

# Hydrosilylation and double silylation of carbonyl compounds with 1,1'-bis(dimethylsilyl)ferrocene using nickel- and platinum-catalysts

Young Kun Kong,<sup>a,\*</sup> Jinsik Kim,<sup>a</sup> Sungkeun Choi<sup>a</sup> and Seok-Bong Choi<sup>b</sup>

<sup>a</sup>Department of Chemistry, Kyonggi University, Suwon, Kyonggido 440-760, Republic of Korea

<sup>b</sup>Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota 58105, USA

Received 1 October 2006; revised 18 December 2006; accepted 3 January 2007

Available online 7 January 2007

**Abstract**—A series of ferrocene-based organosilicon compounds have been prepared via hydrosilylation or double silylation of carbonyl compounds with 1,1'-bis(dimethylsilyl)ferrocene using  $(C_2H_4)Pt(PPh_3)_2$  or  $Ni(PEt_3)_4$  catalysts. In general, while the platinum catalyst  $(C_2H_4)Pt(PPh_3)_2$  preferentially produced cyclic double-silylated products, the  $Ni(PEt_3)_4$  catalyst led to the hydrosilylated ferrocene products from aldehydes or ketones.

© 2007 Elsevier Ltd. All rights reserved.

## 1. Introduction

Recent discoveries in a broad range of applications such as electrical, magnetic, optical, biomedical, coatings, aerospace, and catalysis greatly increased the interest in the incorporation of transition metals into organic monomers and polymers.<sup>1,2</sup> The catalytically facilitated addition of Si–H bond into unsaturated organic substrates has a long history as a major synthetic tool for the formation of organosilicon materials.<sup>3</sup> However, in contrast to well established hydrosilylation reaction, the dehydrogenative double silylation of carbonyls has seen little development even though it has shown importance for the formation of tailored molecular architectures.<sup>4</sup>

We have demonstrated that the platinum and nickel complexes,  $(C_2H_4)Pt(PPh_3)_2$  and  $Ni(PEt_3)_4$ , are efficient catalysts not only for hydrosilylation, but also for dehydrogenative double silylation of unsaturated organic functionalities such as acetylenes, olefins, dienes, enones, and nitriles with 1,2-bis(dimethylsilyl)carborane.<sup>5</sup> In addition, we found that the platinum and nickel catalyst exhibit differences in catalytic activity depending on the type of silanes and on the type of unsaturated organics used in the reaction. In order to extend this research to

organometallic substrates instead of the previously studied benzene<sup>4</sup> or carborane<sup>5</sup> substrates, here we report the reaction of 1,1'-bis(dimethylsilyl)ferrocene with aldehydes and ketones in the presence of platinum or nickel catalysts to give new types of organosilylferrocene derivatives. To our knowledge, this is a first example of the dehydrogenative double silylation reaction leading to products containing a transition metal. In a typical experiment, the starting material 1,1'-bis(dimethylsilyl)ferrocene<sup>6</sup> and the platinum<sup>7</sup> and nickel<sup>8</sup> catalyst complex were prepared according to methods previously published.

## 2. Platinum catalyst $(C_2H_4)Pt(PPh_3)_2$

The reactions of 1,1'-bis(dimethylsilyl)ferrocene with aldehydes (1:1.0–1.58 mmol ratio) in the presence of a catalytic amount of  $(C_2H_4)Pt(PPh_3)_2$  are summarized in Table 1. The products obtained were purified by chromatography and/or fractional distillation and their structure were determined by <sup>1</sup>H and <sup>13</sup>C NMR, FT-IR, and GC–MS. For example, the mixture of benzaldehyde (1.86 mmol), 1,1'-bis(dimethylsilyl)ferrocene (1.18 mmol) and  $(C_2H_4)Pt(PPh_3)_2$  (0.074 mmol) in toluene 15 mL was stirred at 80 °C for 2 h. The mixture was treated with a short silica gel column to remove the platinum catalyst from the reaction mixture. The solution was chromatographed using benzene/hexane (1:1) as the eluant ( $R_f = 0.45$ ). The oily dark red liquid was obtained in the yield of 70%.

