ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 617–618 (2001) 741–743

Journal of Organo metallic Chemistry

Communication

Reactions of silyl-substituted Fischer-type carbene complexes with silanes

Nobuharu Iwasawa [a,*], Masatoshi Saitou [b], Hiroyuki Kusama [a]

[a] *Department of Chemistry, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan*
[b] *Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received 2 August 2000; accepted 28 September 2000

Abstract

Silyl-substituted Fischer-type carbene complexes show unique behavior when treated with silanes. In toluene, all three kinds (Cr, Mo, W) of methyldiphenylsilyl-substituted carbene complex react with silanes to give direct insertion products in moderate to high yield. On the other hand, the reactions in THF give different kinds of product depending on the center metal. Thus, in addition to the direct insertion products (Mo), novel reduction-insertion (W) and reduction-carbonyl insertion-silicon migration (Cr) products are obtained in good yields. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silyl-substituted Fischer-type carbene complexes; Insertion; Silane reduction; Carbonyl insertion; Silicon migration

1. Introduction

The insertion reaction of the Fischer-type carbene complexes of Group 6 metals into Si–H bonds is a well-known process, and sometimes gives synthetically useful silylated compounds [1–8]. For example, Chan et al. have reported that reaction of α,β-unsaturated carbene complexes with triethylsilane gives allylmethoxysilane derivatives in good yields [4,5]. However, although silanes are reductants, there are no reports of hydride-reduction reactions of silanes with such Fischer-type carbene complexes[1,2].

During a study of the chemistry of silyl-substituted Fischer-type carbene complexes of Group 6 metals [10], interesting behavior was observed in their reaction with silanes. In this paper, we report the silane-induced transformation of silyl-substituted carbene complexes into three types of product depending on the solvent and the center metal of the complex employed.

2. Results and discussion

Three kinds (Cr, Mo, W) of methyldiphenylsilyl-substituted carbene complex **1** were prepared based on literature procedures [11,12], and the reaction of these complexes with dimethylphenylsilane was examined.

When each of the three kinds of silyl carbene complex **1** (M = Cr, Mo, W) was treated with 1.5 molar amounts of dimethylphenylsilane in toluene, the reactions of the chromium and molybdenum complexes proceeded at room temperature.[3] While the reaction of the chromium complex was rather sluggish, the corresponding reaction of the molybdenum complex proceeded cleanly to give (dimethylphenylsilyl)(methyl-

---

* Corresponding author. Tel.: +81-3-57342746; fax: +81-3-57342746.

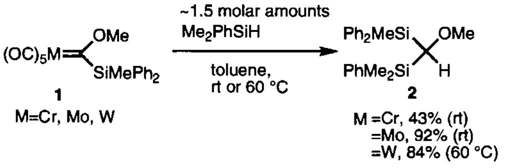
E-mail address: niwasawa@chem.titech.ac.jp (N. Iwasawa).

[1] To our knowledge, one report refers to this possibility. On reaction of triphenylsilane with chromium *p*-methylphenylmethoxycarbene complex, formation of 4,4′-dimethylstilbene along with the normal insertion product was noted. See Ref. [2].

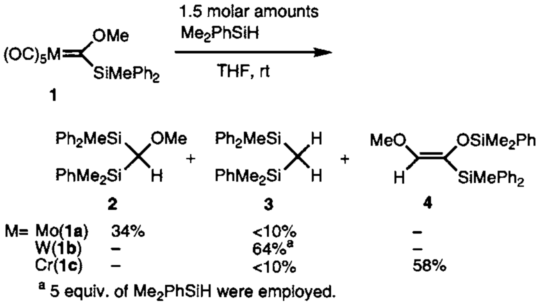
[2] For hydride-reduction of Fischer-type carbene complexes, see Ref. [9].

[3] It is noteworthy that the reaction of phenyl or alkenyl carbene complexes of Group 6 metals with silanes usually necessitates heating in a hydrocarbon solvent, sometimes in the presence of a donor ligand such as pyridine [1–5]. Compared to these, the reactivity of silyl-substituted carbene complexes towards insertion into the Si–H bond is considerably higher.

PII: S0022-328X(00)00721-X



Scheme 1.

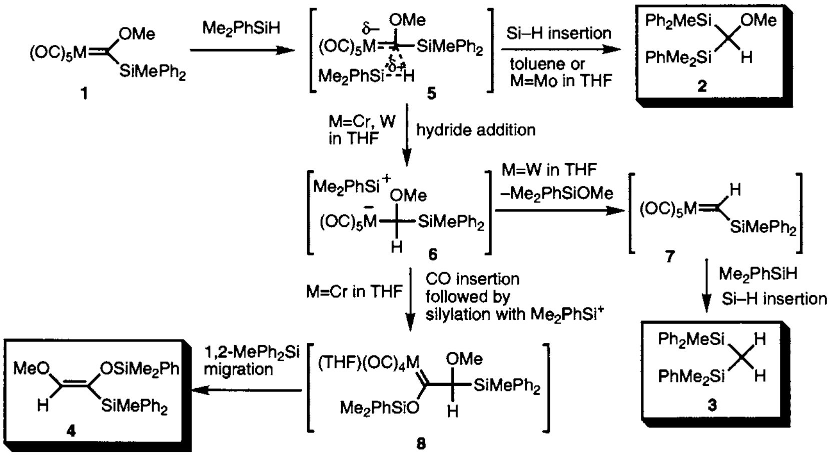


Scheme 2.

diphenylsilyl)methoxymethane (**2**), a normal insertion product, in 92% yield. The corresponding reaction of the tungsten complex did not proceed at room temperature, but on heating at 60°C the complex was consumed within 7 h to give the same insertion product **2** in 84% yield (Scheme 1).

