

Structural Insight into (2-Oxy- π -allyl)palladium and -platinum Complexes as Precursors of Oxodimethylenemethane Complexes

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X-ray crystallographic structures of η^3 -allylpalladium and -platinum complexes bearing an acetal group at the 2-position $\{[M(\eta^3\text{-CH}_2\text{C}(\text{OCH}_2\text{OCH}_3)\text{CH}_2)(\text{PPh}_3)_2](\text{PF}_6) (M = \text{Pd} (\mathbf{1a}), \text{Pt} (\mathbf{1b}))$ and $[M(\eta^3\text{-CH}_2\text{C}(\text{O}-2\text{-C}_5\text{H}_9\text{O})\text{CH}_2)(\text{PPh}_3)_2](\text{PF}_6) (M = \text{Pd} (\mathbf{2a}), \text{Pt} (\mathbf{2b}))\}$ reveal that they have a large contribution of oxonium structure, regardless of the kind of metal. Depending on the structure of the acetal moiety, these η^3 -allyl complexes show different reactivities toward hydroxide and methoxide ion as nucleophiles. The generation mechanism of oxodimethylenemethane complexes $\{[M(\eta^3\text{-CH}_2\text{C}(\text{O})\text{CH}_2)(\text{PPh}_3)_2](\text{PF}_6) (M = \text{Pd} (\mathbf{3a}), \text{Pt} (\mathbf{3b}))\}$ from these acetal compounds was discussed on the basis of the X-ray crystallographic structures, the analysis of reaction products, and the ^{18}O isotope-labeling technique. Nucleophilic displacement at the 2-position of η^3 -allylpalladium complexes was directly proved for the first time by the isotope technique.

Introduction

Unsubstituted (oxodimethylenemethane)palladium (ODMM-palladium) and -platinum complexes (**3a,b**) were generated from the corresponding η^3 -allylmetal complexes bearing an acetal group at the 2-position (**1a,b**, **2a,b**) through reaction with a base under mild conditions,^{1,2} although it was known that acetal compounds are generally stable in basic conditions.³

Meanwhile, alkyl 2-[(1-(butyloxy)ethyl)oxy]allylcarbonate (**4**) afforded the corresponding ODMM complexes **3a,b** only upon mixing with palladium(0) or platinum(0) via the η^3 -allyl complexes as intermediates.⁴

Since there are many possible reactive sites in η^3 -allylpalladium and -platinum complexes bearing a ((methyloxy)methyl)oxy group at the 2-position (**1a,b**), namely the terminal methyl and the central methylene carbons of the acetal group and the 1- and 2-position carbons of the allyl moiety, it is very interesting to clarify the electronic structures of these η^3 -allyl complexes and the mechanism of their reaction with nucleophiles and to learn the correlation between them.

In this paper, X-ray crystallographic structures of these unique η^3 -allylpalladium and -platinum complexes bearing a ((methyloxy)methyl)oxy group at the 2-position (**1a,b**) were determined, and the generation mechanism of ODMM complexes **3a,b** from these acetal compounds was discussed on the basis of the X-ray crystallographic structures, the analysis of reaction products, and the results obtained by using the ^{18}O isotope-labeling technique.

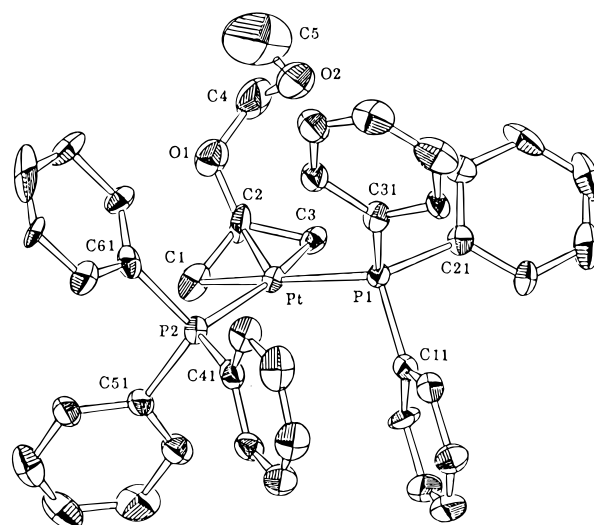


Figure 1. ORTEP plot of **1b** at the 50% probability level (counterion PF_6^- and all hydrogen atoms are omitted).

Results and Discussion

Structure of η^3 -Allyl Complexes **1a,b.** Complexes **1a,b**¹ readily crystallized in prisms from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Their structures were determined by X-ray diffraction. The X-ray crystallographic structure of **1b** is shown in Figure 1 (the structures of both complexes are similar, and therefore only one is shown here).

Selected bond lengths and angles of **1a,b** are given in Table 1, the structural parameters in Table 2, and the data for X-ray diffraction analysis of **1a,b** in Table 3.

