

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

Masaki Morita, Katsuharu Inoue, Sensuke Ogoshi,* and Hideo Kurosawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

Received August 22, 2003

The reaction of (η^2 -CH₂=CHCHO)ML₂ (M = Pd, Pt; L = PPh₃, L₂ = DPPF) with methyl triflate gave η^3 -methoxyallyl complexes [(η^3 -CH₃OCHCHCH₂)ML₂][OTf]. X-ray diffraction analysis on [(η^3 -CH₃OCHCHCH₂)M(dppf)][OTf] (M = Pd, Pt) showed a distorted η^3 -allyl structure. The enone complexes (η^2 -CH₂=CHCOCH₃)M(PPh₃)₂ also reacted with methyl triflate to give [(η^3 -CH₃OC(CH₃)CHCH₂)M(PPh₃)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 Me₃SiOTf, 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., AlR₃, ZnR₂, and R₃SiSiR₃, 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 Me₃-SiOTf addition. Nevertheless we obtained evidence for the exclusive occurrence of the attack of a proton at the oxygen. This prompted us to use carbon electrophiles⁵ 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, ³¹P, and ¹³C 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

(1) (a) Kurosawa, H., Yamamoto, A., Eds. *Fundamentals of Molecular Catalysis*; Elsevier: Amsterdam, 2003; Chapter 8. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-VCH: New York, 2001; Chapter 8. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987; Chapter 8.

(2) Lewis acid: (a) Ogoshi, S.; Yoshida, T.; Nishida, T.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 1944–1950. Me₃SiOTf: (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.

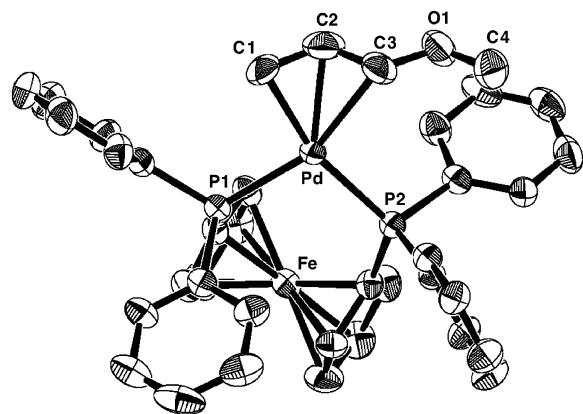
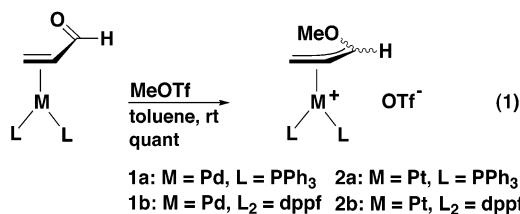


Figure 1. ORTEP drawing of **1b**·3/2C₆H₆. Thermal ellipsoids are drawn at the 50% probability level. All H atoms and the OTf anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C1 = 2.136(6); Pd–C2 = 2.214(7); Pd–C3 = 2.373(7); C1–C2 = 1.40(1); C2–C3 = 1.33(1); C3–O1 = 1.387(8); O1–C4 = 1.397(9); C2–C3–O1–C4 = 171.9(7).

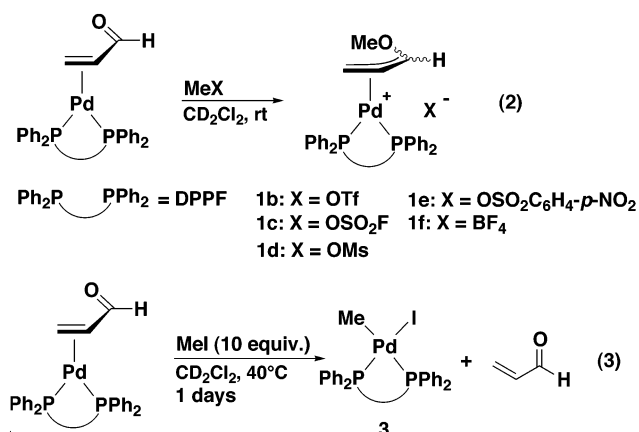
at the 1-position of an allyl moiety bearing the alkoxy group despite the steric disadvantage.⁶ However, there are very few reports on their isolation, structure, and reactivity.⁷ The present reaction represents a very convenient route to prepare η^3 -1-alkoxyallyl complexes, demonstrating the first 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 -allylpalladium⁸ 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 -acroleinplatinum complex (eq 2). The reaction with MeOSO₂F 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 MeOSO₂-(C₆H₄-*p*-NO₂) (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 MeOSO₂-(C₆H₄-*p*-NO₂) 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 -CH₂=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)(PPh₃)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 MMe₂L₂ (M = Pd faster than M = Pt) is taken into account.¹¹ The oxidative addition

