Reaction of Palladium and Platinum Complexes Bearing α,β-Unsaturated Carbonyl Compounds with Carbon Electrophiles: Control over Site of Electrophilic Attack, Oxygen or Metal

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The reaction of (η^2-CH_2=CHCHO)ML_2 (M = Pd, Pt; L = PPh_3, L_2 = DPPF) with methyl triflate gave η^3-methoxyallyl complexes [(η^3-$CH_3OCHCHCH_2$)ML_2][OTf]. X-ray diffraction analysis on [(η^3-$CH_3OCHCHCH_2$)M(dppf)][OTf] (M = Pd, Pt) showed a distorted η^3-allyl structure. The enone complexes (η^2-CH_2=$CHCOCH_3$)M(PPh_3)$_2$ also reacted with methyl triflate to give [(η^3-$CH_3OC(CH_3)CHCH_2$)M(PPh_3)$_2$][OTf]. It was proposed that these complexes were formed by the direct electrophilic attack of methyl triflate at the carbonyl oxygen of the enal or enone ligand on the palladium and platinum. In fact, no insertion of acrolein into the platinum−methyl bond of the separately isolated methylplatinum complex proceeded. On the other hand, methyl iodide underwent oxidative addition with zerovalent enal or enone complexes to give methylmetal complexes concomitant with dissociation of an enal or enone molecule.

Introduction

Both nucleophilic and electrophilic addition reactions of organic reagents to transition metal complexes are among the most important transformations in organometallic chemistry.[1] There are two reaction sites, the metal center and coordinated ligands, which receive both nucleophilic and electrophilic attacks. In the electrophilic addition the attack at metal converts the electrophile into a new metal-bound ligand (e.g., H^+ to hydride), while that at an unsaturated ligand modifies this into the other (e.g., acyl + Me^+ to carbene). Recently, we reported that the addition of several metallic electrophiles, such as a Lewis acid or Me_3SiOTf, to the carbonyl oxygen of α,β-unsaturated carbonyl compounds coordinated to zerovalent palladium led to the formation of η^3-allyl complexes bearing a metalloxy or siloxy group at the allyl terminal.[2,3] These new compounds served as model intermediates in palladium-catalyzed conjugate addition of various organometallic reagents, e.g., AlR_3, ZnR_2, and R_3SiSiR_3, to α,β-unsaturated carbonyl compounds.

We also reported the reaction of η^2-enal and enone complexes of palladium and platinum with Brønsted acid to give η^3-1-hydroxyallyl complexes.[4] It is conceivable that in the case of the reaction of Brønsted acid there is a greater chance of the electrophilic addition to the metal center than the case of Lewis acid or Me_3SiOTf addition. Nevertheless we obtained evidence for the exclusive occurrence of the attack of a proton at the oxygen. This prompted us to use carbon electrophiles[5] next as the reagent in the reaction with the coordinated enal or enone. Here, we report the reaction of palladium and platinum complexes bearing α,β-unsaturated carbonyl compounds with some methyl electrophiles which results in the electrophilic attack at the carbonyl oxygen or the metal center depending on the nature of the leaving group of the methyl substrate.

Results and Discussion

The reaction of η^2-acroleinpalladium complexes with MeOTf in toluene at room temperature quantitatively gave palladium complexes having expected compositions in elemental analysis (eq 1). The ^1H, ^{31}P, and ^{13}C NMR indicate that these complexes have an η^3-methoxyallyl structure. η^3-1-Alkoxyallylpalladium complexes have been proposed as an important intermediate in several catalytic reactions, where they have a great tendency to direct the nucleophilic attack of stabilized carbanions

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(2) Lewis acid: (a) Ogoshi, S.; Yoshida, T.; Nishida, T.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 1944−1950. Me_3SiOTf: (b) Ogoshi, S.; Tomiyasu, S.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 11598−11599.

(3) α,β-Unsaturated carbonyl compounds have been used as precursors to η^3-1-siloxyallyl complexes of a number of metals. Ni: (a) Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172−6177. (b) Grisso, B. A.; Johnson, J. R.; Mackenzie, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 5160−5165. Co: (c) Chatani, N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, *24*, 5649−5652. Mo: (d) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4201−4210. (e) Moretto, A. F.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 7445−7455.

(4) Brønsted acid: Ogoshi, S.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 9020−9021.

(5) A similar reaction of *C,O*-η^2-crotonaldehyde complex of osmium with methyl triflate has been reported. Spera, M. L.; Chen, H.; Moody, M. W.; Hill, M. M.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 12772−12778.