The dihedral angles θ' between the $\text{P}(1)\text{-M-P}(2)$ and $\text{C}(1)\text{-C}(2)\text{-C}(3)$ planes of **1a,b** were almost equal to or a little smaller than those of typically reported η^3 -allyl

[Ⓢ] Abstract published in *Advance ACS Abstracts*, June 1, 1997.
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 (2) Ohsuka, A.; Hirao, T.; Kurosawa, H.; Ikeda, I. *Organometallics* **1995**, *14*, 2538.
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(5) η^3 -Allylpalladium and -platinum complexes ($\theta' = 61\text{--}72^\circ$): (a) Mason, R.; Wheeler, A. G. *J. Chem. Soc. A* **1968**, 2549. (b) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, p 721.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1a,b

| bond | 1a | 1b | angle | 1a | 1b |
|------------|----------|----------|----------------|----------|----------|
| P(1)–M | 2.328(3) | 2.292(4) | P(2)–M–P(1) | 102.3(1) | 101.2(1) |
| P(2)–M | 2.331(4) | 2.297(4) | C(1)–M–P(1) | 163.5(4) | 163.9(5) |
| C(1)–M | 2.13(1) | 2.17(2) | C(1)–M–P(2) | 93.3(5) | 93.8(5) |
| C(2)–M | 2.24(1) | 2.22(2) | C(2)–M–P(1) | 130.9(5) | 130.9(5) |
| C(3)–M | 2.15(1) | 2.15(2) | C(2)–M–P(2) | 124.7(4) | 125.6(4) |
| C(2)–C(3) | 1.39(2) | 1.40(2) | C(2)–M–C(1) | 36.4(6) | 37.3(7) |
| C(1)–C(2) | 1.37(2) | 1.41(3) | C(3)–M–P(1) | 98.1(4) | 98.2(4) |
| O(1)–C(2) | 1.33(2) | 1.33(2) | C(3)–M–P(2) | 159.4(4) | 160.3(5) |
| O(1)–C(4) | 1.38(2) | 1.39(3) | C(3)–M–C(1) | 66.1(6) | 66.5(7) |
| O(2)–C(4) | 1.37(3) | 1.36(4) | C(3)–M–C(2) | 37.0(5) | 37.3(5) |
| O(2)–C(5) | 1.39(4) | 1.46(7) | C(3)–C(2)–C(1) | 115(1) | 115(1) |
| C(11)–P(1) | 1.83(1) | 1.83(1) | O(1)–C(2)–C(1) | 117(1) | 118(1) |
| C(21)–P(1) | 1.83(1) | 1.84(1) | O(1)–C(2)–C(3) | 125(1) | 126(1) |
| C(31)–P(1) | 1.83(1) | 1.83(2) | C(2)–O(1)–C(4) | 120(1) | 120(1) |
| C(41)–P(2) | 1.84(1) | 1.83(1) | O(1)–C(4)–O(2) | 111(1) | 110(2) |
| C(51)–P(2) | 1.83(1) | 1.86(1) | C(4)–O(2)–C(5) | 110(2) | 112(2) |
| C(61)–P(2) | 1.83(1) | 1.85(1) | | | |

Table 2. Structural Parameters of 1a,b

| structural parameter ^a | 1a (M = Pd) | 1b (M = Pt) |
|-----------------------------------|-------------|-------------|
| M–P | 2.330(4) | 2.295(4) |
| M–C(1) | 2.14(1) | 2.16(3) |
| M–C(2) | 2.24(1) | 2.22(2) |
| C(1)–C(2) | 1.38(2) | 1.41(3) |
| C(2)–O | 1.33(2) | 1.33(2) |
| P(1)–M–P(2) | 102.3(1) | 101.2(1) |
| C(1)–C(2)–C(3) | 115(1) | 115(1) |
| θ | 62.3 | 66.5 |
| θ' | 57.5 | 61.1 |

^a θ is the fold angle between the C(1)–M–C(3) and C(1)–C(2)–C(3) planes. θ' is the dihedral angle between the P(1)–M–P(2) and C(1)–C(2)–C(3) planes.

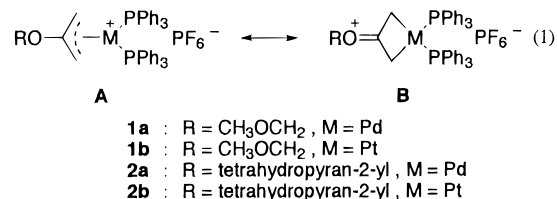
Table 3. Data for X-ray Diffraction Analysis of 1a,b

| | 1a | 1b |
|---|-----------------------------|-----------------------------|
| A. Crystal Data | | |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| lattice parameters | | |
| <i>a</i> , Å | 16.552(4) | 16.518(4) |
| <i>b</i> , Å | 22.378(4) | 22.396(4) |
| <i>c</i> , Å | 11.126(2) | 11.117(3) |
| β , deg | 90.72(2) | 90.83(2) |
| <i>V</i> , Å ³ | 4120(1) | 4112(1) |
| fw | 877.07 | 965.76 |
| <i>D</i> (calcd), g/cm ³ | 1.414 | 1.560 |
| <i>Z</i> value | 4 | 4 |
| μ , cm ⁻¹ | 6.27 | 35.76 |
| λ (Mo K α), Å | 0.71069 | 0.71069 |
| B. Data Collection and Analysis Summary | | |
| cryst dimens, mm | 0.70 × 0.25 × 0.25 | 0.60 × 0.25 × 0.25 |
| 2 θ range for centered reflns | 22.11 ≤ 2 θ ≤ 26.60° | 27.19 ≤ 2 θ ≤ 27.49° |
| total no. of reflns measd | 10549 | 10034 |
| no. of unique data used | 9724 | 9711 |
| max transm factor | 0.9993 | 0.9997 |
| min transm factor | 0.9533 | 0.8743 |
| <i>R</i> | 0.071 | 0.060 |
| <i>R</i> _w | 0.088 | 0.078 |
| <i>F</i> (000) | 1784.00 | 1912.00 |

complexes (61–72°),⁵ while the C(2)–O(1) bonds of **1a,b** (1.33 Å) were shorter than a typical C–O single bond (1.43 Å) and almost equal to the mean of this length and the C–O bond length of ODMM complexes (1.22 Å (**3a**), 1.257 Å (**3b**)),^{2,6} though the result shows that the C(4)–O(1), C(4)–O(2), and C(5)–O(2) bonds were also

