

# One-Step Synthesis of Oxodimethylenemethane–Transition Metal Complexes and Palladium-Catalyzed Cycloaddition Reaction

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Some alkyl allyl carbonates and an allylammonium chloride bearing (1-(butyloxy)ethyl)oxy group at the 2-position of the allyl group were synthesized and successfully transformed to oxodimethylenemethane–palladium and –platinum complexes in one step by mixing with a transition metal(0) and triphenylphosphine. On the basis of the confirmation of vinyl ether formation by <sup>1</sup>H NMR, the generation of oxodimethylenemethane complexes was rationalized to occur through abstraction of the β-hydrogen on the acetal carbon by an alkoxide ion which was generated from the allyl carbonate upon oxidative addition of the transition metal. The palladium-catalyzed cycloaddition of the acetonilidene group to strained olefins also proceeded successfully by using these alkyl allyl carbonates.

## Introduction

Synthetic equivalents of trimethylenemethane and its derivatives are of immense interest in cycloaddition reactions. Transition metal complexes of trimethylenemethane and its heteroatom analogs such as oxodimethylenemethane (ODMM)<sup>1–4</sup> or iminodimethylenemethane<sup>5,6</sup> are expected to exist in a variety of coordination modes, which have attracted much attention in the field of structural organometallic chemistry.<sup>1–9</sup> From a synthetic chemical viewpoint, the ODMM complex **3a** has been invoked as a transient intermediate in the palladium-catalyzed cyclopropanation of electron-rich strained olefins with 1-(acetyloxy)-3-(trimethylsilyl)-2-propanone.<sup>2</sup>

In a previous paper, a novel synthetic route to ODMM–palladium and –platinum complexes **3** via the unexpected carbon–oxygen bond cleavage of the ((methyloxy)methyl)oxy group attached to the π-allyl moiety of **2** at

the 2-position with hydroxide ion has been developed (Scheme 1).<sup>4</sup> This procedure required many steps to afford the ODMM complexes. Here we described the one-step synthesis of the complexes from alkyl allyl carbonates or an allylammonium chloride bearing a (1-(butyloxy)ethyl)oxy group at the 2-position of the allyl group. The palladium-catalyzed cycloaddition of an acetonilidene group to electron-rich strained olefins using the alkyl allyl carbonate is also described.

## Results and Discussion

The carbon–oxygen bond of an acetal moiety attached to π-allyl transition metal complexes **2** at the 2-position was cleaved by hydroxide ion to give ODMM complexes as shown in Scheme 1. This π-allyl palladium complex **2a**, however, was inert to methoxide ion for the same cleavage reaction. Thus, no ODMM complex **3a** was generated by added methoxide ion, while the platinum complex **2b** afforded complex **3b** by this treatment though in low yield. On the basis of these facts, the one-step synthesis of ODMM transition metal complexes was investigated for the purpose of developing a catalytic reaction system for the cycloaddition reaction.

In order to accomplish our goals, it was necessary to change the structure of the metal–π-allyl complex active toward the alkoxide ion. It is well-known that some alkyl allyl carbonates generate a π-allyl complex and an alkoxide ion upon oxidative addition of a metal(0);<sup>10,11</sup> therefore, for this purpose, we synthesized alkyl allyl carbonates **6a–c** and allyltrimethylammonium chloride **6d** from the corresponding allyl chloride as illustrated in Scheme 2.