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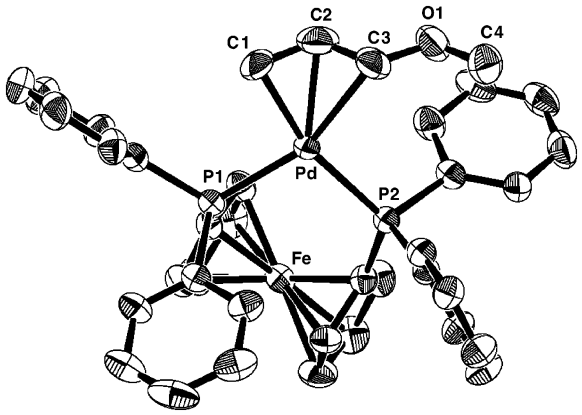
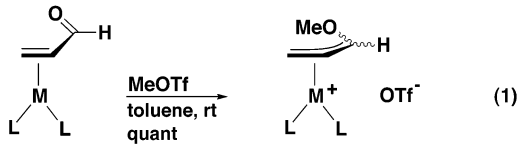


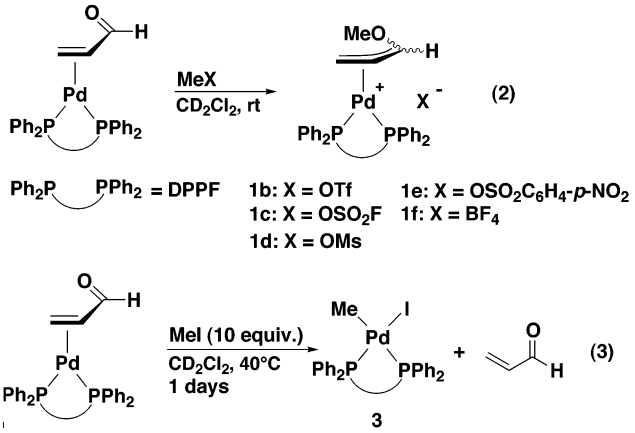
Figure 1. ORTEP drawing of **1b**·3/2C_6H_6. Thermal ellipsoids are drawn at the 50% probability level. All H atoms and the OTf anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C1 = 2.136(6); Pd−C2 = 2.214(7); Pd−C3 = 2.373(7); C1−C2 = 1.40(1); C2−C3 = 1.33(1); C3−O1 = 1.387(8); O1−C4 = 1.397(9); C2−C3−O1−C4 = 171.9(7).

at the 1-position of an allyl moiety bearing the alkoxy group despite the steric disadvantage.[6] However, there are very few reports on their isolation, structure, and reactivity.[7] The present reaction represents a very convenient route to prepare η^3-1-alkoxyallyl complexes, demonstrating the first preparation of the simplest η^3-1-alkoxyallyl complex of palladium. Similar treatment of η^2-acroleinplatinum complex with MeOTf also led to quantitative formation of the corresponding platinum analogues, **2a** and **2b**.



The structures of **1b** and **2b**, determined by X-ray diffraction analysis, are consistent with the anticipated structure. The structure of **1b** is shown in Figure 1, and that of **2b** is very similar to this. The Pd−C3 bond distance (2.373 Å) is somewhat longer than those in usual η^3-allylpalladium complexes, e.g., Pd−C1 = 2.136 Å in **1b**, and the C2−C3 bond distance (1.33 Å) is shorter than the C1−C2 bond distance (1.40 Å). The two atoms in the methoxy group are almost coplanar with the three allyl carbons. This unsymmetrical coordination of an allyl moiety to palladium is similar to that in the other distorted η^3-allylpalladium[8] and η^3-1-methoxyallylpalladium complexes.[7b,c] The unsymmetrical η^3-allyl coordination would control the position of the nucleophilic attack.[1a]

To evaluate the scope of carbon electrophiles to generate η^3-1-methoxyallyl complexes under similar reaction conditions, we set out to apply various methylating agents to the reaction with η^2-acroleinpalladium complex (eq 2). The reaction with $MeOSO_2F$ at room temperature proceeded as readily as eq 1 to give a similar complex **1c** quantitatively. The corresponding η^3-1-methoxyallyl complex **1d** was obtained by use of MeOMs (10 equiv) in excellent yield (98%), but higher temperature (60 °C in DCE-d_4) and longer reaction time (3 days) were required. The reaction with $MeOSO_2$-(C_6H_4-*p*-NO_2) (10 equiv) at room temperature in 12 h also led to the formation of the complex **1e** in good yield (85%). The lower reactivity of MeOMs and $MeOSO_2$-(C_6H_4-*p*-NO_2) would be attributed to the lesser facility of mesylate and *p*-nitrophenylsulfonate anion to leave from the methyl cation than that of the triflate anion.[9] Trimethyloxonium salt was also available for this reaction to give the complex **1f** quantitatively, although somewhat longer time (3 h) was required because of its insolubility. Of particular note is the reaction of MeI with Pd(η^2-CH_2=CHCHO)(dppf), though very slow, which gave the oxidative addition product PdMe(I)(dppf) (**3**). The yield was 18%, as determined by NMR, in 1 day along with the release of acrolein even when 10 equiv of MeI was employed (eq 3).



