

Reactions of Hydrido(hydrosilylene)tungsten Complexes with  $\alpha,\beta$ -Unsaturated Carbonyl Compounds: Selective Formation of ( $\eta^3$ -Siloxyallyl)tungsten Complexes

Takahito Watanabe, Hisako Hashimoto,\* and Hiromi Tobita\*

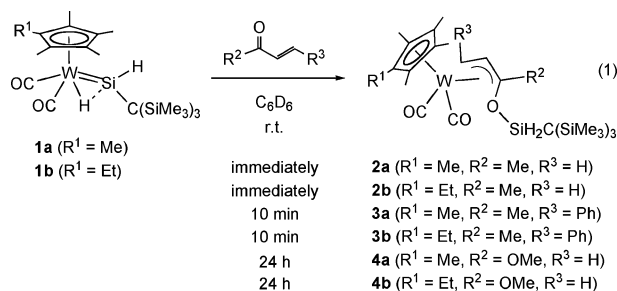
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Received July 9, 2007; E-mail: tobita@mail.tains.tohoku.ac.jp

In contrast to that of transition-metal carbene complexes, the development of transition-metal silylene complexes has been slow. Earlier studies on such silylene complexes have concentrated on their syntheses, structures, and fundamental reactions with simple nucleophiles.<sup>1</sup> Recently, because of improved synthetic methodologies, a new stage in the development of silylene complexes has opened.<sup>2–5</sup> For example, a cationic silylene–ruthenium complex has been found to react with enolizable ketones to afford silyl enol ethers.<sup>2</sup> Some silylene complexes, through their M–Si double bonds, can undergo [2+2] cycloaddition reactions with isocyanates.<sup>3</sup> Examples of stoichiometric and catalytic hydrosilylations of alkenes and carbonyl compounds using silylene complexes have also been demonstrated.<sup>4</sup> However, [2+4] cycloaddition reactions involving silylene complexes have yet to be reported.

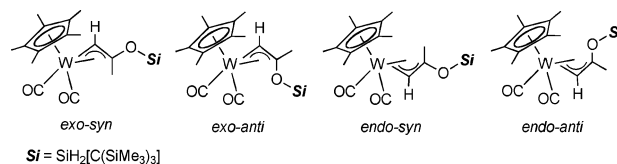
Recently, we have found the stoichiometric hydrosilylation reactions of acetone<sup>5a</sup> and nitriles<sup>5b</sup> with neutral hydrido(hydrosilylene)tungsten complexes, Cp\*(CO)<sub>2</sub>(H)W=Si(H)[C(SiMe<sub>3</sub>)<sub>3</sub>] (**1a**, Cp' = Cp\*; **1b**, Cp' =  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et). Herein, we report on the new and unique reactions of **1** with  $\alpha,\beta$ -unsaturated carbonyl compounds to afford  $\eta^3$ -siloxyallyl complexes. These reactions are highly regioselective, nearly quantitative, and, presumably, proceed via a [2+4] cycloaddition reaction as the main process.

Treatment of hydrido(hydrosilylene)tungsten complex **1a** with methyl vinyl ketone at room temperature resulted in the immediate and quantitative formation of  $\eta^3$ -siloxyallyl complex Cp\*(CO)<sub>2</sub>W-[ $\eta^3$ -H<sub>2</sub>CCHCMeOSiH<sub>2</sub>{C(SiMe<sub>3</sub>)<sub>3</sub>}] (**2a**) as the sole product (eq 1).<sup>6,7</sup> Similarly, the  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et analogue, **2b**, was obtained by the reaction of **1b** with methyl vinyl ketone.<sup>6</sup> Transformations of such silylene complexes into the corresponding  $\eta^3$ -allyl complexes have yet to be reported.