As expected, the ODMM–palladium and –platinum complexes were obtained by only mixing allyl carbonate **6c** with the tetrakis(triphenylphosphine)metal complex in dichloromethane at room temperature. The yields were 58% and 87%, respectively. To determine the reaction conditions suitable for this one-step synthesis of the complexes **3**, all the prepared allyl carbonates and allylammonium chloride were transformed to ODMM

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(1) Trost, B. M.; Urabe, H. *Tetrahedron Lett.* **1990**, 131, 615. Inoue, Y.; Matsusita, K.; Yen, I.-F.; Imaizumi, S. *Chem. Lett.* **1991**, 1377. Ohe, K.; Matsuda, H.; Ishihara, T.; Ogosi, S.; Chatani, N.; Murai, S. *J. Org. Chem.* **1993**, 58, 1173. Kemmitt, R. D. W.; McKenna, P.; Russell, D. R.; Sherry, L. J. S. *J. Chem. Soc., Dalton Trans.* **1985**, 259. Imran, A.; Kemmitt, R. D. W.; Markwick, A. J. W.; McKenna, P.; Russell, D. R.; Sherry, L. J. S. *J. Chem. Soc., Dalton Trans.* **1985**, 549. Jones, M. D.; Kemmitt, R. D. W.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1986**, 427. Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, 112, 5670.

(2) Trost, B. M.; Schneider, S. *J. Am. Chem. Soc.* **1989**, 111, 4430.

(3) Fawcett, J.; Henderson, W.; Jones, M. D.; Kemmitt, R. D. W.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, 8, 1991.

(4) Ohsuka, A.; Fujimori, T.; Hirao, T.; Kurosawa, H.; Ikeda, I. *J. Chem. Soc., Chem. Commun.* **1993**, 1039.

(5) Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1990**, 112, 9646.

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

(7) Binger, P.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1977**, 16, 249. Binger, P.; Schuchardt, U. *Chem. Ber.* **1980**, 3334. Binger, P.; Schuchardt, U. *Chem. Ber.* **1981**, 3313. Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, 105, 2326. Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, 25, 5183. Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* **1985**, 107, 8277. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 1. Jones, M. D.; Kemmitt, R. D. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1201. Trost, B. M.; Seoane, P. R. *J. Am. Chem. Soc.* **1987**, 109, 615. Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, 109, 3483. Trost, B. M.; Grease, T. A.; Chan, D. M. T. *J. Am. Chem. Soc.* **1991**, 113, 7350. Trost, B. M.; Grease, T. A.; Chan, D. M. T. *J. Am. Chem. Soc.* **1991**, 113, 7363.

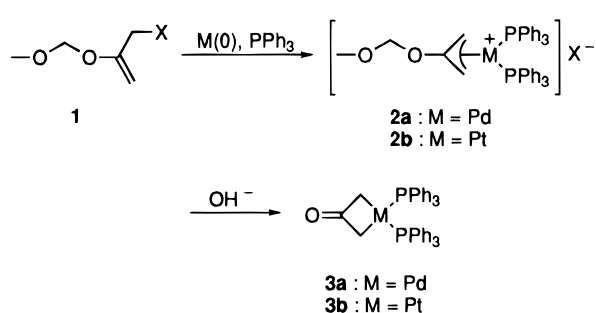
(8) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, 105, 2315.

(9) Ando, W.; Yamamoto, T.; Sasso, H.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, 113, 2791.

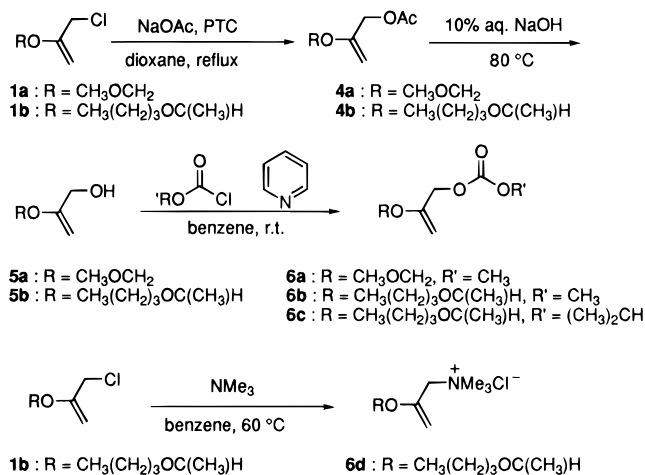
(10) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, 23, 4809.