We also examined the effect of the substituent in the carbonyl compound. The reaction of η^2-methylvinyl ketone complexes of palladium and platinum with MeOTf gave corresponding η^3-methoxyallyl complexes,[10] while M(Me)(I)(PPh_3)$_2$ (M = Pd, Pt) were formed by the reaction with MeI (eq 4). Oxidative addition of MeI to the palladium complex proceeded faster than that to the platinum complex (5 vs 47 h). This is a somewhat unexpected order of reactivity, if the relative ease of the reductive elimination of MMe_2L_2 (M = Pd faster than M = Pt) is taken into account.[11] The oxidative addition

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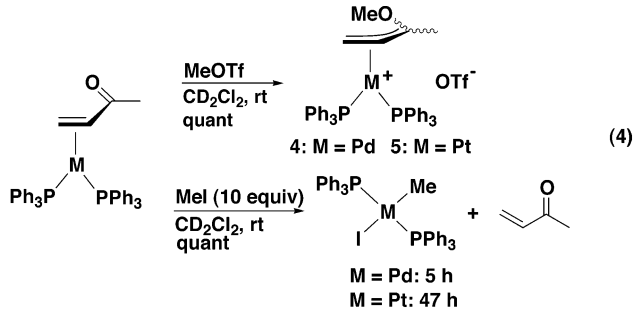
(9) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643−2647.

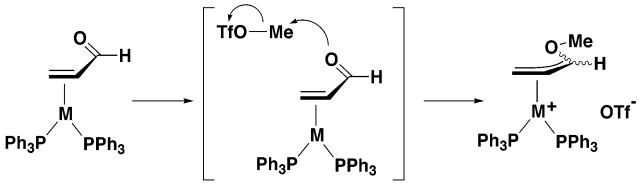
(10) NMR studies revealed that the complexes **4** and **5** were formed as a mixture of almost equal amounts of syn and anti isomers at the early stage of the reaction. The isomerization between these two isomers proceeded gradually to give a thermodynamic mixture (syn/anti = 98/2 for **4**, 94/6 for **5**, respectively).

(11) (a) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115−6128. (b) Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609−622.



may proceed via an initial slow olefin dissociation step,[12] which is particularly sluggish for the Pt(0) complex. In contrast, the formation of [Pt(η^3-$CH_3OCHCHCH_2$)(dppf)]-[(C_6H_4-*p*-NO_2)OSO_2] involving the attack of $MeOSO_2$-(C_6H_4-*p*-NO_2) at the coordinated enal of Pt(η^2-CH_2=CHCHO)(dppf) required a reaction time (20 h) almost similar to that for **1e**. The reaction of (η^2-CH_2=$CHCOOCH_3$)$Pt(PPh_3)_2$ with MeOTf in C_6D_6 at room temperature gave Pt(Me)(OTf)$(PPh_3)_2$ and [Pt(Me)-$(PPh_3)_3$]$^+$ by oxidative addition.[13]

Scheme 1. Proposed Mechanism for Formation of η^3-1-Methoxyallyl Complexes



For the purpose of understanding the course of the reaction to form η^3-methoxyallyl complexes, reaction of Pt(Me)(OTf)(dppf) with acrolein was attempted. However, no insertion of acrolein into the Pt−Me bond occurred at room temperature in CD_2Cl_2 after 48 h. Therefore, the sequence of oxidative addition of MeOTf to the Pt(0) complex followed by the insertion of acrolein into the Pt−Me bond would be unlikely for eq 1. On the basis of these results, we propose that the η^3-1-methoxyallyl complexes of palladium and platinum would be formed by the nucleophilic substitution of MeOTf by the carbonyl oxygen of the acrolein complex, described in Scheme 1.