**Keywords:** Hydrosilylation; Dehydrogenative double silylation; Catalyst; Ferrocene; Silane.

\* Corresponding author. Tel.: +1 82 31 249 9635; fax: +1 82 31 258 4845; e-mail: [ykkong@kyonggi.ac.kr](mailto:ykkong@kyonggi.ac.kr)

**Table 1.** The platinum complex  $(C_2H_4)Pt(PPh_3)_2$  catalyzed dehydrogenative double silylation of carbonyls

	Substrates	Products	Reaction			Yield <sup>b</sup> (%)
			Ratio <sup>a</sup>	Temperature °C	Time (h)	
1			1.58	80	2	70
2			1.0	110	16	75
3			1.25	80	2	55
4			1.54	80	2	80

<sup>a</sup> Ratio of aldehydes versus 1,1'-bis(dimethylsilyl)ferrocene used.

<sup>b</sup> Isolation yield after column chromatography.

The key feature for the formation of cyclic product in <sup>1</sup>H NMR spectrum includes complete disappearance of Si–H peak and aldehyde peak H–C=O (4.6<sup>1(a)</sup> and 9.48 ppm respectively) and appearance of new peak at 4.89 ppm assigned the O–C–H proton. A significant chemical shift of aldehyde in <sup>13</sup>C NMR resonance from 205.83 ppm to 68.46 ppm is, also, a clear evidence for a single bond formation of C–O from the C=O double bond of aldehyde.

In contrast to the double silylation of the above carbonyls, **1–3**, when isobutyraldehyde **4** was employed in the reaction under the same conditions, non-cyclic hydrosilylated product was isolated as a dark red liquid instead of the cyclic bis(silyl)ferrocene. Overall, despite the fact that we previously reported that the platinum complex  $(C_2H_4)Pt(PPh_3)_2$  has no catalytic activity for 1,2-double silylation with aldehydes when 1,2-bis(dimethylsilyl)carborane is used,<sup>9</sup> we found that the platinum complex  $(C_2H_4)Pt(PPh_3)_2$  is active for either the 1,2-double silylation of aldehydes as well as hydrosilylation, depending on the aldehyde reactant, when 1,1'-bis(dimethylsilyl)ferrocene is used.

### 3. Nickel catalyst Ni(PEt<sub>3</sub>)<sub>4</sub>

In general, all synthetic processes, purification methods, and characterization methods were identical except the use of the Ni catalyst. The results for the reactions involving Ni(PEt<sub>3</sub>)<sub>4</sub> catalyst are summarized in Table

**2.** In contrast to the reaction products obtained using the Pt catalyst, the reaction of 1,1'-bis(dimethylsilyl)ferrocene (1.48 mmol) with aldehydes or ketones (1.1–1.78 mmol) in the presence of a catalytic amount tetrakis(triethyl-phosphino)nickel produced linear products instead of cyclic compounds. This is confirmed by the existence of Si–H peak at 4.3–4.7 ppm from the <sup>1</sup>H NMR spectrum as well as a peak at around 2100 cm<sup>-1</sup> in the FT-IR spectrum. As an example, the mixture of 1,1'-bis(dimethylsilyl)ferrocene (1.18 mmol), phenylaldehyde (1.91 mmol), and Ni(PEt<sub>3</sub>)<sub>4</sub> (0.074 mmol) in 15 mL of toluene was heated to 80 °C for 14 h. After removal of the residual nickel catalyst using a silica column and following fractional column chromatography (benzene:hexane = 1:1), the product was obtained as a dark red oily liquid in a 75% yield.

In conclusion, a series of ferrocene-based organosilicon compounds have been prepared via dehydrogenative double silylation and hydrosilylation of carbonyl compounds with 1,1'-bis(dimethylsilyl)ferrocene using  $(C_2H_4)Pt(PPh_3)_2$  and Ni(PEt<sub>3</sub>)<sub>4</sub>. The structures of products were identified using <sup>1</sup>H, and <sup>13</sup>C NMR spectroscopy, FT-IR, X-ray crystallography, and gas chromatography–mass spectrometry. Our results indicate that both platinum and nickel catalysts are capable of catalytic activity for either dehydrogenative double silylation or hydrosilylation with distinctive discrimination against the type of carbonyls when 1,1'-bis(dimethylsilyl)ferrocene is used. Thus, while the platinum catalyst favors dehydrogenative silylation to make cyclic

**Table 2.** Nickel catalyzed hydrosilylation of carbonyl compounds

Entry	Substrate	Products	Reaction			Yield <sup>b</sup> (%)
			Ratio <sup>a</sup>	Temperature (°C)	Time (h)	
1			1.62	80	14	75
2			1.21	80	16	40
3			1.10	110	14	45
4			1.45	80	14	60
5			1.78	80	14	60

<sup>a</sup> Ratio of aldehydes versus 1,1'-bis(dimethylsilyl)ferrocene used.