Our synthetic scheme was subsequently applied to other  $\alpha,\beta$ -unsaturated carbonyl compounds. The reaction of **1a** with benzylideneacetone was complete within 10 min to afford Cp\*(CO)<sub>2</sub>W-[ $\eta^3$ -PhCHCMeOSiH<sub>2</sub>{C(SiMe<sub>3</sub>)<sub>3</sub>}] (**3a**) in 81% isolated yield. The reaction of **1a** with methyl acrylate required more time (24 h) to afford Cp\*(CO)<sub>2</sub>W-[ $\eta^3$ -H<sub>2</sub>CCHC(OMe)OSiH<sub>2</sub>{C(SiMe<sub>3</sub>)<sub>3</sub>}] (**4a**) in 82% yield (eq 2). The  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et analogues **3b** and **4b** were similarly obtained.<sup>6</sup> In contrast to the linear  $\alpha,\beta$ -unsaturated

Chart 1

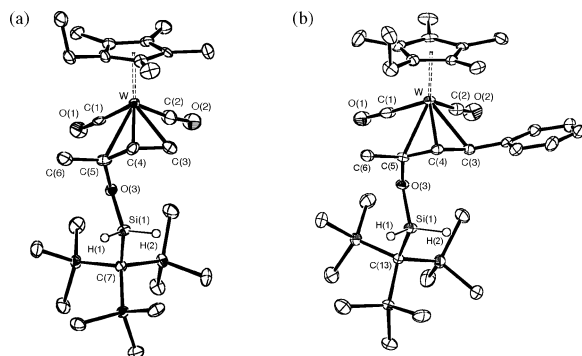


carbonyl compounds, the reaction of **1a** with cyclohex-2-en-1-one, a cyclic derivative, resulted in a complicated mixture of unidentified products.

All  $\eta^3$ -siloxyallyl products were fully characterized using <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy and elemental analysis.<sup>6</sup> Existence of the  $\eta^3$ -siloxyallyl ligands was indicated by the <sup>1</sup>H NMR spectra. In the case of **2a**, the three <sup>1</sup>H signals in the vicinity of 2 ppm were assigned to the central methine proton ( $\delta$  = 2.08 ppm) and to the terminal methylene protons ( $\delta$  = 1.47 and 2.40 ppm), and were confirmed using <sup>13</sup>C{<sup>1</sup>H}-<sup>1</sup>H COSY NMR experiments.<sup>6</sup> The two doublet signals, with AB pattern, at  $\delta$  = 4.93 and 5.02 ppm (<sup>2</sup>J<sub>HH</sub> = 16.5 Hz) were assigned to the diastereotopic Si–H protons on the siloxy group. The <sup>29</sup>Si NMR spectrum of **2a** exhibited signals for the siloxy ( $\delta$  = –19.9) and the silyl ( $\delta$  = –0.7) groups. Importantly, in all cases, the formation of a single isomer was observed among four possible isomers, the syn and anti geometrical isomers of the siloxy group in the  $\eta^3$ -allyl ligand and their exo and endo rotomers, as shown in Chart 1.<sup>8</sup>

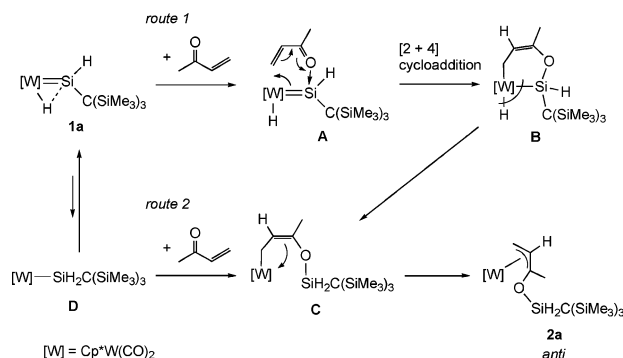
Structural analysis using X-ray crystallography was employed to determine the stereochemistries of  $\eta^3$ -siloxyallyl complexes **2b**, **3b**, and **4b**.<sup>9</sup> The results indicated that the three complexes have identical stereochemistries<sup>6</sup> (ORTEP drawings of **2b** and **3b** are shown in Figure 1), and possess the exo-anti configuration as illustrated in Chart 1. For all three complexes, the C–C bond between the three allyl carbons [1.405(11)–1.444(10) Å] are shorter than the C–C single bond of ethane (1.54 Å) but longer than the C–C double bond of ethene (1.34 Å), thus supporting their  $\eta^3$ -allyl coordination mode. In all cases, the W–C(5) bond is longer than the W–C(3) and W–C(4) bonds, which can be attributed to the steric repulsion between the carbonyl ligand and the oxygen atom of the siloxy group.