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

## Scheme 1



## Scheme 2

Table 1. One-Step Synthesis of ODMM Complexes (**3**)

run	substrate	complex	solvent	yield (%) <sup>a</sup>
1	<b>6a</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	0
2	<b>6a</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	C <sub>6</sub> D <sub>6</sub>	0
3	<b>6b</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	59
4	<b>6b</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	CDCl <sub>3</sub>	45
5	<b>6b</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>3</sub> CN	3
6	<b>6b</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	C <sub>6</sub> D <sub>6</sub>	59
7	<b>6c</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	63
8	<b>6d</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	3
9	<b>6a</b>	Pt(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	33
10	<b>6b</b>	Pt(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	83
11	<b>6c</b>	Pt(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	87
12	<b>6d</b>	Pt(PPh <sub>3</sub> ) <sub>4</sub>	CD <sub>2</sub> Cl <sub>2</sub>	48

<sup>a</sup> By <sup>1</sup>H NMR.

complexes in some solvents by mixing with the tetrakis(triphenylphosphine)metal(0) complex in an NMR tube. The results obtained under the conditions described below are summarized in Table 1. Thus, allyl carbonate **6a–c** (0.01 mmol) or allyltrimethylammonium chloride **6d** (0.01 mmol) was mixed with the tetrakis(triphenylphosphine)palladium or -platinum complex (0.01 mmol) dissolved in organic solvent (0.5 mL) and stirred under an argon atmosphere at room temperature for 1 h. The yields of the ODMM complexes were determined by comparing the signal area of the methylene protons of the complex with all phenyl protons (for runs 1, 3, and 7–12) or 1,1,2,2-tetrachloroethane (added as internal standard, for runs 2 and 4–6) in the <sup>1</sup>H NMR spectra.

The platinum complex of ODMM (**3b**) was produced in a higher yield than the palladium complex (**3a**) from any starting allyl compounds. Carbonate **6a**, which has no β-hydrogen at the acetal moiety, gave no palladium complex end product (runs 1 and 2) or the end product of the platinum complex in a lower yield (run 9). Although the formation of the cationic palladium complex

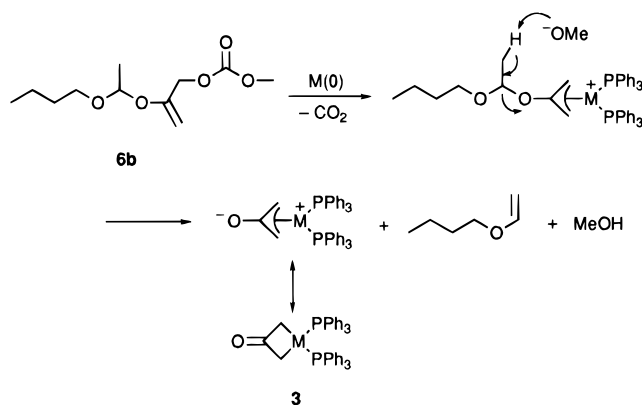
Figure 1. Generation mechanism of ODMM complexes (**3**).

Table 2. Palladium-Catalyzed Cycloaddition Reaction

olefin	product (yield %) <sup>a</sup>
	(71)  (12)
	(74)
	(46)

<sup>a</sup> By <sup>1</sup>H NMR.

**2a** starting from **6a** was confirmed in the <sup>1</sup>H NMR spectra, complex **2a** had no reactivity for transformation to the ODMM complex **3a** under the present conditions (runs 1 and 2). The ammonium chloride **6d** was also converted to the ODMM complex. However, the yields were not satisfactory, as the trimethylamine generated during the reaction was not strong enough to effect the β-elimination.

With respect to the effect of solvent on the yield, there was a slight difference except for CD<sub>3</sub>CN, in which the ODMM–palladium complex was generated in a very low yield, since this solvent has a low solubilization ability toward tetrakis(triphenylphosphine)palladium (run 5). Other solvents gave the palladium complex in good yield from **6b** (runs 3, 4, and 6).

