9).



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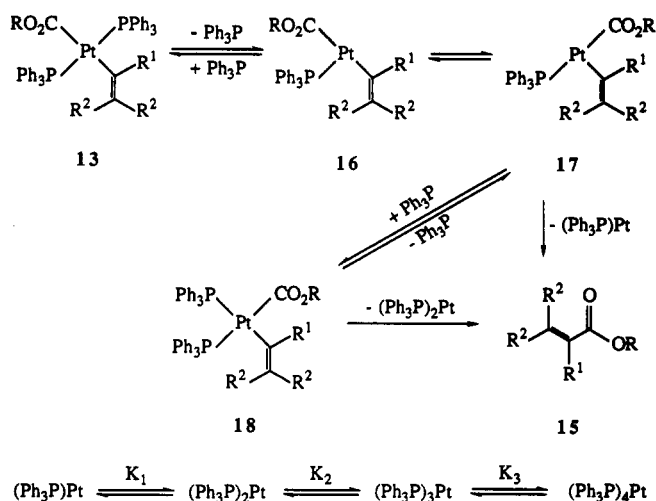
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Table IV. Rate Constants and Activation Parameters for Thermal Decomposition of 13

entry	compd	solvent	temp. ^a °C	k ₁ ^b min ⁻¹	ΔH [‡] , kcal/mol	ΔS [‡] , eu
1	13a	C ₆ D ₅ CD ₃	60.0	0.0034 ± 0.0002	25.5	6.5
2	13a	C ₆ D ₅ CD ₃	70.0	0.011 ± 0.001		
3	13a	C ₆ D ₅ Cl	70.0	0.0095 ± 0.0002		
4	13a	C ₆ D ₅ CD ₃	79.9	0.032 ± 0.002		
5	13a	C ₆ D ₅ Cl	79.9	0.030		
6	13a	C ₆ D ₅ NO ₂	69.9	0.028		
7	13b	C ₆ D ₅ CD ₃	90.1	0.0026	19.7	-16.2
8	13b	C ₆ D ₅ CD ₃	100.1	0.0063 ± 0.0003		
9	13b	C ₆ D ₅ CD ₃	110.4	0.012 ± 0.001		
10	13c	C ₆ D ₅ Cl	60.3	0.0030	24.9	4.5
11	13c	C ₆ D ₅ Cl	70.3	0.0094		
12	13c	C ₆ D ₅ Cl	79.9	0.025		

^a Temperature controlled to ±0.5 °C. ^b Average of runs.

Scheme I. Likely Mechanism of Reductive Elimination Reactions of Alkoxy carbonyl Pt(II) Complexes



13a: R¹ = CH₃, R² = H, R = C₂H₅;

13b: R¹ = H, R² = CH₃, R = CH₃;

13c: R¹ = CH₃, R² = H, R = CH₃.

The product was confirmed by GC and GC–MS analysis and comparison with authentic materials. ³¹P NMR spectra showed no distinct phosphorus-containing compounds, although ester formation is accompanied by the decomposition of a large amount of 13a. Likewise, the thermal decomposition of 13b and 13c produces acrylic esters 15b and 15c, respectively (eq 9).

Having demonstrated the formation of α,β -unsaturated carboxylic esters from alkoxy carbonyl Pt(II) complexes 13, we undertook a more detailed kinetic investigation of these coupling reactions. Both the disappearance of starting complexes and appearance of substituted acrylic esters could be followed by monitoring the ethoxyl methylene proton resonances of complex 13a (3.10 ppm) and ester 15a (3.98 ppm) or the methoxyl proton resonances of the complexes (2.72 ppm for 13b, 2.49 ppm for 13c) and esters (3.43 ppm for 15b and 3.40 ppm for 15c). The first-order decomposition reactions were followed to at least 3 half-lives by variable-temperature ¹H NMR spectroscopy. The thermal decomposition of 13a was performed at 60–80 °C, and the data are summarized in Table IV. The yields of the ester formation are 40–50% in all decomposition reactions of 13 presumably due to acrylate polymerization.

Theoretical calculations clearly indicate that reductive elimination from d⁸ metal complexes must proceed via a cis or trigonal-planar orientation.³⁴ Therefore, these trans