Experimental Section

General Procedures. All manipulations were conducted under a nitrogen atmosphere using standard Schlenck or drybox techniques. ^{1}H, ^{31}P, and ^{13}C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. The chemical shifts in the ^{1}H nuclear magnetic resonance spectra were recorded relative to Me_4Si, CD_2Cl_2 (δ 5.32), C_6D_6 (δ 7.16), or $CDCl_3$ (δ 7.26). The chemical shifts in the ^{13}C nuclear magnetic resonance spectra were recorded relative to Me_4Si, CD_2Cl_2 (δ 53.8) or $CDCl_3$ (δ 77.0). The chemical shifts in ^{31}P nuclear magnetic resonance spectra were recorded using 85% H_3PO_4 as an external standard. Elemental analyses were preformed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by a Rigaku RAXIS-RAPID imaging plate diffractometer.

Materials. All solvents used in this work were distilled prior to use. THF, hexane, benzene, and C_6D_6 were distilled from sodium benzophenone ketyl; CD_2Cl_2 and $CDCl_3$, from CaH_2. All commercially available reagents were distilled and degassed prior to use.

[(CH_2CHCH(OCH$_3$))Pd(PPh_3)$_2$][CF_3SO_3] (1a). To a solution of Pd(CH_2=CHCHO)$(PPh_3)_2$ (153.8 mg, 0.224 mmol) in 5 mL of toluene was added 26.0 μL of MeOTf (37.7 mg, 0.230 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give brown solids quantitatively. The solids were washed with hexane to give 181.6 mg of the complex **1a** in 95% isolated yield. **Anti isomer (95%).** ^{1}H NMR (CD_2Cl_2): δ 2.74 (t, J = 12.4 Hz, 1H), 2.85 (s, 3H), 3.22 (dt, J = 3.0, 7.8 Hz, 1H), 5.30 (dt, J = 1.6, 11.1 Hz, 1H), 6.63 (dd, J = 9.2, 10.8 Hz, 1H), 7.1−7.5 (m, 30H). ^{31}P NMR (CD_2Cl_2): δ 23.27 (d, J_{PP} = 36.6 Hz), 27.11 (d, J_{PP} = 36.6 Hz). ^{13}C NMR (CD_2Cl_2): δ 60.3 (s), 60.4 (dd, J_{CP} = 2.9, 27.4 Hz), 96.4 (dd, J_{CP} = 4.0, 6.1 Hz), 121.4 (q, J_{CF} = 319.9 Hz), 129−135 (m), 142.0 (dd, J_{CP} = 1.7, 16.5 Hz, *C*OMe). **Syn isomer (5%).** ^{1}H NMR (CD_2Cl_2): δ 3.17 (m, 1H), 3.63 (m, 1H), 5.01 (m, 1H), 6.48 (m, 1H). The other resonances are hidden by those of the major isomer. ^{31}P NMR (CD_2Cl_2): δ 21.52 (d, J_{PP} = 41.5 Hz), 28.60 (d, J_{PP} = 41.5 Hz). Anal. Calcd for $C_{41}H_{37}F_3O_4P_2SPd$ (a mixture of anti and syn isomers): C, 57.85; H, 4.38. Found: C, 58.11; H, 4.47.

[(CH_2CHCH(OCH$_3$))Pd(dppf)][CF_3SO_3] (1b). To a solution of Pd(CH_2=CHCHO)(dppf) (163.1 mg, 0.228 mmol) in 5 mL of toluene was added 30 μL of MeOTf (43.5 mg, 0.265 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give yellow solids quantitatively. The solids were washed with hexane to give 197.7 mg of the complex **1b** in 99% isolated yield. **Syn isomer (85%).** ^{1}H NMR (CD_2Cl_2): δ 2.58 (ddd, J = 2.7, 10.3, 13.0 Hz, 1H), 2.89 (s, 3H), 3.27 (dt, J = 3.0, 8.1 Hz, 1H), 4.0−4.6 (m, 8H), 5.32 (m, 1H), 6.70 (dd, J = 9.2, 10.8 Hz, 1H), 7.2−7.8 (m, 20H). ^{31}P NMR (CD_2Cl_2): δ 20.12 (d, J_{PP} = 45.6 Hz), 25.69 (d, J_{PP} = 45.6 Hz). ^{13}C NMR (CD_2Cl_2): δ 59.7 (dd, J_{CP} = 3.4, 29.3 Hz), 59.9 (s), 73−78 (m), 97.7 (dd, J_{CP} = 3.0, 6.3 Hz), 128−135 (m), 138.9 (dd, J_{CP} = 2.8, 19.1 Hz, *C*OMe). **Anti isomer (15%).** ^{1}H NMR (CD_2Cl_2): δ 3.12 (s, 3H), 3.67 (t, J = 7.8 Hz, 1H), 4.83 (m, 1H), 6.52 (m, 1H). The other resonances are hidden by those of the major isomer. ^{31}P NMR (CD_2Cl_2): δ 20.59 (d, J_{PP} = 47.7 Hz), 28.48 (d, J_{PP} = 47.7 Hz). Anal. Calcd for $C_{39}H_{35}F_3O_4P_2SFePd$ (a mixture of syn and anti isomers): C, 53.17; H, 4.00. Found: C, 53.25; H, 4.05. X-ray data for **1b**·3/2C_6H_6. M = 998.12, red, triclinic, $P\bar{1}$ (No. 2), a = 10.0513(5) Å, b = 10.3216(4) Å, c = 22.1580(7) Å, α = 98.078(2)°, β = 102.590(1)°, γ = 91.862(2)°, V = 2216.5(2) Å^3, Z = 2, D_{calcd} = 1.495 g/cm^3, T = −70.0 °C, R (R_w) = 0.056 (0.108).