A possible mechanism for this reaction is illustrated in Figure 1. During the first step of the reaction, the transition metal(0) oxidatively adds to the allyl carbonate, resulting in the formation of carbon dioxide and a π-allyl cationic complex paired with an alkoxide ion. A β-hydrogen at the acetal moiety is then abstracted by the thus generated alkoxide ion, resulting in the elimination of the π-allyl 2-oxide moiety complex, which is another canonical form of the ODMM complex **3**. The formation of the vinyl ether was confirmed in a separate <sup>1</sup>H NMR experiment.

We then considered that the procedure for the one-step synthesis of the ODMM complexes could be applied to the construction of a catalytic reaction system. Thus the reaction of carbonate **6b** with some olefins in the presence of a catalytic amount of a palladium(0) complex and triphenylphosphine at room temperature was studied (Table 2).

It has been reported that electron-poor olefins react with trimethylenemethane–Pd complexes generated *in*

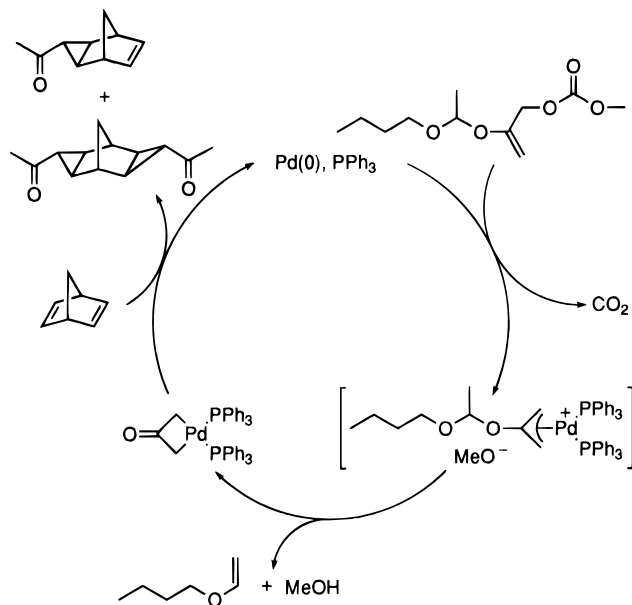


Figure 2. Catalytic cycle of the cycloaddition reaction.

*situ* to produce five-membered-ring compounds by [2 + 3] cycloaddition reactions in good yields.<sup>8</sup> But in the present catalytic reaction with **6b**, no product from the reaction with [3,2,1] and [3,1,1] strained bicyclic olefins and electron-poor olefins was found in their GC-mass spectra.<sup>12</sup> On the other hand, electron-rich strained olefins such as norbornadiene reacted with **6b** to give some products containing three-membered rings by [1 + 2] cycloaddition reactions in good yield (Table 2). Only these products have been catalytically prepared through the supposed intermediate of **3a** by Trost and co-workers.<sup>2</sup>

### Conclusion

ODMM-palladium and -platinum complexes were prepared in a one-step synthesis using alkyl allyl carbonates (**6b,c**) bearing an (1-(alkyloxy)ethyl)oxy group at the 2-position of the allyl moiety. A palladium-catalyzed cycloaddition reaction system forming acetylcyclopropane compounds was successfully constructed with these alkyl allyl carbonates, as shown in Figure 2. It is an important point for this synthetic method that the alkyl allyl carbonates **6b** and **6c** can be easily obtained in good yield from commercially available reagents.

### Experimental Section

**General Information.** Most of the commercially available reagents were used without further purification. Complexes Pd<sub>2</sub>(dba)<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, and Pt(PPh<sub>3</sub>)<sub>4</sub> were prepared according to the literature.<sup>13</sup> Solvents were dried and distilled under an argon atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 600.14 and 150.90 MHz with SiMe<sub>4</sub> (0.00 ppm) as the internal reference at 25 °C.