Table V. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B, \text{\AA}^2$
Pt	0.01612 (4)	0.10628 (3)	0.26312 (3)	2.628 (7)
P1	-0.0026 (3)	0.2893 (2)	0.2300 (2)	2.81 (5)
P2	0.0498 (3)	-0.0788 (2)	0.2889 (2)	2.70 (5)
O1	-0.1698 (8)	0.0211 (7)	0.1049 (5)	4.9 (2)
O2	-0.2890 (8)	0.0646 (7)	0.2114 (4)	4.3 (2)
C1	0.212 (1)	0.1502 (9)	0.3355 (8)	4.4 (3)
C2	0.326 (1)	0.143 (1)	0.3034 (6)	3.9 (2)
C3	0.221 (1)	0.192 (1)	0.4298 (7)	4.3 (3)
C4	-0.168 (1)	0.0565 (8)	0.1776 (8)	3.9 (2)
C5	-0.418 (1)	0.012 (1)	0.158 (1)	6.3 (4)
C6	-0.489 (1)	0.092 (1)	0.100 (1)	6.5 (4)
C7	0.071 (1)	0.3114 (9)	0.1351 (7)	3.4 (2)
C8	0.105 (1)	0.4192 (9)	0.1160 (7)	4.1 (3)
C9	0.162 (1)	0.435 (1)	0.0432 (7)	5.0 (3)
C10	0.188 (1)	0.341 (1)	-0.0076 (8)	5.2 (3)
C11	0.158 (1)	0.235 (1)	0.0107 (8)	5.2 (3)
C12	0.099 (1)	0.219 (1)	0.0849 (7)	4.3 (2)
C13	-0.183 (1)	0.3334 (8)	0.2071 (6)	3.2 (2)
C14	-0.268 (1)	0.3224 (9)	0.2648 (7)	3.8 (2)
C15	-0.405 (1)	0.355 (1)	0.2513 (8)	4.7 (3)
C16	-0.461 (1)	0.395 (1)	0.1760 (9)	4.9 (3)
C17	-0.379 (1)	0.404 (1)	0.1122 (8)	4.9 (3)
C18	-0.240 (1)	0.374 (1)	0.1278 (7)	4.0 (2)
C19	0.087 (1)	0.4023 (8)	0.3072 (6)	3.3 (2)
C20	0.016 (1)	0.470 (1)	0.3589 (8)	5.0 (3)
C21	0.089 (2)	0.553 (1)	0.4179 (9)	5.7 (3)
C22	0.232 (2)	0.568 (1)	0.4256 (8)	5.8 (3)
C23	0.304 (1)	0.502 (1)	0.3728 (8)	5.2 (3)
C24	0.230 (1)	0.4192 (9)	0.3149 (7)	4.2 (3)
C25	0.149 (1)	-0.1049 (8)	0.3931 (6)	2.7 (2)
C26	0.078 (1)	-0.1272 (9)	0.4586 (6)	3.4 (2)
C27	0.151 (1)	-0.140 (1)	0.5406 (7)	4.2 (3)
C28	0.297 (1)	-0.1328 (9)	0.5551 (7)	4.0 (2)
C29	0.367 (1)	-0.1111 (9)	0.4907 (7)	3.7 (2)
C30	0.294 (1)	-0.0960 (9)	0.4100 (6)	3.5 (2)
C31	-0.107 (1)	-0.1685 (8)	0.2822 (6)	3.2 (2)
C32	-0.121 (1)	-0.279 (1)	0.2537 (9)	5.0 (3)
C33	-0.238 (1)	-0.346 (1)	0.257 (1)	5.9 (3)
C34	-0.344 (1)	-0.303 (1)	0.293 (1)	6.3 (3)
C35	-0.333 (1)	-0.191 (1)	0.3252 (9)	5.4 (3)
C36	-0.216 (1)	-0.124 (1)	0.3206 (7)	4.1 (2)
C37	0.148 (1)	-0.1489 (8)	0.2161 (6)	3.3 (2)
C38	0.145 (1)	-0.1058 (9)	0.1363 (7)	3.8 (2)
C39	0.220 (1)	-0.155 (1)	0.0785 (7)	5.0 (3)
C40	0.296 (1)	-0.248 (1)	0.0979 (7)	5.3 (3)
C41	0.298 (1)	-0.293 (1)	0.1734 (8)	5.3 (3)
C42	0.224 (1)	-0.2444 (9)	0.2336 (7)	3.9 (2)

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

σ -alkoxycarbonyl σ -vinyl Pt(II) complexes, **13**, must first undergo phosphine dissociation to provide an intermediate capable of reductive elimination (Scheme I). Indeed, the coupling reaction of **13a** can be completely inhibited by added Ph_3P . In the presence of 2 equiv of Ph_3P , no reaction could be detected by ^1H NMR spectroscopy even after heating at 70 °C overnight (>15 h).

In the presence of less than 1 equiv of added Ph_3P (0.29–1.0 equiv), the decomposition of **13a** took place with rates convenient to monitor at 80 °C in $\text{C}_6\text{D}_5\text{Cl}$. At the early stages the reaction distinctly deviates from first-order kinetics as the amount of Ph_3P increases (Figure 2). Furthermore, the reaction rates accelerate as a function of time until first-order kinetics are established. This observation clearly indicates that an induction period is required for the reductive coupling in the presence of Ph_3P . The induction period $T_{\text{induction}}$ is derived by extrapolating

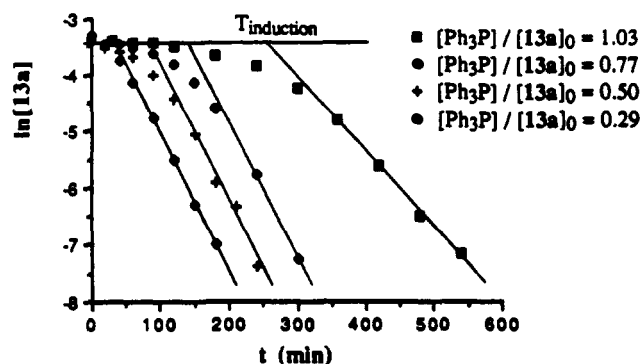


Figure 2. First-order plot of thermal decomposition of **13a** with added Ph_3P .