(6) (a) Chaptal, N.; Colovray-Gotteland, V.; Grandjean, C.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1991**, *32*, 1795–1798. (b) Vicart, N.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1995**, *36*, 535–538. (c) Trost, B. M.; Jäkel, C.; Plietker, B. *J. Am. Chem. Soc.* **2003**, *125*, 4438–4439.

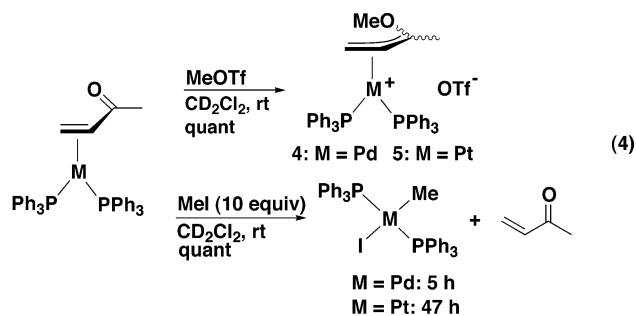
(7) (a) Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Murai, S. *Organometallics* **1991**, *10*, 3813–3818. (b) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Inorg. Chim. Acta* **1994**, *222*, 1–4. (c) Milani, B.; Paronetto, F.; Zangrando, E. *J. Chem. Soc., Dalton Trans.* **2000**, 3055–3057.

(8) (a) van Haaren, R. J.; Goubitz, K.; Fraanje, J.; van Strijdonck, G. P. F.; Oevering H.; Coussens, B.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Inorg. Chem.* **2001**, *40*, 3363–3372. (b) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmänn, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031–1037. (c) Burckhardt, U.; Gramlich, V.; Hofmann, P.; Nesper, R.; Pregosin, P. S.; Salzmänn, R.; Togni, A. *Organometallics* **1996**, *15*, 3496–3503.

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

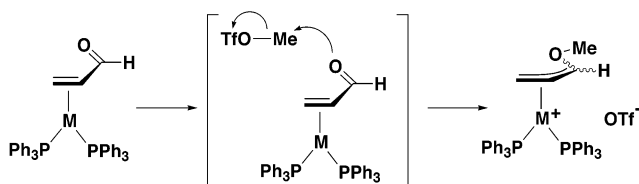
(10) NMR studies revealed that the complexes **4** and **5** were formed as a mixture of almost equal amounts of syn and anti isomers at the early stage of the reaction. The isomerization between these two isomers proceeded gradually to give a thermodynamic mixture (syn/anti = 98/2 for **4**, 94/6 for **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 -CH₃OCHCHCH₂)(dppf)]-[(C₆H₄-*p*-NO₂)OSO₂] involving the attack of MeOSO₂-(C₆H₄-*p*-NO₂) at the coordinated enal of Pt(η^2 -CH₂=CHCHO)(dppf) required a reaction time (20 h) almost similar to that for **1e**. The reaction of (η^2 -CH₂=CHCOOCH₃)Pt(PPh₃)₂ with MeOTf in C₆D₆ at room temperature gave Pt(Me)(OTf)(PPh₃)₂ and [Pt(Me)-(PPh₃)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 CD₂Cl₂ 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. ¹H, ³¹P, and ¹³C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. The chemical shifts in the ¹H nuclear magnetic resonance spectra were recorded relative to Me₄Si, CD₂Cl₂ (δ 5.32), C₆D₆ (δ 7.16), or CDCl₃ (δ 7.26). The chemical shifts in the ¹³C nuclear magnetic resonance spectra were recorded relative to Me₄Si, CD₂Cl₂ (δ 53.8) or CDCl₃ (δ 77.0). The chemical shifts in ³¹P nuclear magnetic resonance spectra were recorded using 85% H₃PO₄ as an external standard. Elemental analyses were performed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data

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

(13) The reaction of Pt(CH₂=CH₂)(PPh₃)₂ with MeOTf under the same conditions gave Pt(Me)(OTf)(PPh₃)₂ at first, which then decomposed gradually to [Pt(Me)(PPh₃)₃]⁺.