(12) Reactions with (*S*)-*cis*-verbenol, (1*S*)-(-)- $\beta$ -pinene, (1*R*)-(+)- $\alpha$ -pinene, 3,4-dichlorobicyclo[3.2.1]oct-2-ene, methyl acrylate, methyl *trans*-cinnamate, dimethyl maleate, acrylonitrile, and *trans*-cinnamaldehyde were tried under the same conditions mentioned in the text. However, none of these substrates gave any peak in the GC-mass spectrum except for the raw olefin.

(13) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253. Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121. Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* **1968**, *11*, 105.

(14) Ohsuka, A.; Hirao, T.; Kurosawa, H.; Ikeda, I. *Organometallics* **1995**, *14*, 2538.

**Preparation of 2-(Chloromethyl)-4-methyl-3,5-dioxanon-1-ene (1b).** Into a 300 mL round-bottomed flask fitted with a stopper carrying a glass tube reaching nearly to the bottom of the flask was placed 100 g (1.00 mol) of *n*-butyl vinyl ether. 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 allowed to run for about an extra 15 min to ensure the absorption of hydrogen chloride. Nitrogen gas was then bubbled through the glass tube for 15 min to evacuate the excess hydrogen chloride. The reaction mixture was slowly added to a solution of 92.5 g (1.00 mol) of epichlorohydrin and 2.64 g (0.01 mol) of dodecyltrimethylammonium chloride dissolved in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> under cooling in an ice bath. The mixture was then stirred for 1 h. After removal of the solvent by evaporation, the liquid material containing 1-chloro-2-(chloromethyl)-4-methyl-3,5-dioxanonane was extracted with 500 mL of ether and the dichloride was isolated by distillation (75 °C/0.2 mmHg). An aqueous solution of 50% NaOH (160 g, 2 mol) and tetra-*n*-butylammonium hydrogen sulfate (16.9 g, 0.05 mol) was added to the distillate of the dichloride and heated at 80 °C for 24 h. The reaction mixture was extracted with ether and the solvent removed by evaporation. The oily material was fractionally distilled to give **1b** (51 °C/0.7 mmHg): yield 109 g (57%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.92 (t, *J* = 7.4 Hz, 3H), 1.35–1.40 (m, 2H), 1.44 (d, *J* = 5.3 Hz, 3H), 1.54–1.59 (m, 2H), 3.44 (dt, *J* = 9.3, 6.7 Hz, 1H), 3.72 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.95 (d, *J* = 11.8 Hz, 1H), 3.98 (d, *J* = 11.8 Hz, 1H), 4.26 (d, *J* = 2.2 Hz, 1H), 4.38 (d, *J* = 2.2 Hz, 1H), 5.20 (q, *J* = 5.3 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.8, 19.2, 19.2, 31.5, 45.3, 65.8, 88.5, 98.9, 155.8; IR (neat) 2940, 1625 cm<sup>-1</sup>. Anal. Calcd for C<sub>9</sub>H<sub>17</sub>O<sub>2</sub>Cl: C, 56.10; H, 8.89; Cl, 18.40. Found: C, 55.88; H, 9.01; Cl, 18.20.

**Preparation of 4-Methyl-2-methylene-3,5-dioxanonyl Acetate (4b).** Sodium acetate (47.4 g, 0.58 mol) and tetra-*n*-butylammonium hydrogen sulfate (8.91 g, 0.026 mol) were added to 2-(chloromethyl)-4-methyl-3,5-dioxanon-1-ene (**1b**) (101 g, 0.52 mol) dissolved in 300 mL of 1,4-dioxane. The mixture was heated to reflux for 6 h. After removal of the solvent by evaporation, the generated solid materials were removed by filtration and the resulting oil was fractionally distilled to give **4b** (65 °C/0.6 mmHg): yield 79 g (70%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.92 (t, *J* = 7.7 Hz, 3H), 1.36 (m, 2H), 1.41 (d, *J* = 5.2 Hz, 3H), 2.09 (s, 3H), 3.41 (dt, *J* = 9.2, 6.8 Hz, 1H), 3.66 (dt, *J* = 9.2, 6.6 Hz, 1H), 4.24 (d, *J* = 1.9 Hz, 1H), 4.29 (d, *J* = 1.9 Hz, 1H), 4.49 (s, 1H), 5.19 (q, *J* = 5.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.1, 20.0, 18.7, 18.8, 31.1, 63.8, 65.0, 86.7, 98.0, 154.8, 169.3; IR (neat) 2945, 1740, 1640 cm<sup>-1</sup>. Anal. Calcd for C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>: C, 61.09; H, 9.32. Found: C, 61.60; H, 9.42.