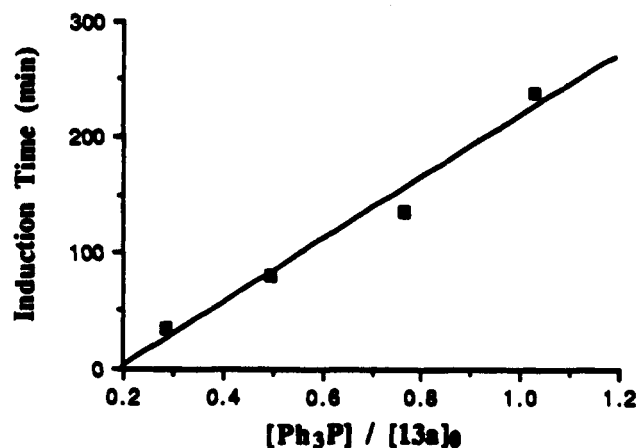


Figure 3. Plot of induction time versus $[\text{Ph}_3\text{P}]/[\text{13a}]_0$.

the curve to the initial concentration of **13a** (Figure 2). Interestingly, $T_{\text{induction}}$ is directly proportional to the amount of added Ph_3P , as shown in Figure 3, where $[\text{Ph}_3\text{P}]/[\text{13a}]_0$ is the ratio of the phosphine concentration and the initial concentration of complex **13a**. The data clearly indicate that the reductive elimination occurs via a preequilibrium involving phosphine dissociation, which in turn could be affected by possible equilibrations between various platinum–phosphine species generated during the reaction (Scheme I).

The reaction is also affected by solvent polarity. When complex **13a** was decomposed in a more polar solvent $\text{C}_6\text{D}_5\text{NO}_2$ (entry 6), the rate of decomposition is twice as fast as in $\text{C}_6\text{D}_5\text{CD}_3$.

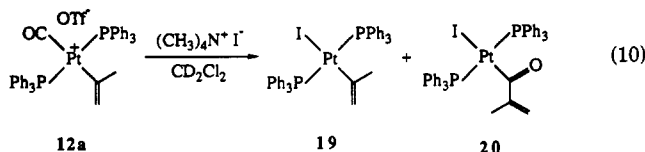
This solvent effect shows that more polar solvents facilitate dissociation and therefore accelerate the reaction. No significant change was observed when the reaction was performed in a less polar solvent $\text{C}_6\text{D}_5\text{Cl}$ rather than $\text{C}_6\text{D}_5\text{NO}_2$ as compared to $\text{C}_6\text{D}_5\text{CD}_3$ (entries 3 and 5). The positive entropies of activation, solvent effect, and phosphine inhibition all suggest the dissociative nature of the coupling reaction.

The effect of substrate structure was also examined. Since complex **13c** was completely insoluble in $\text{C}_6\text{D}_5\text{CD}_3$, its reductive elimination to methyl methacrylate, **15c**, was accomplished in $\text{C}_6\text{D}_5\text{Cl}$ at 60–80 °C (entries 10–12). Previous experiments showed that chlorobenzene does not affect the decomposition rate of **13a** (entries 3 and 5). Therefore the influence of methoxycarbonyl and ethoxycarbonyl ligands is negligible.

On the other hand, there appears to be a strong dependence of the coupling on the substitution pattern of the vinyl moiety. The reductive coupling of the β -substituted **13b** is a much slower process than that of **13a** and

13c. Complex **13b** was thus thermalized in $C_6D_5CD_3$ at 90–110 °C (entries 7–9). The negative value of the activation entropy strongly suggests an ordered transition state in the rate-determining step. Hence, trans-cis isomerization from **13b** to **18b** (Scheme I; $18 R^1 = H, R^2 = CH_3, R = CH_3$) is likely to be the rate-determining step and a concerted transition state for the direct reductive elimination from the cis isomer **18b** may be invoked.

Interconversion of Acyl Pt(II) and Alkoxy carbonyl Pt(II) Complexes. In the preceding paper, we have shown that the interaction of the cationic σ -vinyl Pt(II) carbonyl **12a** with the iodide anion leads to the formation of the covalent vinylic acyl Pt(II) iodide **20** (eq 10).²



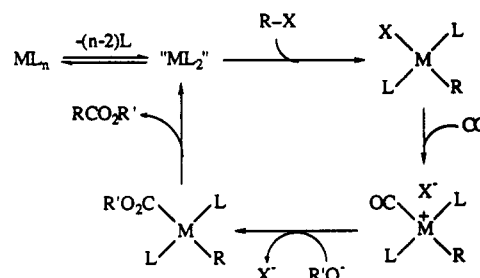
Clearly, vinylic acyl Pt(II) complexes are thermodynamically more stable than the carbonyl species. This implies that the formation of an acyl intermediate may be a facile route for the catalytic carbalkoxylation process in the presence of a halide source. However, in the systems containing the more reactive triflates, in the absence of halide anions, the addition of alkoxy nucleophiles to the CO ligand of the carbonyl intermediates may become important. Under such halide-free conditions, an alkoxy-carbonyl intermediate could be generated, which then reductively eliminates carboxylic ester.