[(CH_2CHCH(OCH$_3$))Pd(dppf)][FSO_3] (1c). To a solution of Pd(CH_2=CHCHO)(dppf) (10.8 mg, 0.015 mmol) in 0.5 mL of CD_2Cl_2 was added 1.3 μL of $MeOSO_2F$ (1.9 mg, 0.016 mmol) at room temperature. The complex **1c** was formed quantitatively.

[(CH_2CHCH(OCH$_3$))Pd(dppf)][CH_3SO_3] (1d). To a solution of Pd(CH_2=CHCHO)(dppf) (10.8 mg, 0.015 mmol) in 0.5 mL of $C_2D_4Cl_2$ was added 12.7 μL of MeOMs (16.5 mg, 0.150 mmol) at room temperature. The tube was heated to 60 °C, and the reaction was monitored by NMR measurement. After 3 days the complex **1d** was formed in 98% yield along with $PdCl_2$(dppf) in 2% yield.

[(CH_2CHCH(OCH$_3$))Pd(dppf)][*p*-$NO_2C_6H_4SO_3$] (1e). Pd(CH_2=CHCHO)(dppf) (10.8 mg, 0.015 mmol) and $MeOSO_2C_6H_4$-*p*-NO_2 (22.7 mg, 0.151 mmol) were charged in an NMR sample tube, then CD_2Cl_2 was added at room temperature. After 12 h, the complex **1e** was formed in 85% yield along with $PdCl_2$-(dppf) in 15% yield.

[(CH_2CHCH(OCH$_3$))Pd(dppf)][BF_4] (1f). Pd(CH_2=CHCHO)(dppf) (10.8 mg, 0.015 mmol) and [$(CH_3)_3O$][BF_4] (2.2 mg,

(12) Birk, J. P.; Halpern, J.; Pickard, A. L. *J. Am. Chem. Soc.* **1968**, *90*, 4491−4492.

(13) The reaction of Pt(CH_2=CH_2)$(PPh_3)_2$ with MeOTf under the same conditions gave Pt(Me)(OTf)$(PPh_3)_2$ at first, which then decomposed gradually to [Pt(Me)$(PPh_3)_3$]$^+$.

0.015 mmol) were charged in an NMR sample tube, and CD_2Cl_2 was added at room temperature. After 3 h, the complex **1f** was formed quantitatively.