<sup>b</sup> Isolation yield after column chromatography.

organosilyl-ferrocenes, use of the nickel catalyst led exclusively to the linear products through hydrosilylation process. We anticipate future studies involving the systematic variation of dihydrosilanes containing two adjacent Si-H functional groups ( $\text{HSiR}_2 - \text{R}^2 - \text{SiR}_2\text{H}$ ) and unsaturated organic functional groups to add essential background knowledge for the design of tailored molecular structures in polymer and material chemistry.

### Acknowledgments

This work was supported by the fund from the Korea Science and Engineering Foundation (KOSEF, Grant R01-2001-00053). The useful discussions from Philip Boudjouk are gratefully acknowledged.

### Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2007.01.009](https://doi.org/10.1016/j.tetlet.2007.01.009).

### References and notes

- (a) Itazaki, M.; Kitami, O.; Tanabe, M.; Nishihara, Y.; Osakada, K. *J. Organomet. Chem.* **2005**, *690*, 3957; (b) Manners, I. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 179; (c) Gates, D. P. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2002**, *98*, 479; (d) Archer, R. D. *Inorganic and Organometallic Polymers*; Wiley-VCH: Weinheim, 2001; (e) Nishihara, H.; Nalwa, H. S. In *Handbook of Organic Conductive Molecules and Polymers*; John Wiley & Sons: New York, 1997; *2*, p 799.
- (a) Hudson, R. D. A. *J. Organomet. Chem.* **2001**, *637–639*, 47–69, and references cited therein; (b) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G. *Adv. Organomet. Chem.* **1998**, *42*, 291; (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1996**, *88*, 201; (d) Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270.
- (a) Nishiyama, H. In *Comprehensive Asymmetric Catalysis I–III*; Jacobsen, E., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; *1*, p 267; (b) Brunner, H. In Beller, M., Bolm, C., Eds. *Trans. Met. Org. Synth.* **1998**, *2*, 131; (c) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994, p 124; (d) Brunner, H.; Nishiyama, H.; Itoh, K. In *Catalytic Asymmetric synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 303; (e) Ojima, I. In *The Chemistry of Silicon Compounds*; Patai, S., Ed.; Wiley: New York, 1989; p 1479.
- (a) Phan, S. T.; Lim, W. C.; Han, J. S.; Yoo, B. R.; Jung, I. N. *Organometallics* **2004**, *23*, 169–171; (b) Hodgson, D. M.; Kirton, E. H. M. *Synth. Lett.* **2004**, *9*, 1610–1612; (c) Takaki, K.; Sonoda, K.; Kousaka, T.; Koshiji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 9211–9214; (d) Tishkov, A. A.; Lyapkalo, I. M.; Ioffe, S. L.; Strelenko, Y. A.; Tartakovskiy, V. A. *Tetrahedron* **2001**, *57*, 2221–2230; (e) Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, *39*, 9697–9698; (f) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853–2856; (g)

- Uchimaru, Y.; Lautenschlager, H. J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639–2643, and references cited therein; (h) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H. J. *J. Organomet. Chem.* **1992**, *428*, 1–12; (i) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280–281; (j) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, *3*, 467.
5. (a) Kong, Y. K.; Lee, J. *J. Korean Chem. Soc.* **2002**, *46*, 139–144; (b) Kim, J.; Kang, Y.; Lee, J.; Kong, Y. K.; Gong, M. S.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 937; (c) Kang, Y.; Kim, J.; Kong, Y. K.; Lee, J.; Lee, S. W.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 5026; (d) Kang, Y.; Kang, S. O.; Ko, J.; Lee, J.; Kong, Y. K. *Chem. Commun.* **1998**, *21*, 2343–2344.
  6. Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.
  7. Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119.
  8. Browning, J.; Cundy, C. S.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 20.
  9. Kang, Y.; Kim, J.; Kong, Y. K.; Lee, J.; Lee, S. W.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 5026.