Conclusions

The current studies have described the preparation of several new platinum complexes which serve as the isostructural analogues to the possible intermediates in the catalytic carbalkoxylation process. These σ -vinyl Pt(II) complexes represent a possible model for the catalytic carbalkoxylation of organic triflates. Oxidative addition of triflates yields the σ -organo M(II) triflate complexes.²⁴ While interaction with alkoxide nucleophiles results in the formation of transition-metal hydrides, carbon monoxide replaces the labile triflate group to generate the cationic σ -organo M(II) carbonyls via nucleophilic substitution. Subsequent addition of alkoxides on the CO ligand forms the σ -bonded alkoxy carbonyl moieties. The resulting σ -alkoxy carbonyl σ -organo M(II) complexes then reductively eliminate carboxylic esters. Phosphine inhibition experiments and kinetic studies indicate that the reductive couplings of trans σ -alkoxy carbonyl σ -vinyl Pt(II) complexes occur via a preequilibrium involving phosphine dissociation, followed by the rate-determining trans-cis isomerization prior to the elimination of the α,β -unsaturated carboxylic esters. Activation parameters show that the reaction is greatly dependent on the substitution pattern of the vinyl ligands but little upon the alkoxy-carbonyl moieties.

The catalytic cycle of the nickel triad metal-mediated carbalkoxylation of vinyl triflates can be generalized in Scheme II, with most of the key intermediates isolated and fully characterized. Since covalent vinylic acyl M(II) halides are thermodynamically more stable than the cationic σ -vinyl M(II) carbonyls, the formation of the acyl M(II) intermediate is the more facile route for the carbalkoxylation process in the presence of a halide source. Due to the superior leaving group ability of the triflate ligand, however, the alkoxy carbonyl species could be generated with triflate substrates under halide-free conditions, which then reductively eliminate α,β -unsaturated

Scheme II. Catalytic Cycle of the Metal Mediated Carbalkoxylation of Vinyl Triflates



M = Ni, Pd, Pt; R = vinyl; R' = alkyl; L = phosphines; X = triflate.

carboxylic esters. To the best of our knowledge, this is the first example of an extensive investigation, involving both acyl M(II)² and alkoxy carbonyl M(II) complexes, on the transition-metal-mediated carbalkoxylation of vinyl electrophiles. Although our reactions were performed stoichiometrically with platinum complexes, we believe that this system is an excellent model for the nickel triad metal-mediated catalytic carbalkoxylation of vinyl electrophiles.

Experimental Section

Materials. Hydrocarbon solvents (hexanes, pentane, and toluene) and methylene chloride either were reagent grade or were purified as described in the preceding paper.² Methanol was directly collected from distillation over CaH_2 . Chlorobenzene and 1,2-dichloroethane 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-transferred or directly used as packaged without purification ($C_6D_5CD_3$, C_6D_5Cl , CD_2Cl_2 , $C_6D_5NO_2$). Triphenylphosphine and fluorene were recrystallized from hexanes and vacuum-dried. Sodium methoxide and ethoxide (Aldrich) and carbon monoxide (Matheson) were directly used as purchased without purification. The covalent σ -vinyl Pt(II) triflates, **8**, were prepared according to known procedures.²⁴

Physical Methods. 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 (300 MHz) spectrometer. ^1H NMR chemical shifts are reported in ppm relative to the residual proton resonance of the NMR solvents: CDCl_3 (7.24 ppm), CD_2Cl_2 (5.32 ppm), $C_6D_5CD_3$ (methyl, 2.09 ppm). ^{13}C NMR spectra were acquired 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). ^{31}P NMR spectra were measured at 121 MHz with broad-band ^1H decoupling with the magnet locked on the deuterated solvents. An external 85% H_3PO_4 reference was used, and the ^{31}P downfield shifts were assigned positive value and reported in ppm. ^{19}F NMR spectra were obtained at 282 MHz, and resonances are reported in ppm relative to external CFC_3 at 0.0 ppm.

Fast atom bombardment mass spectra were obtained with a VG Analytical 7050-E mass spectrometer. X-ray data were collected on a Syntex P1 automated diffractometer at ambient temperature (16 ± 1 °C). A crystal of the compound was grown from $\text{ClCH}_2\text{CH}_2\text{Cl}$ /pentane solution. The crystal was glued onto a glass fiber and mounted for data collection. Cell constants (Table I) were obtained from 30 reflections with $18.0 < 2\theta < 28.0$. The space group was determined from subsequent least-squares refinement. Standard reflections showed no decay during collection.