[(CH_2CHCH(OCH_3))Pt(PPh_3)$_2$][CF_3SO_3] (2a). To a solution of Pt(CH_2=CH_2)(PPh_3)$_2$ (228.0 mg, 0.305 mmol) in 6 mL of toluene was added 30.0 μL of CH_2=CHCHO (25.2 mg, 0.449 mmol) and 37.0 μL of MeOTf (53.7 mg, 0.327 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give white solids quantitatively. The solids were washed with hexane to give 278.9 mg of the complex **2a** in 97% isolated yield. **Syn isomer (75%).** ^{1}H NMR (CD_2Cl_2): δ 2.06 (t, J = 12.2 Hz, 1H), 2.81 (m, 1H), 2.84 (s, 3H), 4.90 (dtt, J = 3.0, 8.1, 11.1 Hz, 1H), 6.30 (dd, J = 9.5, 10.8 Hz, J_{HPt} = 48.6 Hz, 1H), 7.1−7.5 (m, 30H). ^{31}P NMR (CD_2Cl_2): δ 19.08 (d, J_{PP} = 1.5 Hz, J_{PPt} = 4532 Hz), 22.52 (d, J_{PP} = 1.5 Hz, J_{PPt} = 3815 Hz). ^{13}C NMR (CD_2Cl_2): δ 50.1 (d, J_{CP} = 30.6 Hz, J_{CPt} = 149.4 Hz), 59.9 (s), 93.3 (dd, J_{CP} = 1.6, 4.3 Hz, J_{CPt} = 23.0 Hz), 121.4 (q, J_{CF} = 321.7 Hz), 128−135 (m). The resonance for the carbon-bearing methoxy group was observed at 134.9 ppm by the C−H COSY measurement. **Anti isomer (25%).** ^{1}H NMR (CD_2Cl_2): δ 2.43 (m, 1H), 3.18 (s, 3H), 3.43 (m, 1H), 4.79 (m, 1H), 6.01 (d, J = 4.6 Hz, 1H). The other resonances are hidden by those of the major isomer. ^{31}P NMR (CD_2Cl_2): δ 16.57 (d, J_{PP} = 7.6 Hz, J_{PPt} = 3901 Hz), 17.97 (d, J_{PP} = 7.6 Hz, J_{PPt} = 4154 Hz). Anal. Calcd for $C_{41}H_{37}F_3O_4P_2SPt$ (a mixture of syn and anti isomers): C, 52.40; H, 3.97. Found: C, 51.71; H, 3.81.

[(CH_2CHCH(OCH_3))Pt(dppf)][CF_3SO_3] (2b). To a solution of Pt(CH_2=CH_2)(dppf) (161.0 mg, 0.207 mmol) in 6 mL of benzene was added 16.0 μL of CH_2=CHCHO (13.4 mg, 0.239 mmol) and 25.0 μL of MeOTf (36.3 mg, 0.221 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give yellow solids quantitatively. The solids were washed with hexane to give 194.8 mg of the complex **2b** in 97% isolated yield. An analytical sample was prepared by recrystallization from THF/benzene/hexane solution. **Syn isomer (80%).** ^{1}H NMR (CD_2Cl_2): δ 1.95 (t, J = 11.6 Hz, J_{HPt} = 61.6 Hz, 1H), 2.83 (m, 4H, allylic syn proton at the terminal carbon overlaps with the methoxy proton), 3.9−4.6 (m, 8H), 4.89 (q, J = 9.7 Hz, 1H), 6.16 (q, J = 9.7 Hz, J_{HPt} = 41.6 Hz, 1H), 7.3−7.8 (m, 20H). ^{31}P NMR (CD_2Cl_2): δ 18.96 (d, J_{PP} = 11.7 Hz, J_{PPt} = 4527 Hz), 21.03 (d, J_{PP} = 11.7 Hz, J_{PPt} = 3948 Hz). ^{13}C NMR (CD_2Cl_2): δ 50.1 (d, J_{CP} = 32.1 Hz, J_{CPt} = 144.5 Hz) 59.5 (s), 73−77 (m), 94.6 (dd, J_{CP} = 1.6, 4.0 Hz, J_{CPt} = 22.0 Hz), 121.4 (q, J_{CF} = 321.7 Hz), 128−138 (m). The resonance for the carbon-bearing methoxy group was observed at 132.2 ppm by the C−H COSY measurement. **Anti isomer (20%).** ^{1}H NMR (CD_2Cl_2): δ 2.42 (td, J = 2.7, 11.8 Hz, J_{HPt} = 60.2 Hz, 1H), 3.08 (s, 3H), 3.43 (m, 1H), 6.04 (m, 1H). The other resonances are hidden by the major isomer. ^{31}P NMR (CD_2Cl_2): δ 16.65 (d, J_{PP} = 16.0 Hz, J_{PPt} = 3948 Hz), 18.90 (d, J_{PP} = 16.0 Hz, J_{PPt} = 4243 Hz). Anal. Calcd for $C_{45}H_{41}F_3O_4P_2SFePt$ (a mixture of syn and anti isomers): C, 51.59; H, 3.94. Found: C, 51.57; H, 3.92. X-ray data for **2b**·3/2C_6H_6. M = 1086.81, yellow, triclinic, $P\bar{1}$ (No. 2), a = 9.9669(8) Å, b = 10.3655(7) Å, c = 22.007(1) Å, α = 98.413(1)°, β = 102.4313(6)°, γ = 91.7362(7)°, V = 2191.9(3) Å^3, Z = 2, D_{calcd} = 1.647 g/cm^3, T = −60.0 °C, R = 0.056.