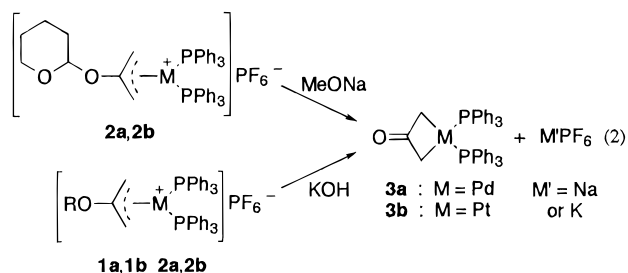
(6) Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; Lin, Y.-C.; Wang, Y. *Organometallics* **1992**, *11*, 1761.

somewhat shorter than ordinary single bonds. From these data, it can be concluded that the η^3 -allyl complexes **1a,b** are in resonance between the formal acetal (**A**) and the oxonium ion (**B**) structures, as shown in eq 1.



The fact that the C(2)–M bonds (2.24 Å (**1a**), 2.22 Å (**1b**)) are longer than C(1)–M and C(3)–M, as shown in Table 1, may also support the contribution of oxonium ion structure. Usually, the length of C(2)–M is almost the same to the other two C–M lengths for an η^3 -allyl complex, especially in the case of unsubstituted η^3 -allyl complexes.⁷ In the case of 2-methyl- η^3 -allylpalladium and -platinum complexes, however, C(2)–M was reported to be slightly longer than the others.⁸

Reactivities of η^3 -Allyl Complexes with Nucleophiles. Depending on the structure of the acetal group, these η^3 -allylpalladium and -platinum complexes revealed different reactivities toward hydroxide ion and methoxide ion. Upon treating the η^3 -allylpalladium complex bearing an acetal group with methoxide ion, only **2a**, which has β -hydrogen atoms on the acetal central carbon, gave ODMM-palladium complex (**3a**) in good yields (eq 2), while **1a**, which has no β -hydrogen atom, did not yield the same product. In the case of the platinum complex, however, **3b** was obtained by reaction with methoxide ion, even from **1b** which has no β -hydrogen atom, though in a poor yield. On the contrary, upon using hydroxide ion, the complexes **3a,b** were afforded not only from **2a,b** but also from **1a,b** which have no β -hydrogen atom on the acetal group (eq 2).



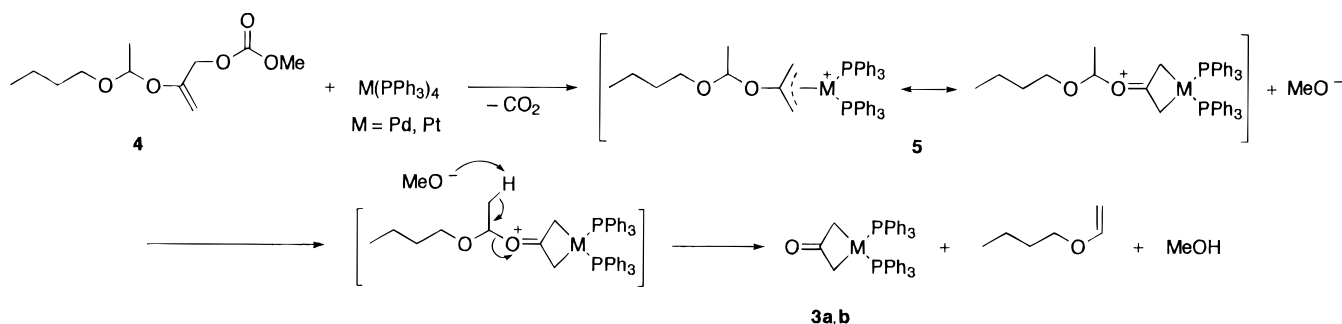
Generation Mechanism of ODMM Complexes from the Reaction of 2a,b with Methoxide Ion.

Upon considering the synthetic utilization of complexes **3a,b**, it would be very important to clarify the multiplicity of the mechanisms of these reactions. In a previous paper,⁴ we reported that alkyl 2-[(1-(butyloxy)ethyl)oxy]-allylcarbonate (**4**) afforded complexes **3a,b** only upon mixing with M(PPh₃)₄ (M = Pd, Pt). Thus, in an NMR experiment, the appearance of signals due to the

(7) For palladium complexes, see: (a) De Munno, G.; Bruno, G.; Rotondo, E.; Giordano, G.; Lo Schiavo, S.; Piraino, P.; Tresoldi, G. *Inorg. Chim. Acta* **1993**, *208*, 67. (b) Canty, A. J.; Jin, H.; Roberts, A. S.; Traill, P. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *489*, 153.

(8) Ozawa, F.; Son, T.-i.; Ebina, S.; Osakada, K.; Yamamoto, A. *Organometallics* **1992**, *11*, 171.