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_0 about 0.023. 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.³⁶

Gas chromatograms were obtained on a Hewlett-Packard 5711 GC instrument equipped with a flame ionization detector and a Hewlett-Packard 3380 integrator, using a 0.125 in. \times 6 ft. UCW-98 on 80/100 Chromosorb W analytical column, or a Hewlett-Packard 5890 Series II GC instrument equipped with a flame ionization detector and a Hewlett-Packard 3396A integrator, using a 25 m \times 0.32 mm \times 0.3 mm film thickness Carbowax 20M (HP-20M) capillary column.

Reaction of 8a with Sodium Ethoxide. A solution of triflate complex 8a (123 mg, 0.135 mmol) in 5 mL of ethanol was degassed through three freeze-pump-thaw cycles. The addition of sodium ethoxide (46 mg, 0.68 mmol) immediately resulted in a white precipitate. After stirring for 3 h under N₂, the solid was filtered out and washed with ethanol. Recrystallization from CH₂Cl₂/hexane gave 40 mg (39%) of microcrystalline σ -vinyl Pt(II) hydride 10: mp 151–152 °C dec; IR 3048 (m), 2906 (m), 1996 (br m), 1573 (w), 1478 (m), 1435 (s), 1184 (m), 1096 (s), 1027 (w), 854 (m), 745 (m), 693 cm⁻¹ (s); ¹H NMR (CDCl₃) δ -5.43 (mt, ²J_{PH} = 19.3 Hz, ¹J_{PH} = 595.9 Hz, 1 H, H_{Pt}), 1.19 (s, ³J_{PH} = 29.4 Hz, 3 H, CH₃), 4.42 (m, ³J_{PH} = 38.4 Hz, 1 H, (Z)-CH=), 5.46 (m, ³J_{PH} = 81.3 Hz, 1 H, (E)-CH=), 7.3 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ³¹P NMR (CDCl₃) δ 31.7 (s, ¹J_{PP} = 3190 Hz); ¹³C NMR (CDCl₃) δ 31.6 (s, ¹J_{PC} = 35.4 Hz, CH₃), 115.4 (t, ³J_{PC} = 2.8 Hz, ²J_{PC} = 31.2 Hz, CH₂=), 127.8 (t, ³J_{PC} = 5.1 Hz, *m*-C), 129.8 (s, *p*-C), 133.9 (t, ¹J_{PC} = 27.4 Hz, ²J_{PC} = 31.9 Hz, *ipso*-C), 134.7 (t, ²J_{PC} = 6.7 Hz, *o*-C), 174.6 (t, ²J_{PC} = 9.7 Hz, C(CH₃)=); FAB MS 761 (24%), 760 (27%), 720 (19%), 719 (30%), 457 (13%). Anal. Calcd for C₃₉H₃₆Pt: C, 61.49; H, 4.76. Found: C, 61.22; H, 4.83.

General Procedure for the Preparation of Cationic σ -Vinyl Pt(II) Carbonyls: [*trans*-CH₂=C(CH₃)Pt(PPh₃)₂(CO)](OTf) (12a). Carbon monoxide was bubbled through dry CH₂Cl₂ (50 mL) for 15 min to saturation. Complex 8a (1/2 C₆H₅CH₃ solvate, 597 mg, 0.632 mmol) was then added, leading to a brown solution. CO was bubbled through the solution for 4 h. The solution was concentrated to about 4 mL by evaporation on a rotovap. After filtration, toluene was added to precipitate the product. The solid was filtered out, washed with toluene and hexane, and dried in high vacuo for 5 h to yield 388 mg (65%) of 12a. Characterization of 12a has been previously reported.²⁶

[*trans*-(CH₃)₂C=CHPt(PPh₃)₂(CO)](OTf) (12b). This complex was prepared by bubbling CO through the suspension of 8b (246 mg, 0.266 mmol) in toluene for 2 h. Workup as above afforded 126 mg (50%) of carbonyl product 12b as white microcrystals: mp 143–144 °C dec; IR 3059 (m), 2899 (w), 2089 (s), 1482 (m), 1436 (s), 1264 (s), 1223 (m), 1150 (s), 1099 (s), 1031 (s), 998 (m), 752 (m), 693 (s), 637 cm⁻¹ (s); ¹H NMR (CD₂Cl₂) δ 0.59 (t, ³J_{PH} = 1.8 Hz, 3 H, CH₃), 1.02 (td, ⁵J_{PH} = 3.1 Hz, ⁴J_{HH} = 1.2 Hz, 3 H, CH₃), 5.80 (t, ³J_{PH} = 4.9 Hz, 1 H, CH=), 7.5–7.7 (30 H, aromatics); ³¹P NMR (CD₂Cl₂) δ 16.8 (s, ¹J_{PP} = 2666 Hz); ¹³C NMR (CD₂Cl₂) δ 26.4 (s, ³J_{PC} = 47.8 Hz, (Z)-CH₃), 28.7 (s, ³J_{PC} = 62.5 Hz, (E)-CH₃), 121.5 (q, ¹J_{PC} = 321.5 Hz, CF₃), 128.0 (t, ¹J_{PC} = 30.8 Hz, ²J_{PC} = 30.5 Hz, *ipso*-C), 129.6 (t, ³J_{PC} = 5.6 Hz, *m*-C), 131.3 (t, ²J_{PC} = 11.5 Hz, =C_{Pt}), 132.8 (s, *p*-C), 134.7 (t, ²J_{PC} = 6.2 Hz, *o*-C), 141.2 (t, ³J_{PC} = 5.0 Hz, C(CH₃)₂), 179.6 (t, ²J_{PC} = 8.0 Hz, CO); FAB MS 802 (5%), 774 (100%), 747 (6%), 719 (61%), 457 (28%). Anal. Calcd for C₄₂H₃₇O₄F₃P₂Spt: C, 53.00; H, 3.92. Found: C, 53.07; H, 3.96.