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 C₆D₆ were distilled from sodium benzophenone ketyl; CD₂Cl₂ and CDCl₃, from CaH₂. All commercially available reagents were distilled and degassed prior to use.

[(CH₂CHCH(OCH₃))Pd(PPh₃)₂][CF₃SO₃] (1a**).** To a solution of Pd(CH₂=CHCHO)(PPh₃)₂ (153.8 mg, 0.224 mmol) in 5 mL of toluene was added 26.0 μ L 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%).** ¹H NMR (CD₂Cl₂): 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). ³¹P NMR (CD₂Cl₂): δ 23.27 (d, *J*_{PP} = 36.6 Hz), 27.11 (d, *J*_{PP} = 36.6 Hz). ¹³C NMR (CD₂Cl₂): 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, COMe). **Syn isomer (5%).** ¹H NMR (CD₂Cl₂): 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. ³¹P NMR (CD₂Cl₂): δ 21.52 (d, *J*_{PP} = 41.5 Hz), 28.60 (d, *J*_{PP} = 41.5 Hz). Anal. Calcd for C₄₁H₃₇F₃O₄P₂SPd (a mixture of anti and syn isomers): C, 57.85; H, 4.38. Found: C, 58.11; H, 4.47.

[(CH₂CHCH(OCH₃))Pd(dppf)][CF₃SO₃] (1b**).** To a solution of Pd(CH₂=CHCHO)(dppf) (163.1 mg, 0.228 mmol) in 5 mL of toluene was added 30 μ L 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%).** ¹H NMR (CD₂Cl₂): 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). ³¹P NMR (CD₂Cl₂): δ 20.12 (d, *J*_{PP} = 45.6 Hz), 25.69 (d, *J*_{PP} = 45.6 Hz). ¹³C NMR (CD₂Cl₂): 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, COMe). **Anti isomer (15%).** ¹H NMR (CD₂Cl₂): 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. ³¹P NMR (CD₂Cl₂): δ 20.59 (d, *J*_{PP} = 47.7 Hz), 28.48 (d, *J*_{PP} = 47.7 Hz). Anal. Calcd for C₃₉H₃₅F₃O₄P₂SFePd (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**·3/2C₆H₆. *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) Å³, *Z* = 2, *D*_{calcd} = 1.495 g/cm³, *T* = –70.0 °C, *R* (*R*_w) = 0.056 (0.108).

[(CH₂CHCH(OCH₃))Pd(dppf)][FSO₃] (1c**).** To a solution of Pd(CH₂=CHCHO)(dppf) (10.8 mg, 0.015 mmol) in 0.5 mL of CD₂Cl₂ was added 1.3 μ L of MeOSO₂F (1.9 mg, 0.016 mmol) at room temperature. The complex **1c** was formed quantitatively.

[(CH₂CHCH(OCH₃))Pd(dppf)][CH₃SO₃] (1d**).** To a solution of Pd(CH₂=CHCHO)(dppf) (10.8 mg, 0.015 mmol) in 0.5 mL of C₂D₄Cl₂ was added 12.7 μ L 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 PdCl₂(dppf) in 2% yield.

[(CH₂CHCH(OCH₃))Pd(dppf)][*p*-NO₂C₆H₄SO₃] (1e**).** Pd-(CH₂=CHCHO)(dppf) (10.8 mg, 0.015 mmol) and MeOSO₂C₆H₄-*p*-NO₂ (22.7 mg, 0.151 mmol) were charged in an NMR sample tube, then CD₂Cl₂ was added at room temperature. After 12 h, the complex **1e** was formed in 85% yield along with PdCl₂(dppf) in 15% yield.