Scheme 1



complexes **3a,b**⁹ and butyl vinyl ether¹⁰ was confirmed. On the other hand, alkyl allylcarbonate, having no β -hydrogen at the central carbon of the acetal moiety on the 2-position of the allyl group, did not afford end products **3a,b**, even when mixed with $M(\text{PPh}_3)_4$ ($M = \text{Pd}, \text{Pt}$), although generation of the corresponding η^3 -allyl complex was confirmed in ^1H NMR.

A possible mechanism for this reaction is illustrated in Scheme 1. During the first step of the reaction, the transition metal (0) adds to the carbonate **4** oxidatively to result in the formation of carbon dioxide and a cationic complex paired with a methoxide ion (**5**).^{11,12} A β -hydrogen atom is abstracted from the acetal moiety by the generated methoxide ion, resulting in the elimination of the ODMM complex, i.e., the η^3 -(2-oxyallyl) complex moiety.

In the case of the reaction of **2a,b** with methoxide ion, this mechanism is also likely.

One important factor by which this reaction proceeded smoothly with these acetal compounds was supposed to be the easy elimination of the η^3 -(2-oxyallyl) complex moiety, assisted by a large contribution of oxonium ion structure (**B** in eq 1), as shown in **1a,b**. The difference of reactivity toward methoxide ion between palladium and platinum complexes is obvious (**1b** afforded **3b**, though in a poor yield, while **1a** did not afford **3a** at all) but is left unexplained at present.

Generation Mechanism of ODMM Complexes from the Reaction of 1a,b and 2a,b with Hydroxide Ion. For the purpose of clarifying this difference, the formation mechanism was investigated by analyzing the ODMM complex generated from the reaction of **1a,b** with hydroxide ion labeled with ^{18}O (ca. 80% enriched)¹³ using mass spectrum.

As a result, both of the generated ODMM complexes **3a,b** were found to be ^{18}O atom enriched, by 63% for the palladium complex and 76% for the platinum complex, as calculated from their mass spectra (Table 4). To find out why the ^{18}O enrichment decreased, the

Table 4. Intensity of $[M + 1]^+$ Peaks of ODMM Complexes **3a,b**

| $[M + 1]$ (m/e) | intensity (3a) | | | $[M + 1]$ (m/e) | intensity (3b) | | |
|------------------------|----------------------------|----------------------------------|--|------------------------|----------------------------|----------------------------------|--|
| | from KOH | from K^{18}OH | 63% ^{18}O -labeled (calcd) | | from KOH | from K^{18}OH | 76% ^{18}O -labeled (calcd) |
| 682 | 1.15 | 0.73 | 0.93 | 772 | 0.84 | 0.47 | 0.46 |
| 683 | 4.11 | 1.81 | 2.28 | 773 | 3.21 | 1.32 | 1.27 |
| 684 | 6.33 | 3.13 | 3.30 | 774 | 10.86 | 3.86 | 3.87 |
| 685 | 38.07 | 18.07 | 17.95 | 775 | 75.35 | 24.70 | 24.50 |
| 686 | 80.06 | 36.86 | 36.17 | 776 | 100 | 39.19 | 38.50 |
| 687 | 100 | 67.27 | 65.63 | 777 | 85.53 | 91.33 | 92.85 |
| 688 | 47.79 | 75.60 | 73.31 | 778 | 32.44 | 100 | 100 |
| 689 | 80.85 | 100 | 100 | 779 | 21.58 | 82.34 | 83.76 |
| 690 | 36.24 | 47.27 | 46.83 | 780 | 7.84 | 30.67 | 31.67 |
| 691 | 40.45 | 71.79 | 70.93 | 781 | 1.87 | 19.74 | 20.11 |
| 692 | 16.14 | 32.37 | 31.00 | 782 | 0.43 | 7.09 | 7.23 |
| 693 | 3.93 | 30.16 | 28.99 | 783 | 0.21 | 1.63 | 1.76 |
| 694 | 1.02 | 11.58 | 11.35 | 784 | 0.15 | 0.37 | 0.43 |
| 695 | 0.69 | 2.64 | 2.94 | | | | |

resulting complexes **3a,b** enriched with ^{18}O were further treated with water saturated in benzene at room temperature for a day, and the unlabeled complexes **3a,b** were treated with K^{18}OH in 2-propanol/THF for 1 h. However, the degree of ^{18}O enrichment in both cases was not changed, as confirmed in the mass spectra, suggesting no exchange of hydroxide group with water under neutral conditions at ambient temperature, which are the same conditions as in the workup process, nor with OH^- under the conditions of the preparation reaction.

A possible mechanism for the generation reaction is illustrated in Scheme 2. During the first step of the reaction, nucleophilic attack by a hydroxide ion takes place at the 2-position carbon atom of allyl moiety to generate η^2 -metallacyclobutane complex **6** as a reaction intermediate. The proton of the hydroxy group in this intermediate is transferred, then, to the ((methoxy)methyl)oxy group as the result of a four-centered reaction, to result in the elimination of a hemiacetal molecule and the formation of the ODMM complexes **3a,b**. In the case of the reaction of **1a,b** with methoxide ion, even if the intermediate of η^2 -metallacyclobutane complex is generated, ODMM complexes **3a,b** are considered not to be generated, due to the impossibility of the methyl group transfer via the four-centered reaction.