**Preparation of 4-Methyl-2-methylene-3,5-dioxanonan-1-ol (5b).** An aqueous solution of 10% NaOH (213 g, 0.53 mol) and tetra-*n*-butylammonium hydrogen sulfate (6.02 g, 0.018 mol) was mixed with 4-methyl-2-methylene-3,5-dioxanonyl acetate (**4b**) (76.7 g, 0.35 mol) and then stirred at 80 °C for 1 h. After cooling, the suspension was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL  $\times$  2). The extracted oily material was fractionally distilled to give **5b** (53 °C/0.3 mmHg): yield 48 g (78%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.92 (t, *J* = 7.4 Hz, 3H), 1.38 (m, 2H), 1.42 (d, *J* = 5.2 Hz, 3H), 1.56 (m, 2H), 1.94 (br, 1H), 3.42 (dt, *J* = 9.3, 6.7 Hz, 1H), 3.66 (dt, *J* = 9.3, 6.6 Hz, 1H), 4.03 (s, 2H), 4.14 (d, *J* = 2.1 Hz, 1H), 4.27 (d, *J* = 2.1 Hz, 1H), 5.22 (q, *J* = 5.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.0, 18.6, 18.8, 31.0, 67.8, 69.3, 97.6, 99.1, 156.9; IR (neat) 3400, 2940, 1630 cm<sup>-1</sup>. Anal. Calcd for C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>: C, 62.04; H, 10.41. Found: C, 61.75; H, 10.60.

**Preparation of Methyl 4-Methyl-2-methylene-3,5-dioxanon-1-ol (5b).** 4-Methyl-2-methylene-3,5-dioxanon-1-ol (**5b**) (5.05 g, 29.0 mmol) was dissolved in a mixture of benzene (15 mL) and pyridine (10 mL) under an argon atmosphere. Methyl chlorocarbonate (2.67 g, 28.3 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred at the same temperature for 5 min. After removal of the low boiling point materials by evaporation, the precipitate formed was removed by filtration. The oily material was fractionally distilled to give **6b** (68 °C/0.2 mmHg): yield 3.9 g (59%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, *J* = 7.5 Hz, 3H), 1.35 (m,

2H), 1.41 (d,  $J = 5.5$  Hz, 3H), 1.54 (m, 2H), 3.40 (dt,  $J = 9.2$ , 6.6 Hz, 1H), 3.64 (dt,  $J = 9.2$ , 6.4 Hz, 1H), 3.79 (s, 3H), 4.27 (d,  $J = 2.2$  Hz, 1H), 4.33 (d,  $J = 2.2$  Hz, 1H), 4.53 (s, 2H), 5.18 (q,  $J = 5.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.6, 19.1, 19.1, 31.5, 54.7, 65.6, 67.6, 87.8, 98.5, 154.4, 155.4; IR (neat) 2890, 1720, 1635  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_5$ : C, 56.88; H, 8.68. Found: C, 57.13; H, 8.91.