Oxidative Addition of CH_3I to Pd(CH_2=CHCHO)(dppf). To a solution of Pd(CH_2=CHCHO)(dppf) (10.8 mg, 0.015 mmol) in 0.5 mL of CD_2Cl_2 was added 9.3 μL of MeI (21.3 mg, 0.150 mmol) at room temperature. The tube was heated to 40 °C, and the reaction was monitored by NMR measurement. After 24 h the complex **3** was formed in 18% yield with 82% of Pd(CH_2=CHCHO)(dppf) remaining unreacted.

Pd(CH_3)(I)(dppf) (3). An authentic sample of complex **3** was generated by the reaction of *trans*-Pd(Me)(I)(PPh_3)$_2$[14] (5.1 mg, 0.007 mmol) with DPPF (3.7 mg, 0.007 mmol) in CD_2Cl_2. Selected NMR data for **3**. ^{1}H NMR (CD_2Cl_2): δ 0.86 (t, J = 7.6 Hz, 3H). ^{31}P NMR (CD_2Cl_2): δ 12.24 (d, J_{PP} = 31.8 Hz), 33.88 (d, J_{PP} = 31.8 Hz).

[(CH_2CHCCH_3(OCH_3))Pd(PPh_3)$_2$][CF_3SO_3] (4). To a solution of Pd(CH_2=CHCOCH_3)(PPh_3)$_2$ (194.7 mg, 0.278 mmol) in 6 mL of toluene was added 32.0 μL of MeOTf (46.6 mg, 0.283 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give brown solids quantitatively. The solids were washed with hexane to give 198.3 mg of the complex **4** in 83% isolated yield. **Syn isomer (46%).** ^{1}H NMR (CD_2Cl_2): δ 1.75 (dd, J = 3.2, 4.9 Hz, 3H), 2.33 (ddt, J = 2.2, 3.2, 8.6 Hz, 1H), 3.08 (s, 3H), 3.34 (dt, J = 3.8, 7.8 Hz, 1H), 5.00 (tt, J = 1.6, 10.5 Hz, 1H), 7.1−7.5 (m, 30H). ^{31}P NMR (CD_2Cl_2): δ 23.13 (d, J_{PP} = 33.3 Hz), 29.97 (d, J_{PP} = 33.3 Hz). ^{13}C NMR (CD_2Cl_2): δ 23.0 (dd, J_{CP} = 1.0, 4.3 Hz, *C*H$_3$), 54.8 (dd, J_{CP} = 2.8, 30.6 Hz), 57.4 (s), 82.9 (dd, J_{CP} = 2.9, 5.4 Hz), 128−135 (m), 163.9 (d, J_{CP} = 11.6 Hz, *C*OMe). **Anti isomer (54%).** ^{1}H NMR (CD_2Cl_2): δ 1.38 (dd, J = 4.6, 11.3 Hz, 3H), 2.94 (m, 2H), 3.49 (s, 3H), 4.61 (dd, J = 8.1, 13.5 Hz, 1H). The other resonances are hidden by those of the major isomer. ^{31}P NMR (CD_2Cl_2): δ 22.93 (d, J_{PP} = 36.0 Hz), 33.71 (d, J_{PP} = 36.0 Hz). ^{13}C NMR (CD_2Cl_2): δ 19.6 (dd, J_{CP} = 0.9, 4.9 Hz, *C*H$_3$), 52.6 (dd, J_{CP} = 3.4, 31.5 Hz), 86.3 (dd, J_{CP} = 3.8, 5.7 Hz), 167.2 (d, J_{CP} = 13.1 Hz). The other resonances are hidden by those of the major isomer. Anal. Calcd for $C_{42}H_{39}F_3O_4P_2SPd$ (a mixture of anti and syn isomers): C, 58.31; H, 4.54. Found: C, 58.41; H, 4.47.