One of the reasons why nucleophilic attack by hydroxide ion at the 2-position of the η^3 -allyl complexes

(9) ^1H NMR (25 °C, 400 MHz) signals of methylene protons are as follows. Pd complex (**3a**): in CD_2Cl_2 , δ 2.39 (s, br). Pt complex (**3b**): in CD_2Cl_2 , δ 2.19 (s, $J(\text{PtH}) = 48$ Hz).

(10) ^1H NMR (CD_2Cl_2 , 25 °C, 400 MHz) signals are δ 0.92 (t, 3H), 1.38 (sext, 2H), 1.60 (quint, 2H), 3.65 (t, 2H), 3.39 (d, 1H), 4.13 (d, 1H), 6.45 (dd, 1H).

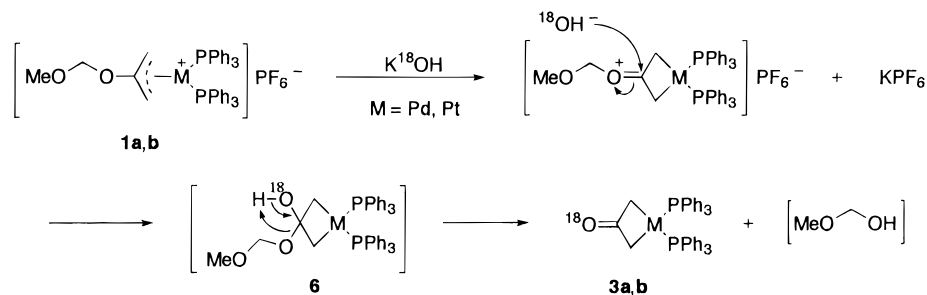
(11) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, 23, 4809.

(12) Ikeda, I.; Gu, X.-P.; Okuhara, T.; Okahara, M. *Synthesis* **1990**, 32.

(13) Enrichment of ^{18}O was confirmed by mass spectrum of the product (intensity of fragment ($m/e = 150$)/intensity of fragment ($m/e = 148$)); ^{18}O -enriched cinnamic acid, $M = 150$) from the reaction of methyl cinnamate with potassium hydroxide prepared from H_2^{18}O (purchased as 96.9 atom %-enriched reagent from Isotec Inc., Dayton, OH) and *t*-BuOK (purified by sublimation before use) in absolute 2-propanol and followed by neutralization with hydrochloric acid.

(14) Direct observation of nucleophilic displacement reaction at the 2-position of η^3 -allylplatinum complex and indirect observation (deduction from organic products analysis) for nucleophilic displacement reaction at the 2-position of η^3 -allylpalladium complex: Ohe, K.; Matsuda, H.; Morimoto, T.; Ogoshi, S.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1994**, 116, 4125.

Scheme 2



proceeded smoothly may also be the large contribution of oxonium ion structure (**B** in eq 1), that is, the high density of positive charge on the 2-position carbon atom connected to the oxonium-characteristic oxygen atom.

The isolation of ODMM complexes **3a,b** enriched with ^{18}O is the first direct observation of nucleophilic displacement reaction at the 2-position of η^3 -allylpalladium complexes.^{14–16}

Recently, nucleophilic attack at the 2-position of η^3 -propargyl/allenyl complexes was reported.¹⁷ While the nucleophilic substitution in our studies presumably proceeds via the η^2 -metallacyclobutane intermediate **6**, these reports showed an addition of pronucleophile toward the triple-bonded η^3 -allenyl intermediate moiety, with the hydrogen atom (or possibly transferred as a hydride ion) selectively adding to the terminal carbon.

The reason for about 4–17% loss of ^{18}O enrichment during the preparation of **3a,b** from **1a,b** and $^{18}\text{OH}^-$ remained unknown.

Conclusion

It was clarified that, concerning the generation mechanism of ODMM-palladium and -platinum complexes from η^3 -allyl complexes bearing an acetal group at the 2-position, there are at least two different paths leading to the ODMM complexes, and their reactivities toward bases were based on the high positive charge density on the 2-position carbon atom and the oxygen atom connected to this carbon, i.e., a large contribution of oxonium ion structure, which was confirmed by the X-ray crystallographic analysis.

Nucleophilic displacement at the 2-position of the η^3 -allylpalladium complex was first directly proved by the isotope technique.

Experimental Section

Preparation of Platinum η^3 -2-[(Tetrahydropyran-2-yl)oxy]allyl Hexafluorophosphate (2b). In an argon atmosphere, a solution of 377 mg (2.13 mmol) of 2-[(tetrahydropyran-2-yl)oxy]allyl chloride in 3 mL of benzene was added to a

(15) Direct observation of nucleophilic addition reaction at the 2-position of η^3 -allylpalladium complex: Hoffmann, H. M. R.; Otte, A. R.; Wilde, A.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1.

(16) Indirect observation (deduction from organic products analysis) for nucleophilic addition reaction at the 2-position of η^3 -allylpalladium complex: (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173. (b) Hoffmann, H. M. R.; Otte, A. R.; Wilde, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 234. (c) Wilde, A.; Otte, A. R.; Hoffmann, H. M. R. *J. Chem. Soc., Chem. Commun.* **1993**, 615. (d) Otte, A. R.; Wilde, A.; Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1280.