All three  $\eta^3$ -siloxyallyl complexes are suggested to take the exo-anti configuration also in solution, because steric repulsion between the large siloxy and Cp\* groups is likely to prevent the formation of other isomers according to the X-ray structures. Similarities between the <sup>1</sup>H NMR spectra of the Cp\* and the  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et analogues (Table S1, in the Supporting Information) further indicate that **2a**, **3a**, and **4a** possess the same exo-anti configuration.<sup>6</sup> Interestingly, the anti selectivity of our methodology is opposite to the syn selectivity for the formation of structurally related Tp-(CO)<sub>2</sub>Mo[ $\eta^3$ -H<sub>2</sub>CCHCMeOSiBuMe<sub>2</sub>] [Tp = tris-1-(pyrazolyl)-borate],<sup>10</sup> which was obtained using a significantly different route



**Figure 1.** ORTEP drawings of **2b** (a) and **3b** (b) showing 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg). **2b**: W–C(1), 1.966(7); W–C(2), 1.941(7); W–C(3), 2.298(8); W–C(4), 2.223(7); W–C(5), 2.412(6); C(3)–C(4), 1.427(10); C(4)–C(5), 1.444(10); C(5)–O(3), 1.414(8); O(3)–Si(1), 1.650(6). **3b**: W–C(1), 1.951(5); W–C(2), 1.941(5); W–C(3), 2.343(4); W–C(4), 2.215(4); W–C(5), 2.376(4); C(3)–C(4), 1.418(6); C(4)–C(5), 1.434(6); C(5)–O(3), 1.421(5); O(3)–Si(1), 1.661(3).

#### Scheme 1. Possible Reaction Mechanisms



involving the reaction between (DMF)<sub>3</sub>Mo(CO)<sub>3</sub> and methyl vinyl ketone, followed by the addition of <sup>t</sup>BuMeSiCl and KTp.

Two most possible reaction mechanisms that explain the high stereoselective formation of the anti- $\eta^3$ -siloxyallyl complex are illustrated in Scheme 1. In route 1, the enone is coordinated to the silicon atom of the silylene ligand of **1a** by the carbonyl oxygen atom to form intermediate **A**, which undergoes a [2+4] cycloaddition via a six-membered transition state to give intermediate **B**. Subsequently, **B** undergoes a Si–H reductive elimination to form 16-electron  $\eta^1$ -allyl intermediate **C**, which is then saturated via coordination of the intramolecular C–C double bond, followed by rearrangement to form anti- $\eta^3$ -siloxyallyl complex **2a**. In route 2, the 16-electron silyl complex **D**, which is formed from **1a** by a 1,2-hydrogen migration from W to Si, reacts with the enone to afford **C**, which then rearranges to **2a**.

Murai et al. have previously reported on the reaction between silyl complex (CO)<sub>4</sub>CoSiMe<sub>3</sub> and methyl vinyl ketone to give (CO)<sub>3</sub>Co[ $\eta^3$ -H<sub>2</sub>CCHCMeOSiMe<sub>3</sub>] as a mixture of the syn and anti isomers (syn, 12% yield; anti, 46% yield). For reactions with other  $\alpha,\beta$ -unsaturated carbonyl compounds, the syn/anti selectivity greatly depends on the substituents. Because details of the mechanism remain unclear,<sup>11</sup> it is difficult to select route 2 (via silyl intermediate **D**) as the only mechanism to describe the formation of the anti isomer. In our opinion, route 1 is more likely, not only because of the exclusive formation of the anti isomer, but also because of the

unsuccessful formation of the  $\eta^3$ -siloxyallyl complex using **1a** and cyclohex-2-en-1-one, which does not allow the *s-cis* conformation required for the [2+4] cycloaddition. Although direct observation of **A** has yet to be achieved, there is evidence that indicates the interaction between the oxygen atom of a ketone with the silylene silicon atom of **1a**. Treatment of **1a** with acetone at 250 K resulted in the formation of Cp\*(CO)<sub>2</sub>(H)<sub>2</sub>WSi(H)[OC(Me)=CH<sub>2</sub>][C(SiMe<sub>3</sub>)<sub>3</sub>] (**5**),<sup>12</sup> via coordination of the oxygen atom of acetone to the silylene silicon, followed by the  $\alpha$ -H migration to W, although **5** is transformed into the hydrosilylation product upon warming to room temperature.<sup>5a</sup> This would support that **A** is a key intermediate of route 1 (Scheme 1).<sup>13</sup>

**Acknowledgment.** This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [Grants-in-Aid for Scientific Research Nos. 18350027, 18064003, 16750044, 19550056, and 19029003].