[(CH₂CHCH(OCH₃))Pd(dppf)][BF₄] (1f**).** Pd(CH₂=CHCHO)(dppf) (10.8 mg, 0.015 mmol) and [(CH₃)₃O][BF₄] (2.2 mg,

0.015 mmol) were charged in an NMR sample tube, and CD₂-Cl₂ was added at room temperature. After 3 h, the complex **1f** was formed quantitatively.

[(CH₂CHCH(OCH₃))Pt(PPh₃)₂][CF₃SO₃] (2a). To a solution of Pt(CH₂=CH₂)(PPh₃)₂ (228.0 mg, 0.305 mmol) in 6 mL of toluene was added 30.0 μL of CH₂=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%).** ¹H NMR (CD₂Cl₂): 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). ³¹P NMR (CD₂Cl₂): δ 19.08 (d, *J*_{PP} = 1.5 Hz, *J*_{PtP} = 4532 Hz), 22.52 (d, *J*_{PP} = 1.5 Hz, *J*_{PtP} = 3815 Hz). ¹³C NMR (CD₂Cl₂): 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%).** ¹H NMR (CD₂Cl₂): 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. ³¹P NMR (CD₂Cl₂): δ 16.57 (d, *J*_{PP} = 7.6 Hz, *J*_{PtP} = 3901 Hz), 17.97 (d, *J*_{PP} = 7.6 Hz, *J*_{PtP} = 4154 Hz). Anal. Calcd for C₄₁H₃₇F₃O₄P₂SPt (a mixture of syn and anti isomers): C, 52.40; H, 3.97. Found: C, 51.71; H, 3.81.

[(CH₂CHCH(OCH₃))Pt(dppf)][CF₃SO₃] (2b). To a solution of Pt(CH₂=CH₂)(dppf) (161.0 mg, 0.207 mmol) in 6 mL of benzene was added 16.0 μL of CH₂=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%).** ¹H NMR (CD₂Cl₂): 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). ³¹P NMR (CD₂Cl₂): δ 18.96 (d, *J*_{PP} = 11.7 Hz, *J*_{PtP} = 4527 Hz), 21.03 (d, *J*_{PP} = 11.7 Hz, *J*_{PtP} = 3948 Hz). ¹³C NMR (CD₂Cl₂): 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%).** ¹H NMR (CD₂Cl₂): 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. ³¹P NMR (CD₂Cl₂): δ 16.65 (d, *J*_{PP} = 16.0 Hz, *J*_{PtP} = 3948 Hz), 18.90 (d, *J*_{PP} = 16.0 Hz, *J*_{PtP} = 4243 Hz). Anal. Calcd for C₄₅H₄₁F₃O₄P₂SFepT (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**·3/2C₆H₆. *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) Å³, *Z* = 2, *D*_{calcd} = 1.647 g/cm³, *T* = –60.0 °C, *R* = 0.056.

Oxidative Addition of CH₃I to Pd(CH₂=CHCHO)-(dppf). To a solution of Pd(CH₂=CHCHO)(dppf) (10.8 mg, 0.015 mmol) in 0.5 mL of CD₂Cl₂ 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(CH₂=CHCHO)(dppf) remaining unreacted.

Pd(CH₃)(I)(dppf) (3). An authentic sample of complex **3** was generated by the reaction of *trans*-Pd(Me)(I)(PPh₃)₂¹⁴ (5.1 mg, 0.007 mmol) with DPPF (3.7 mg, 0.007 mmol) in CD₂Cl₂.

Selected NMR data for **3**. ¹H NMR (CD₂Cl₂): δ 0.86 (t, *J* = 7.6 Hz, 3H). ³¹P NMR (CD₂Cl₂): δ 12.24 (d, *J*_{PP} = 31.8 Hz), 33.88 (d, *J*_{PP} = 31.8 Hz).