**Preparation of Isopropyl 4-Methyl-2-methylene-3,5-dioxanon-1-ol (5b).** 4-Methyl-2-methylene-3,5-dioxanon-1-ol (**5b**) (4.76 g, 27.3 mmol) was dissolved in a mixture of benzene (15 mL) and pyridine (10 mL) under an argon atmosphere. Isopropyl chlorocarbonate (3.66 g, 27.3 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred at the same temperature for 5 min. After the same workup as that for **6b**, **6c** was isolated by fractional distillation (85 °C/0.3 mmHg): yield 3.5 g (49%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.91 (t,  $J = 7.5$  Hz, 3H), 1.36 (m, 2H), 1.41 (d,  $J = 5.3$  Hz, 3H), 1.55 (m, 2H), 3.41 (dt,  $J = 9.2$ , 6.7 Hz, 1H), 3.66 (dt,  $J = 9.2$ , 6.6 Hz, 1H), 4.27 (d,  $J = 2.3$  Hz, 1H), 4.33 (d,  $J = 2.3$  Hz, 1H), 4.52 (s, 2H), 4.89 (m, 1H), 5.19 (q,  $J = 5.2$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.6, 19.1, 19.2, 21.4, 31.6, 53.9, 65.5, 70.4, 89.1, 99.6, 154.0, 154.9; IR (neat) 2910, 1730, 1620  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{24}\text{O}_5$ : C, 58.04; H, 9.74. Found: C, 58.37; H, 9.61.

**Preparation of (4-Methyl-2-methylene-3,5-dioxanonyl)-trimethylammonium Chloride (6d).** A large excess amount of dry trimethylamine gas was condensed into the benzene (20 mL) solution of 2-(chloromethyl)-4-methyl-3,5-dioxanon-1-ene (**1b**) (4.10 g, 21.3 mmol) in a sealed tube, and the solution was heated at 60 °C for 12 h. The excess amine and the solvent were evaporated: yield 4.8 g (89%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.90 (t,  $J = 7.4$  Hz, 3H), 1.40 (m, 2H), 1.42 (d,  $J = 5.2$  Hz, 3H), 1.54 (m, 2H), 3.40 (dt,  $J = 9.0$ , 6.5 Hz, 1H), 3.50 (m, 9H), 3.58 (dt,  $J = 9.0$ , 6.4 Hz, 1H), 4.31 (d,  $J = 13.1$  Hz, 1H), 4.38 (d,  $J = 13.1$  Hz, 1H), 4.69 (d,  $J = 2.6$  Hz, 1H), 4.97 (d,  $J = 2.6$  Hz, 1H), 5.20 (q,  $J = 5.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  12.8, 18.2, 18.3, 30.5, 52.7, 65.1, 67.8, 97.1, 97.9, 148.3; IR (KBr) 2950, 1635  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{26}\text{O}_2\text{NCl}$ : C, 57.24; H, 10.41; N, 5.56; Cl, 14.08. Found: C, 57.34; H, 10.41; N, 5.36; Cl, 14.57.

**One-Step Preparation and Isolation of ODMM Complexes (3a,b).**<sup>14</sup> The allyl carbonate **6c** (0.60 mmol) was added to a  $\text{CH}_2\text{Cl}_2$  (10 mL) solution of  $\text{M}(\text{PPh}_3)_4$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) (0.50 mmol) at room temperature under an argon atmosphere. After 1 h, the solution was evaporated to dryness, and the residue was washed with hexane. The product was purified by recrystallization from dichloromethane/hexane.

ODMM palladium complex (**3a**): yellow powder; yield 199.2 mg (58%); mp 165 °C dec; IR  $\nu(\text{CO})$  1526  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.43 (s, br, 2H, *syn*- $\text{CH}_2$ ), 2.71 (s, br, 2H, *anti*- $\text{CH}_2$ ), 7.18–7.31 (m, 30H, Ph);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  58.8, 128.3, 129.9, 133.1, 133.9, 175.1.

ODMM platinum complex (**3b**): white powder; yield 337.4 mg (87%); mp 222 °C dec; IR  $\nu(\text{CO})$  1593  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

( $\text{CDCl}_3$ )  $\delta$  2.36 (d, 4H,  $J = 46.3$  Hz,  $\text{CH}_2$ ) 7.16–7.29 (m, 30H, Ph);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  51.0, 128.0, 130.0, 133.0, 134.0, 180.5.