General Procedure for the Synthesis of σ -Alkoxy carbonyl σ -Vinyl Pt(II) Complexes: *trans*-CH₂=C(CH₃)Pt(PPh₃)₂(COOC₂H₅) (13a). A suspension of 12a (152 mg, 0.162 mmol) in 5 mL of absolute ethanol was degassed through three freeze-pump-thaw cycles. Sodium ethoxide (55 mg, 0.81 mmol) was added all at once under N₂ protection. The mixture immediately turned light yellow clear solution and then changed to a new suspension. After stirring for 2 h, the white solid was filtered out, washed with ethanol and hexanes, and dissolved in about 3 mL of CH₂Cl₂. The insoluble residue was removed by filtration. Slow addition of hexane led to a colorless microcrystalline solid. The product was filtered out, washed with hexanes, and dried in vacuo to yield 103 mg (76%) of 13a. Single crystals of 13a were obtained by diffusion recrystallization from 1,2-dichloroethane/pentane

solution: mp 150–151 °C dec; IR 3053 (m), 2970 (m), 2909 (m), 1627 (s), 1482 (s), 1435 (s), 1379 (w), 1312 (w), 1186 (m), 1157 (w), 1096 (s), 1031 (s), 856 (m), 745 (s), 694 (s), 632 cm⁻¹ (w); ¹H NMR (CDCl₃) δ 0.44 (t, ³J_{HH} = 7.1 Hz, 3 H, CH₃CH₂), 0.85 (s, ³J_{PH} = 21.1, 3 H, CH₃C=), 2.76 (q, ³J_{HH} = 7.1 Hz, 2 H, CH₂O), 4.31 (dt, ²J_{HH} = 3.8 Hz, ⁴J_{PH} = 1.2 Hz, ³J_{PH} = 27.8 Hz, 1 H, (Z)-CH=), 5.30 (dt, ²J_{HH} = 3.8 Hz, ⁴J_{PH} = 1.4 Hz, ³J_{PH} = 59.8 Hz, 1 H, (E)-CH=), 7.3 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ³¹P NMR (CDCl₃) δ 18.0 (s, ¹J_{PP} = 3243 Hz); ¹³C NMR (CDCl₃) δ 14.1 (s, CH₃), 30.7 (s, ²J_{PC} = 21.3 Hz, CH₃C=), 56.2 (s, ³J_{PC} = 18.8 Hz, CH₂O), 119.5 (t, ³J_{PC} = 3.8 Hz, CH₂=), 127.5 (t, ³J_{PC} = 5.3 Hz, *m*-C), 129.9 (s, *p*-C), 131.6 (t, ¹J_{PC} = 28.0 Hz, ²J_{PC} = 32.0 Hz, *ipso*-C), 134.8 (t, ²J_{PC} = 6.1 Hz, *o*-C), 161.7 (t, ²J_{PC} = 11.6 Hz, C_{Pt}=), 205.0 (t, ²J_{PC} = 12.6 Hz, CO); FAB MS 788 (3%), 761 (100%), 760 (90%), 719 (25%), 457 (18%). Anal. Calcd for C₄₂H₄₀O₂Pt: C, 60.50; H, 4.84. Found: C, 60.41; H, 4.85.