**Supporting Information Available:** Experimental procedures and characterization data; X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### References

- (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 24. (b) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds Vol. 2*; Rappaport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Chapter 35. (c) Ogino, H. *Chem. Rec.* **2002**, 2, 291. (d) Okazaki, M.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **2003**, 493. (e) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, 500, 21. (f) Braunstein, P.; Knorr, M.; Stern, C. *Coord. Chem. Rev.* **1998**, 178–180, 903.
- Zhang, C.; Grubbs, S. D.; Tilley, T. D. *Polyhedron* **1991**, 10, 1173.
- Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, 119, 11236.
- (a) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, 21, 4065. (b) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, 21, 4648. (c) Glaser, P. J.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, 125, 13640.
- (a) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, 43, 218. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. *J. Am. Chem. Soc.* **2006**, 128, 2176.
- See the Supporting Information for details.
- 2a**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.33 (s, 27H, SiMe), 1.47 (dd, 1H,  $\eta^3$ -H<sub>2</sub>CCHCMe, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 1.55 (s, 15H, C<sub>3</sub>Me<sub>3</sub>), 2.08 (dd, 1H,  $\eta^3$ -H<sub>2</sub>CCHCMe, <sup>3</sup>J<sub>HH</sub> = 9.1 Hz, <sup>2</sup>J<sub>HH</sub> = 6.9 Hz), 2.19 (s, 3H,  $\eta^3$ -H<sub>2</sub>CCHCMe), 2.40 (dd, 1H,  $\eta^3$ -H<sub>2</sub>CCHCMe, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, <sup>3</sup>J<sub>HH</sub> = 9.1 Hz), 4.93 (d, 1H, SiH, <sup>2</sup>J<sub>HH</sub> = 16.5 Hz), 5.02 (d, 1H, SiH, <sup>2</sup>J<sub>HH</sub> = 16.5 Hz).
- For the definition of exo and anti isomers of  $\eta^3$ -allyl complexes, see: Ariafard, A.; Lin, Z. *Organometallics* **2005**, 24, 3800.
- Crystal data (150 K) for **2b**: C<sub>27</sub>H<sub>52</sub>O<sub>3</sub>Si<sub>4</sub>W; fw = 720.90; orthorhombic; space group Pna2<sub>1</sub> (No. 33); *a* = 13.8869(4) Å, *b* = 8.9296(4) Å, *c* = 26.3746(8) Å, *V* = 3270.6(2) Å<sup>3</sup>, density (calcd) 1.464 Mg/m<sup>3</sup>, *Z* = 4. Final *R* indices *R* = 0.0374, *R*<sub>w</sub> = 0.0851 for all data, 6991 unique reflections. **3b**: C<sub>33</sub>H<sub>56</sub>O<sub>3</sub>Si<sub>4</sub>W; fw = 796.99; monoclinic; space group P2<sub>1</sub>/c (No. 14); *a* = 8.2146(4) Å, *b* = 31.6002(11) Å, *c* = 14.2624(3) Å,  $\beta$  = 89.5622(18)°, *V* = 3702.2(2) Å<sup>3</sup>, density (calcd) 1.430 Mg/m<sup>3</sup>, *Z* = 4. Final *R* indices *R* = 0.0469, *R*<sub>w</sub> = 0.1052 for all data, 8186 unique reflections. For the data of **4b**, see the Supporting Information. Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 608679 for **2b**, No. 608680 for **3b**, and No. 608681 for **4b**).
- Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *Organometallics* **1996**, 15, 4201.
- Chatani, N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, 24, 5649.
- Complex **5** was not isolable but characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR data (250 K).<sup>6</sup>
- Besides the mechanisms described in Scheme 1, the possibility of the [2+2] cycloaddition mechanism suggested by a reviewer cannot be ruled out. But we think at present that the mechanisms described in Scheme 1 are more preferable, because the [2+2] cycloaddition mechanism cannot fully explain the absolute anti selectivity of the products.

JA074629E