[(CH_2CHCCH_3(OCH_3))Pt(PPh_3)$_2$][CF_3SO_3] (5). To a solution of Pt(CH_2=CH_2)(PPh_3)$_2$ (206.1 mg, 0.276 mmol) in 6 mL of benzene was added 24.0 μL of CH_2=CHCOCH_3 (20.2 mg, 0.288 mmol) and 32.0 μL of MeOTf (46.4 mg, 0.283 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give white solids quantitatively. The solids were washed with hexane to give 240.5 mg of the complex **5** in 92% isolated yield. **Syn isomer (94%).** ^{1}H NMR (CD_2Cl_2): δ 1.59 (dddd, J = 3.5, 4.9, 8.9, 14.6 Hz, 1H), 1.70 (d, J = 3.0 Hz, 3H), 2.89 (q, J = 7.6, Hz, 1H), 3.01 (s, 3H), 4.59 (ddd, J = 4.1, 7.8, 11.6 Hz, J_{HPt} = 51.8 Hz, 1H), 7.0−7.5 (m, 30H). ^{31}P NMR (CD_2Cl_2): δ 20.28 (d, J_{PP} = 2.2 Hz, J_{PPt} = 4640 Hz), 24.25 (d, J_{PP} = 2.2 Hz, J_{PPt} = 3718 Hz). ^{13}C NMR (CD_2Cl_2): δ 21.1 (dd, J_{CP} = 1.0, 4.0 Hz, J_{CPt} = 19.8 Hz), 44.4 (d, J_{CP} = 34.8 Hz, J_{CPt} = 179.7 Hz), 56.8 (s), 76.9 (d, J_{CP} = 4.3 Hz, J_{CPt} = 19.9 Hz), 121.6 (q, J_{CF} = 322.1 Hz), 128−136 (m), 160.6 (dd, J_{CP} = 2.1, 11.6 Hz, *C*OMe). **Anti isomer (6%).** ^{1}H NMR (CD_2Cl_2): δ 1.47 (dd, J = 2.4, 8.9 Hz, 3H), 2.19 (m, 1H), 2.60 (m, 1H), 3.50 (s, 3H), 4.33 (ddd, J = 3.8, 7.8, 11.9 Hz, 1H). The other resonances are hidden by those of the major isomer. ^{31}P NMR (CD_2Cl_2): δ 21.33 (s, J_{PPt} = 4711 Hz), 22.72 (s, J_{PPt} = 3652 Hz). Anal. Calcd for $C_{42}H_{39}F_3O_4P_2SPt$ (a mixture of syn and anti isomers): C, 52.89; H, 4.12. Found: C, 52.59; H, 4.07.

Oxidative Addition of CH_3I to Pd(CH_2=CHCOCH_3)(PPh_3)$_2$. To a solution of Pd(CH_2=CHCOCH_3)(PPh_3)$_2$ (8.0 mg, 0.011 mmol) in 0.5 mL of CD_2Cl_2 was added 7.1 μL of MeI (16.2 mg, 0.114 mmol) at room temperature. The reaction was monitored by NMR measurement. After 7 h *trans*-Pd(CH_3)(I)(PPh_3)$_2$ was quantitatively formed.

Oxidative Addition of CH_3I to Pt(CH_2=CHCOCH_3)(PPh_3)$_2$. To a solution of Pt(CH_2=CHCOCH_3)(PPh_3)$_2$ (8.3 mg, 0.011 mmol) in 0.5 mL of CD_2Cl_2 was added 6.6 μL of MeI (14.9 mg, 0.105 mmol) at room temperature. The reaction was monitored by NMR measurement. After 47 h *trans*-Pt(CH_3)(I)(PPh_3)$_2$[15] was quantitatively formed.

[(CH_2CHCH(OCH_3))Pt(dppf)][*p*-$NO_2C_6H_4SO_3$]. Pt(CH_2=CHCHO)(dppf) (12.1 mg, 0.015 mmol) and MeO$SO_2C_6H_4$-*p*-NO_2 (32.6 mg, 0.150 mmol) were charged in an NMR sample tube, then CD_2Cl_2 was added at room temperature. After 20 h, [(CH_2CHCH(OCH_3))Pt(dppf)][p-$NO_2C_6H_4SO_3$] was formed quantitatively.

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Reaction of $Pt(CH_2{=}CHCOOCH_3)(PPh_3)_2$ with MeOTf. To a solution of $Pt(CH_2{=}CHCOOCH_3)(PPh_3)_2$ (12.1 mg, 0.015 mmol) in 0.5 mL of C_6D_6 was added 1.7 μL of MeOTf (2.5 mg, 0.015 mmol) at room temperature. After 48 h colorless solids precipitated from the solution. In this solution, $Pt(Me)(OTf)(PPh_3)_2$ was formed in 39% yield. The solution was removed by decantation, and the solids were resolved in CD_2Cl_2 with toluene (5.0 μL, 0.047 mmol) as internal standard. $[Pt(Me)(PPh_3)_3][OTf]$ was formed in 33% yield.

Attempted Insertion of Acrolein into the Pt−Me Bond. To a solution of *cis*-Pt(Me)(OTf)(dppf)[16] (12.1 mg, 0.013 mmol) in 0.5 mL of CD_2Cl_2 was added 0.9 μL of acrolein (0.8 mg, 0.013 mmol) at room temperature. After 48 h, no reaction occurred.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **1b** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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