**Comparison of Reaction Conditions for One-Step Preparation of ODMM Complexes (3a,b).** The allyl derivative (**6a–d**) and  $\text{M}(\text{PPh}_3)_4$  ( $\text{M} = \text{Pd}, \text{Pt}$ ), both 0.01 mmol, were dissolved in solvent (0.5 mL) in a NMR tube under an argon atmosphere. After 1 h, the yields of the ODMM complexes (**3a,b**) were calculated by comparing the signal areas of the methylene and phenyl protons (for runs 1, 3, and 7–12) or protons of 1,1,2,2-tetrachloroethane added (for runs 2 and 4–6) in the  $^1\text{H}$  NMR spectra.

ODMM palladium complex (**3a**):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  2.39 (br, 4H); ( $\text{CDCl}_3$ )  $\delta$  2.43 (br, 2H), 2.71 (br, 2H); ( $\text{CD}_3\text{CN}$ )  $\delta$  2.15 (br, 2H), 2.50 (br, 2H); ( $\text{C}_6\text{D}_6$ )  $\delta$  2.90 (br, 4H).

ODMM platinum complex (**3b**):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  2.19 (s,  $J = 48$  Hz, 4H).

**Palladium-Catalyzed Cycloaddition Reaction.**  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  (51 mg, 0.05 mmol) and  $\text{PPh}_3$  (26 mg, 0.10 mmol) were dissolved in 1.0 mL of  $\text{CH}_2\text{Cl}_2$  under an argon atmosphere. Carbonate **6b** (202 mg, 1.00 mmol) and substrate were added to the solution, and the mixture was stirred at room temperature. After 24 h, the solvent was removed by evaporation, and the residue was extracted with  $\text{CDCl}_3$ . The yield of product was calculated from the  $^1\text{H}$  NMR spectrum using 1,1,2,2-tetrachloroethane added as an internal standard.

**Reaction with Norbornadiene. 3-Acetyltricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene:**<sup>2</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.03 (dm,  $J = 9.9$  Hz, 1H), 1.18 (dm,  $J = 9.9$  Hz, 1H), 1.67 (m, 2H), 2.19 (s, 3H), 2.86 (t,  $J = 2.2$  Hz, 1H), 2.92 (m, 2H), 6.41 (m, 2H). **3,7-Diacetyltetracyclo[3.3.1.0<sup>2,4</sup>.0<sup>6,8</sup>]nonane:**<sup>2</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.55 (m, 2H), 2.31 (m, 2H), 2.17 (s, 6H), 1.69 (m, 4H), 0.57 (m, 2H).

**Reaction with Norbornene. 3-Acetyltricyclo[3.2.1.0<sup>2,4</sup>]octane:**<sup>2</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.62 (dm,  $J = 10.9$  Hz, 1H), 0.86 (dm,  $J = 10.9$  Hz, 1H), 1.20–1.40 (m, 4H), 1.29 (m, 2H), 1.80 (m, 1H), 2.11 (s, 3H), 2.27 (m, 2H).

**Reaction with Dicyclopentadiene. 9-Acetyltetracyclo[5.3.1.0<sup>2,6</sup>.0<sup>8,10</sup>]undec-3-ene:**<sup>2</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.94 (dm,  $J = 10.6$  Hz, 1H), 1.08 (dm,  $J = 10.6$  Hz, 1H), 1.23 (dm,  $J = 7.0$  Hz, 1H), 1.52 (dm,  $J = 7.0$  Hz, 1H), 1.96 (m, 1H), 2.15–2.35 (m, 3H), 2.16 (s, 3H), 2.42 (m, 1H), 2.57 (m, 1H), 3.10 (m, 1H), 5.54 (dm,  $J = 5.8$  Hz, 1H), 5.73 (dm,  $J = 5.8$  Hz, 1H).

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