[(CH₂CHCCH₃(OCH₃))Pd(PPh₃)₂][CF₃SO₃] (4). To a solution of Pd(CH₂=CHCOCH₃)(PPh₃)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%).** ¹H NMR (CD₂Cl₂): 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). ³¹P NMR (CD₂Cl₂): δ 23.13 (d, *J*_{PP} = 33.3 Hz), 29.97 (d, *J*_{PP} = 33.3 Hz). ¹³C NMR (CD₂Cl₂): δ 23.0 (dd, *J*_{CP} = 1.0, 4.3 Hz, CH₃), 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, COMe). **Anti isomer (54%).** ¹H NMR (CD₂Cl₂): 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. ³¹P NMR (CD₂Cl₂): δ 22.93 (d, *J*_{PP} = 36.0 Hz), 33.71 (d, *J*_{PP} = 36.0 Hz). ¹³C NMR (CD₂Cl₂): δ 19.6 (dd, *J*_{CP} = 0.9, 4.9 Hz, CH₃), 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 C₄₂H₃₉F₃O₄P₂-SPd (a mixture of anti and syn isomers): C, 58.31; H, 4.54. Found: C, 58.41; H, 4.47.

[(CH₂CHCCH₃(OCH₃))Pt(PPh₃)₂][CF₃SO₃] (5). To a solution of Pt(CH₂=CH₂)(PPh₃)₂ (206.1 mg, 0.276 mmol) in 6 mL of benzene was added 24.0 μL of CH₂=CHCOCH₃ (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%).** ¹H NMR (CD₂Cl₂): 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). ³¹P NMR (CD₂-Cl₂): δ 20.28 (d, *J*_{PP} = 2.2 Hz, *J*_{PtP} = 4640 Hz), 24.25 (d, *J*_{PP} = 2.2 Hz, *J*_{PtP} = 3718 Hz). ¹³C NMR (CD₂Cl₂): 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, COMe). **Anti isomer (6%).** ¹H NMR (CD₂Cl₂): 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. ³¹P NMR (CD₂Cl₂): δ 21.33 (s, *J*_{PtP} = 4711 Hz), 22.72 (s, *J*_{PtP} = 3652 Hz). Anal. Calcd for C₄₂H₃₉F₃O₄P₂SPt (a mixture of syn and anti isomers): C, 52.89; H, 4.12. Found: C, 52.59; H, 4.07.

Oxidative Addition of CH₃I to Pd(CH₂=CHCOCH₃)-(PPh₃)₂. To a solution of Pd(CH₂=CHCOCH₃)(PPh₃)₂ (8.0 mg, 0.011 mmol) in 0.5 mL of CD₂Cl₂ 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(CH₃)-(I)(PPh₃)₂ was quantitatively formed.

Oxidative Addition of CH₃I to Pt(CH₂=CHCOCH₃)-(PPh₃)₂. To a solution of Pt(CH₂=CHCOCH₃)(PPh₃)₂ (8.3 mg, 0.011 mmol) in 0.5 mL of CD₂Cl₂ 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(CH₃)-(I)(PPh₃)₂¹⁵ was quantitatively formed.

[(CH₂CHCH(OCH₃))Pt(dppf)][*p*-NO₂C₆H₄SO₃]. Pt(CH₂=CHCHO)(dppf) (12.1 mg, 0.015 mmol) and MeOSO₂C₆H₄-*p*-NO₂ (32.6 mg, 0.150 mmol) were charged in an NMR sample tube, then CD₂Cl₂ was added at room temperature. After 20 h, [(CH₂CHCH(OCH₃))Pt(dppf)][*p*-NO₂C₆H₄SO₃] was formed quantitatively.

(14) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6–7.

(15) Chat, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705–716.

Reaction of Pt(CH₂=CHCOOCH₃)(PPh₃)₂ with MeOTf.

To a solution of Pt(CH₂=CHCOOCH₃)(PPh₃)₂ (12.1 mg, 0.015 mmol) in 0.5 mL of C₆D₆ 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)(PPh₃)₂ was formed in 39% yield. The solution was removed by decantation, and the solids were resolved in CD₂Cl₂ with toluene (5.0 μL, 0.047 mmol) as internal standard. [Pt(Me)(PPh₃)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 CD₂Cl₂ was added 0.9 μL of acrolein (0.8 mg, 0.013 mmol) at room temperature. After 48 h, no reaction occurred.

Acknowledgment. Partial support of this work through Grants-in-Aid for scientific research from the Ministry of Education, Science and Culture, Japan, and the JSPS Research Fellowship for Young Scientists (M.M.) is gratefully acknowledged.

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>.

(16) Thorn, D. L.; Fultz, W. C. *J. Phys. Chem.* **1989**, *93*, 1234–1243.