(17) (a) Baize, M. W.; Furilla, J. L.; Wojcicki, A. *Inorg. Chim. Acta* **1994**, *223*, 1. (b) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657. (c) Tsai, F.-Y.; Hsu, R.-H.; Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Organomet. Chem.* **1996**, *520*, 85.

solution of 2.53 g (2.03 mmol) of $\text{Pt}(\text{PPh}_3)_4$ in 30 mL of benzene at room temperature. The solution was stirred for 15 min, and then 200 mL of hexane was added. After removal of the solvent by filtration, solid materials containing **2b** (counterion, Cl^-) were dried under reduced pressure and were again dissolved in CH_2Cl_2 /acetone (40 mL + 40 mL). A solution of 342 mg (2.10 mmol) of ammonium hexafluorophosphate in 20 mL of acetone was added to the CH_2Cl_2 /acetone solution. After the solution was stirred for 15 min, the solvent was evaporated to dryness. Thus obtained, **2b** was purified by recrystallization from CH_2Cl_2 /hexane (1/4 v/v) as colorless prisms. Yield: 1540 mg (70%); mp 135–137 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.38–7.36 (m, 6H, Ph), 7.30–7.26 (m, 18H, Ph), 7.22–7.18 (m, 6H, Ph), 5.08 (t, $J = 2.87$ Hz, 1H, OCHO), 3.72 (m, 1H, OCH_2), 3.33–3.29 (m, 3H, OCH_2 and allyl H), 2.77 (m, $J_{\text{PH}} = 40.3$ Hz, 1H, allyl H), 2.60 (m, $J_{\text{PH}} = 44$ Hz, 1H, allyl H), 1.88–1.87 (m, 1H, 3- CH_2), 1.80–1.61 (m, 5H, 3- CH_2 and 4,5- CH_2). ^{13}C NMR (600 MHz, CDCl_3): δ 18.7, 24.6, 29.8 (3,4,5-carbons of tetrahydropyran-2-yl ring), 53.6 (C_1 -position), 63.6 (s, OCH_2), 97.7 (s, OCHO), 128.2–134.9 (phenyl carbons), 153.5 (C_2 -position). ^{31}P NMR (400 MHz, CDCl_3): δ 17.9 (d, $J_{\text{PP}} = 11.0$ Hz, $J_{\text{PF}} = 3684$ Hz), 17.8 (d, $J_{\text{PP}} = 11.0$ Hz, $J_{\text{PF}} = 3757$ Hz). Anal. Calcd for $\text{C}_{44}\text{H}_{43}\text{O}_2\text{F}_6\text{P}_3\text{Pt}\cdot\text{CH}_2\text{Cl}_2$: C, 49.55; H, 4.16. Found: C, 49.77; H, 4.18.

Preparation of Palladium η^3 -2-[(Tetrahydropyran-2-yl)oxy]allyl Hexafluorophosphate (2a). To a solution of 343 mg (0.604 mmol) of palladium η^3 -2-[(tetrahydropyran-2-yl)oxy]allyl chloride dimer in acetone/ CH_2Cl_2 (50 mL + 40 mL) at 0 °C was added a solution of 635 mg (2.42 mmol) of PPh_3 in 5 mL of CH_2Cl_2 . Ammonium hexafluorophosphate (200 mg, 1.23 mmol) dissolved in 10 mL of acetone was added to the solution at 0 °C. The solution was stirred at room temperature for 15 min, and then the solvent was evaporated. The residual solid materials were washed with ether and dried under reduced pressure. Thus obtained, the end product was purified by recrystallization from CH_2Cl_2 /hexane (1/4 v/v) as yellow needles. Yield: 960 mg (79%); mp 173–176 °C dec. ^1H NMR (600 MHz, CDCl_3): δ 7.39–7.37 (m, 6H, Ph), 7.32–7.24 (m, 18H, Ph), 7.19–7.16 (m, 6H, Ph), 4.98 (t, 1H, $J = 2.72$ Hz, OCHO), 3.66 (dt, $J = 5.83, 10.80$ Hz, 1H, OCH_2), 3.46 (m, 2H, allyl H), 3.24 (dt, $J = 4.72, 10.80$ Hz, 1H, OCH_2), 3.19 (d, $J = 10.18$ Hz, 1H, allyl H), 3.03 (d, $J = 9.75$ Hz, 1H, allyl H), 1.90–1.87 (m, 1H, 3- CH_2), 1.80–1.76 (m, 1H, 3- CH_2), 1.70–1.58 (m, 4H, 4,5- CH_2). ^{13}C NMR (600 MHz, CDCl_3): δ 19.2, 24.7, 30.0 (3,4,5-carbons of tetrahydropyran-2-yl ring), 51.7 (C_1 -position), 63.7 (s, OCH_2), 97.4 (s, OCHO), 128.7–133.7 (phenyl carbons), 154.6 (C_2 -position). ^{31}P NMR (400 MHz, CDCl_3): δ 26.0 (d, $J_{\text{PP}} = 36.8$ Hz), 25.3 (d, $J_{\text{PP}} = 36.8$ Hz). Anal. Calcd for $\text{C}_{44}\text{H}_{43}\text{O}_2\text{F}_6\text{P}_3\text{Pd}\cdot\text{CH}_2\text{Cl}_2$: C, 53.94; H, 4.53. Found: C, 53.85; H, 4.58.