***trans*-(CH₃)₂C=CHPt(PPh₃)₂(COOCH₃) (13b).** The carbonyl complex 12b (311 mg, 0.327 mmol) was dissolved in 15 mL of dry CH₃OH, and the solution was degassed through three freeze-pump-thaw cycles. Sodium methoxide (88 mg, 1.63 mmol) was then added all at once. A white precipitate appeared within minutes after the addition. After stirring for 2 h, the white solid was filtered out and washed with methanol and hexane. Recrystallization from CH₂Cl₂/hexane provided 187 mg (69%) of colorless microcrystalline product 13b: mp 158–159 °C dec; IR 3055 (m), 2896 (m), 1625 (s), 1482 (m), 1434 (s), 1185 (m), 1097 (s), 1024 (s), 927 (m), 745 (s), 693 (s), 628 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 0.48 (br s, 3 H, (Z)-CH₃), 0.98 (br d, ⁴J_{HH} = 1.0 Hz, 3 H, (E)-CH₃), 2.45 (s, 3 H, CH₃O), 5.77 (br s, 1 H, CH=), 7.3 (m, 18 H, aromatics), 7.6 (m, 12 H, aromatics); ³¹P NMR (CDCl₃) δ 19.1 (s, ¹J_{PP} = 3157 Hz); ¹³C NMR (CDCl₃) δ 24.7 (s, ³J_{PC} = 40.5 Hz, (Z)-CH₃), 29.9 (s, ³J_{PC} = 46.8 Hz, (E)-CH₃), 47.7 (s, ³J_{PC} = 20.1 Hz, CH₃O), 127.4 (t, ³J_{PC} = 5.2 Hz, *m*-C), 129.7 (s, *p*-C), 132.1 (t, ¹J_{PC} = 28.1 Hz, ²J_{PC} = 32.7 Hz, *ipso*-C), 134.7 (t, ²J_{PC} = 6.1 Hz, *o*-C), 136.6 (s, C(CH₃)₂=), 137.9 (t, ²J_{PC} = 12.9 Hz, C_{Pt}=), 206.8 (t, ²J_{PC} = 12.1 Hz, CO); FAB MS 802 (3%), 777 (13%), 774 (60%), 719 (76%), 183 (100%). Anal. Calcd for C₄₂H₄₀O₂Pt: C, 60.50; H, 4.84. Found: C, 60.41; H, 4.82.

***trans*-CH₂=C(CH₃)Pt(PPh₃)₂(COOCH₃) (13c).** This complex was prepared according to the above procedure with 12a (124 mg, 0.132 mmol) and sodium methoxide (36 mg, 0.67 mmol) in 5 mL of methanol, affording 85 mg (78%) of colorless microcrystalline solid 13c; mp 156–157 °C dec; IR 3055 (m), 2910 (m), 1620 (s), 1481 (s), 1434 (s), 1312 (w), 1185 (m), 1097 (s), 1033 (s), 932 (m), 858 (m), 745 (s), 694 (s), 635 (m); ¹H NMR (CDCl₃) δ 0.86 (s, ³J_{PH} = 21.3 Hz, 3 H, CH₃C=), 2.38 (s, 3 H, CH₃O), 4.31 (dt, ²J_{HH} = 2.5 Hz, ³J_{PH} = 30.3 Hz, 1 H, (Z)-CH=), 5.31 (m, ³J_{PH} = 59.4 Hz, 1 H, (E)-CH=), 7.3 (m, 18 H, aromatics), 7.7 (m, 12 H, aromatics); ³¹P NMR (CDCl₃) δ 17.8 (s, ¹J_{PP} = 3229 Hz); ¹³C NMR (CDCl₃) δ 30.7 (s, ²J_{PC} = 19.9 Hz, CH₃C=), 47.7 (s, ²J_{PC} = 20.4 Hz, CH₃O), 119.8 (t, ³J_{PC} = 3.8 Hz, CH₂=), 127.6 (t, ³J_{PC} = 5.2 Hz, *m*-C, ⁴J_{PH} = 1.2 Hz), 129.9 (s, *p*-C), 131.7 (t, ¹J_{PC} = 27.8 Hz, ²J_{PC} = 33.0 Hz, *ipso*-C), 134.8 (t, ²J_{PC} = 6.1 Hz, *o*-C), 161.1 (t, ²J_{PC} = 11.4 Hz, C_{Pt}=), 205.0 (t, ²J_{PC} = 12.8 Hz, CO); FAB MS 791 (1%), 788 (5%), 760 (67%), 719 (48%), 457 (24%). Anal. Calcd for C₄₁H₃₈O₂Pt: C, 60.07; H, 4.67. Found: C, 60.07; H, 4.71.

NMR Observation and Kinetics of the Thermal Decomposition of 13a. NMR tubes were charged with 13a (ca. 13.4 mg, 1.61 \times 10⁻² mmol), internal standard fluorene (ca. 1.1 mg), and C₆D₅CD₃ (0.450 mL) and tightly sealed with rubber septums. The mixtures were degassed through three freeze-pump-thaw cycles. The rubber septums were wrapped with parafilm. In order to dissolve the complex, the NMR tubes were vigorously shaken when heated in a 45 °C oil bath, resulting in a clear, light yellow solution. Neither ¹H NMR nor ³¹P NMR spectroscopy shows any reaction. The NMR probe was thermostated with the variable-temperature heater and calibrated using the TEMCAL(E) program. The decomposition was followed by monitoring the methylene (CH₂) resonances of the complex, ethyl methacrylate product, and fluorene internal standard, respectively. Reactions in other solvents (C₆D₅Cl, C₆D₅NO₂) were performed in the same way. ¹H NMR spectral arrays were obtained by creating a preacquisition delay (PAD (1) = 0, 570, 570, 1170, 1170, 1170, 1170, 1170, 1170, 1770, 1770, 1770, 3570, 3570, 3570, etc.). The time of each spectrum was calculated by adding the PAD parameter to the

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

acquisition time (30 s). Concentration of each compound with respect to time was calculated by dividing the integral of resonance by the integral of fluorene internal standard. The concentrations were then plotted versus time to give the reaction profiles. The natural logarithm (\ln) of the concentration of the complex could then be plotted versus time, which provided the first-order rate constants ($k_1 = -(\text{slope})$) from linear least-squares analysis. Activation parameters were determined by plotting $\ln(k/T)$ versus $1/T$ (K^{-1}) at 60, 70, and 80 °C, where $\Delta H^\ddagger = -R(\text{slope})$ in cal/mol and $\Delta S^\ddagger = R(\text{y intercept} - \ln(k/h))$ in eu ($R = \text{ideal gas constant}$, $k = \text{Boltzmann constant}$; $h = \text{Planck constant}$).

NMR Observation and Kinetics of the Thermal Decomposition of 13b. Decomposition of 13b was observed and the kinetics were studied at 90, 100, and 110 °C in the same way as above. The reaction was followed by monitoring the methoxyl proton resonances of 13b and the ester product and the methylene proton resonance (CH_2) of the fluorene internal standard. The reaction rates and activation parameters (ΔH^\ddagger and ΔS^\ddagger) are reported in Table IV.

NMR Observation and Kinetics of the Thermal Decomposition of 13c. Since complex 13c is not soluble in toluene, the decomposition was carried out in $\text{C}_6\text{D}_5\text{Cl}$ (0.450 mL) at 60, 70, and 80 °C. Otherwise, the experiment was accomplished in the same way as above. The reaction was followed by monitoring the methoxyl proton resonances of 13c and the ester product, and the methylene resonance (CH_2) of the fluorene internal standard.

The reaction rates and activation parameters (ΔH^\ddagger and ΔS^\ddagger) are listed in Table IV.

NMR Observation of Phosphine Inhibition on the Thermal Decomposition of 13a. Triphenylphosphine samples (1.2, 2.1, 3.3, and 4.3 mg) were placed in thin-wall 5-mm NMR tubes; each was then charged with 0.450 mL of the stock solution of 13a (0.035 M) in $\text{C}_6\text{D}_5\text{Cl}$. The reactions were accomplished at 80 °C in the same way as without adding Ph_3P . The natural logarithm (\ln) of the concentration of 13a was then plotted versus time. Induction periods ($T_{\text{induction}}$) were derived by extrapolating the curve to the initial concentration of 13a (Figure 3), and then plotted versus the ratio of the phosphine concentration and the initial concentration of 13a (Figure 4).

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Supplementary Material Available: Tables of crystal data, bond distances and angles, torsion angles, least-squares planes, positional parameters and thermal parameters (11 pages); a listing of structure factors (17 pages). Ordering information is given on any current masthead page.

Effect of Ring Size on NMR Parameters: Cyclic Bisphosphine Complexes of Molybdenum, Tungsten, and Platinum. Bond Angle Dependence of Metal Shieldings, Metal-Phosphorus Coupling Constants, and the ^{31}P Chemical Shift Anisotropy in the Solid State

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The ^{31}P chemical shift tensors of bis(phosphine) complexes of the type $[\text{M}][\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$ ($[\text{M}] = (\text{OC})_4\text{Mo}, (\text{OC})_4\text{W}, \text{Cl}_2\text{Pt}; n = 1-5$) and of *fac*- $(\text{OC})_3\text{Mo}[\text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$ were determined by solid-state NMR techniques and correlated with structural features of the compounds. $\delta(^{31}\text{P})$, $^1J_{\text{M-P}}$, and $\delta(\text{M})$ show a dependence on the ring size in the solution NMR spectra of the four- to six-membered chelates; for larger rings this dependence vanishes. A model for the orientation of the ^{31}P shift tensor principal components within the molecular frame is proposed. Each tensor component displays a different dependence on the ring size; the isotropic shift is dominated by the component perpendicular to the ring plane. Changes in this component are explained in terms of variations of the M-P-C angles. Generally speaking, the behavior of each of the tensor components must be regarded as a complex interplay of all six bond angles at phosphorus. The crystal structure of $(\text{OC})_4\text{W}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]$ (2d) was determined by X-ray diffraction. Crystals of 2d are monoclinic, space group $P2_1/n$, $a = 1202.8$ (1) pm, $b = 1531.8$ (1) pm, $c = 1654.1$ (2) pm, $\beta = 104.72$ (1)°, and $Z = 4$.

Introduction

Solution-state ^{31}P NMR spectroscopy has proved to be an invaluable experimental technique for understanding the chemistry and structure of phosphorus-containing molecules.¹ Important parameters in these studies are the chemical shift $\delta(^{31}\text{P})$, the coupling constant $J_{\text{P-X}}$ to an

isotope active in NMR spectroscopy, or relaxation rate data. Since the chemical shift of heavier nuclei is such a small and sensitive effect, it has only been recently with larger and faster computing facilities that reasonably accurate theoretical calculations have been forthcoming,²

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