Preparation of Palladium η^3 -2-[(Tetrahydropyran-2-yl)oxy]allyl Chloride Dimer. $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (dba = dibenzylideneacetone) (1520 mg, 1.47 mmol) and 2-[(tetrahydropyran-2-yl)oxy]-3-chloroprop-1-ene (1000 mg, 5.66 mmol) in acetone (100 mL) were stirred for 24 h at room temperature. The deep purple color turned to yellow upon completion of the reaction. The precipitation was filtered off. The yellow solution was evaporated to dryness and the residue washed with diethyl ether until the washing was no longer tinted. Thus obtained,

the end product was purified by recrystallization from CH₂-Cl₂/hexane (1/4 v/v) as yellow needles. Yield: 634 mg (75%); mp 134–137 °C dec. ¹H NMR (600 MHz, CDCl₃): δ 5.30 (t, *J* = 7.3 Hz, 1H, OCHO), 4.09 (br, 1H, allyl H), 3.92 (t, *J* = 3.0 Hz, 1H, OCH₂), 3.72 (br, 1H, allyl H), 3.71 (t, *J* = 3.4 Hz, 1H, OCH₂), 2.66 (br, 1H, allyl H), 2.52 (br, 1H, allyl H), 1.87–1.26 (m, 6H, 3,4,5-CH₂). Anal. Calcd for C₁₆H₂₆O₄Cl₂Pd₂: C, 33.83; H, 4.97; Cl, 12.48. Found: C, 33.46; H, 4.58; Cl, 12.85.

Preparation of 2-[(Tetrahydropyran-2-yl)oxy]-3-chloroprop-1-ene. A mixture of 30.2 g (0.265 mol) of 2-[(tetrahydropyran-2-yl)oxy]-1,3-dichloropropane, 4.6 g (0.0135 mol) of tetrabutylammonium hydrogen sulfate, 11.6 g (0.291 mol) of sodium hydroxide, and 5.3 g of water was placed in a round-bottomed flask and stirred for 2 h at 80 °C. The end product was isolated directly from the reaction mixture by distillation under reduced pressure. Yield: 30.4 g (65%); bp 60 °C/2.0 mmHg. ¹H NMR (600 MHz, CDCl₃): δ 5.24 (t, *J* = 3.12 Hz, 1H, OCHO), 4.48 (d, *J* = 2.08 Hz, 1H, =CH₂), 4.42 (d, *J* = 2.08 Hz, 1H, =CH₂), 4.00 (s, 2H, CH₂Cl), 3.88 (m, 1H, OCH₂), 3.59 (m, 1H, OCH₂), 1.93 (m, 1H, 3-CH₂), 1.79 (m, 1H, 3-CH₂), 1.67–1.57 (m, 4H, 4,5-CH₂). Anal. Calcd for C₈H₁₃O₂Cl: C, 54.40; H, 7.42; Cl, 20.01. Found: C, 54.20; H, 7.64; Cl, 19.74.

Preparation of 2-[(Tetrahydropyran-2-yl)oxy]-1,3-dichloropropane. Into a round-bottomed flask fitted with a stopper carrying a glass tube reaching nearly to the bottom of the flask was placed 105 g (1.25 mol) of 3,4-dihydro-2*H*-pyran. A rapid stream of hydrogen chloride gas was run into the liquid at 0–5 °C. After about 3 h, no more hydrogen chloride gas was absorbed. The stream of hydrogen chloride gas was continued to run for about additionally 15 min. Nitrogen gas was then bubbled through the glass tube for 15 min. The reaction mixture was slowly added to a solution of 123 g (1.33 mol) of epichlorohydrin and 16.3 g (0.062 mol) of dodecyltrimethylammonium chloride in 100 mL of CH₂Cl₂ cooled in an ice bath and stirred for 1 h. After removal of the solvent by evaporation, the dichloride was extracted with 500 mL of ether and isolated by distillation under reduced pressure. Overall yield: 242 g (91%); bp 83 °C/1.8 mmHg. ¹H NMR (600 MHz, CDCl₃): δ 4.79 (t, *J* = 3.66 Hz, 1H, OCHO), 4.06 (m, 1H, OCH₂), 3.93 (m, 1H, OCH₂), 3.80 (dd, *J* = 11.25, 4.10 Hz, 1H, CH₂Cl), 3.77 (dd, *J* = 11.57, 4.80 Hz, 1H, CH₂-Cl), 3.71 (dd, *J* = 11.25, 6.18 Hz, 1H, CH₂Cl), 3.67 (dd, *J* = 11.57, 5.28 Hz, 1H, CH₂Cl), 3.54 (m, 1H, CH₂Cl), 1.84 (m, 1H, 3-CH₂), 1.75 (m, 1H, 3-CH₂), 1.66–1.54 (m, 4H, 4,5-CH₂). Anal. Calcd for C₈H₁₄O₂Cl₂: C, 45.09; H, 6.62; Cl, 33.27. Found: C, 44.93; H, 6.75; Cl, 33.39.

Preparation of **1a** and **1b** is described in our previous report.¹ Here, we add the ¹³C and ³¹P NMR measurements. **1a** ¹³C NMR (600 MHz, CDCl₃): δ 57.1 (s, OCH₃), 61.5 (C₁-position), 94.3 (s, OCH₂O), 128.9–133.6 (phenyl carbons), 155.0 (C₂-position). ³¹P NMR (400 MHz, CDCl₃): δ 25.7. **1b** ¹³C NMR (600 MHz, CDCl₃): δ 53.2 (C₁-position), 57.3 (s, OCH₃), 94.5 (s, OCH₂O), 127.8–134.8 (phenyl carbons), 153.8 (C₂-position); ³¹P NMR (400 MHz, CDCl₃): δ 17.6 (*J*_{PtP} = 3720 Hz).

X-ray Data Collection and Structure Analysis of 1a,b. A well-shaped colorless prismatic crystal of **1a** or **1b** was mounted on a glass fiber. All measurements were made on a Rigaku AFC-5R diffractometer with graphite-monochromated MO Kα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 25 centered reflections in the range 22.11 < 2θ < 26.60° (M = Pd) or 27.19 < 2θ < 27.49° (M = Pt) corresponded to a monoclinic cell. The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The data and experimental conditions were as follows:

(M = Pd). The ω scan of several intense reflections, made prior to data collection, had an average width at half-height of 0.32° with a take-off angle of 6.0°. Scans of (1.10 + 0.35 tan θ)° were made at a speed of 10.0 deg/min (in ω). The intensities of three monitor reflections which were measured after every 150 reflections remained constant throughout the

data collection. Corrections for Lorentz and polarization effects were applied to the intensity data. The structure was solved by direct methods¹⁸ and expanded using Fourier techniques.¹⁹ Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. The final cycle of refinement was based on 4016 observed reflections (*I* > 3.00 σ(*I*)).

(M = Pt). The ω scan of several intense reflections, made prior to data collection, had an average width at half-height of 0.36° with a take-off angle of 6.0°. Scans of (1.52 + 0.35 tan θ)° were made at a speed of 10.0 deg/min (in ω). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout the data collection. Corrections for Lorentz and polarization effects were applied to the intensity data. The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically. The final cycle of refinement was based on 5665 observed reflections (*I* > 3.00σ(*I*)).

Fractional atomic coordinates for **1a** and **1b** are given in the Supporting Information.

Isotope Experiment for Investigation of the Mechanism of Generation of ODMM Complexes from 1a,b. A solution of 0.10 mmol of the complex **1a** or **1b** in 2 mL of THF was added to 1.5 mL of 0.1 N K¹⁸O (ca. 80% ¹⁸O-enriched)¹⁴ in 2-propanol. The mixture was stirred for 1 h at room temperature in an argon atmosphere. After removal of the solvent by evaporation, the resulting solid materials were washed with hexane and dried under reduced pressure to give ODMM complex **3a** or **3b**, respectively, as the sample for mass spectral analysis.

Since palladium and platinum each consist of a complicated isotope mixture, the ¹⁸O enrichments in **3a,b** were determined by comparing the intensity of the peaks in the [M + 1] vicinity. Natural abundance of ¹⁶O is more than 99%; thus, in the [M + 1] vicinity, a 100% ¹⁸O-labeled product is assumed to have peaks with an intensity pattern similar to that of the peaks of an unlabeled product (Table 4, from KOH), except that the peaks of the labeled product are shifted farther along the *m/e* axis by 2 units, due to the difference in the atomic weights of ¹⁸O and ¹⁶O (eq 3).

$$\left[\frac{\text{intensity of peak } (m/e) \text{ of } 100\% \text{ } ^{18}\text{O-labeled product}}{\text{intensity of peak } (m/e - 2) \text{ of unlabeled product}} \right] = \quad (3)$$

Here, the intensity pattern of peaks in the [M + 1] vicinity of the mass spectrum of a partially labeled product is simulated by adding fractions of the observed peak intensities of the unlabeled product and the estimated peak intensities of a 100% ¹⁸O-labeled product (eq 4; *N*% for an arbitrary enrichment level).

$$\left[\frac{\text{intensity of peak } (m/e) \text{ of } N\% \text{ } ^{18}\text{O-enriched product}}{\text{estimated intensity of peak } (m/e) \text{ of } 100\% \text{ } ^{18}\text{O-labeled product}} \times N\% + \frac{\text{intensity of peak } (m/e - 2) \text{ of unlabeled product}}{\text{intensity of peak } (m/e - 2) \text{ of unlabeled product}} \times (100 - N)\% \right] = \quad (4)$$

By trial and error, several intensity patterns of various ¹⁸O-enrichment levels were simulated, and their deviations from the observed pattern (Table 4, from K¹⁸OH) were calculated. From the intensity pattern with the least deviation, the most probable ¹⁸O-enrichment level was found to be 63% for M = Pd and 76% for M = Pt (Table 4).

Since the mass analysis method applied was FAB-MAS, besides the peaks of [M + 1], peaks of the [M] and [M – 1]

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ionization modes are also observed, although in small amount, depending on the sample and measurement conditions, causing a slight gap between the theoretical pattern and the actually observed pattern. MS spectra were measured on a JMS-DX303 mass spectrometer (JEOL Ltd., Tokyo, Japan). MS spectroscopic parameters: scan range, 20–2050; scan slope, 10 s; scan type, Mf, LI, UP, DA; ionization mode; Xe FAB; tic range, 50–2050; cycle time, 10 s; acceleration voltage, 3.0 kV/DAC; matrix, 3-NBA.

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Supporting Information Available: Tables of atomic coordinates and B_{eq} , anisotropic displacement parameters, bond lengths and bond angles, and least-squares planes for **1a,b** (40 pages). Ordering information is given on any current masthead page.

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