When the same reactions were carried out in THF, they all proceeded at room temperature within 1 day, but different products were obtained depending on the center metal. Thus, when the molybdenum complex **1a** was employed, the same insertion product **2** was obtained as the major product, albeit in moderate yield.[4] However, when the corresponding tungsten complex **1b** was employed, a new product, (methyldiphenylsilyl)-(dimethylphenylsilyl)methane (**3**), was obtained in about 30% yield, without formation of **2**. The yield of this compound improved to 64% on employing 5 molar amounts of dimethylphenylsilane. Furthermore, when the chromium complex **1c** was treated in the same manner, a novel silylsiloxyalkene **4** was obtained as the major product as a single geometrical isomer (Scheme 2). The structure and geometry of this compound were determined by NMR analysis.[5]

Formation of these three types of product can be rationalized as follows (Scheme 3). When the reaction is carried out in a non-polar solvent such as toluene, insertion of the silyl methoxy carbene into the Si–H bond is the major reaction pathway regardless of the center metal. The same direct insertion is observed even in a polar solvent such as THF when the molybdenum complex **1a** is employed. However, when the tungsten or chromium complex is employed, the silane first acts as a reducing reagent to give the hydride-addition intermediate **6**. In the case of the tungsten complex **1b**, elimination of methoxide, presumably as dimethylphenylmethoxysilane, occurs to give a non-heteroatom-stabilized silyl carbene complex **7**, which inserts into the Si–H bond of another molecule of dimethylphenylsi-

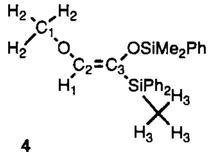


Scheme 3.

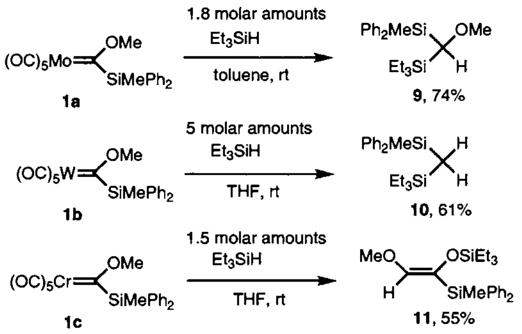
---

[4] Use of 5 molar amounts of the silane improved the yield of **2** to 51%.

[5] The structure of this compound **4** was determined as follows: In the 2D-HMBC spectra, correlations between the olefinic proton (H_1) and the methyl carbon of the methoxy group (C_1), between the olefinic carbon (C_2) and the methyl proton of the methoxy group (H_2), and between the methyl proton of the methyldiphenylsilyl group (H_3) and the olefinic carbon (C_3) were observed. The geometry of the double bond was determined by observation of an NOE between the olefinic proton (H_1) and the methyl protons of the methyldiphenylsilyl group (H_3).



4



Scheme 4.

lane to give the reduction-insertion product **3**.[6] On the other hand, when the chromium complex **1c** is employed, CO insertion followed by silylation on the oxygen atom occurs at the stage of the hydride-addition intermediate **6** to give a new Fischer-type carbene complex **8**.[7] 1,2-Migration of the methyldiphenylsilyl group occurs at this stage to give the product **4**. Such facile 1,2-migration of a silyl group has been observed for several α-silylated carbene complexes [14,15].

The same type of product formation was observed when triethylsilane was employed as silane as shown in Scheme 4.

3. Conclusion

Silyl-substituted Fischer-type carbene complexes show unique behavior when treated with silanes. Depending on the choice of solvent and center metal, three different reaction pathways: direct insertion, reduction-insertion, and reduction-carbonyl insertion-silicon migration can be made to proceed.

Acknowledgements

This research was partly supported by the Toray Science Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] E.O. Fischer, K.H. Dötz, J. Organomet. Chem. 36 (1972) C4.
[2] J.A. Connor, P.D. Rose, R.M. Turner, J. Organomet. Chem. 55 (1973) 111.
[3] J.A. Connor, J.P. Day, R.M. Turner, J. Chem. Soc. Dalton Trans. (1976) 108.
[4] C.C. Mak, K.S. Chan, J. Chem. Soc. Perkin Trans. 1 (1993) 2143.
[5] C.C. Mak, M.K. Tse, K.S. Chan, J. Org. Chem. 59 (1994) 3585.
[6] M. Parisi, A. Solo, W.D. Wulff, I.A. Guzei, A.L. Rheingold, Organometallics 17 (1998) 3696.
[7] E. Nakamura, K. Tanaka, S. Aoki, J. Am. Chem. Soc. 114 (1992) 9715.
[8] C.A. Merlic, J. Albaneze, Tetrahedron Lett. 36 (1995) 1007.
[9] M. Gómez-Gallego, M.J. Mancheno, P. Ramírez, C. Pinar, M.A. Sierra, Tetrahedron 56 (2000) 4893 and references cited therein.
[10] N. Iwasawa, M. Saitou, Chem. Lett. (1994) 231.
[11] E.O. Fischer, H. Hollfelder, P. Friedrich, F.R. Kreissl, G. Huttner, Chem. Ber. 110 (1977) 3467.
[12] U. Schubert, J. Organomet. Chem. 358 (1988) 215.
[13] (a) K.E. Lewis, D.M. Golden, G.P. Smith, J. Am. Chem. Soc. 106 (1984) 3905. (b) I. Lee, N.J. Cooper, J. Am. Chem. Soc. 115, 4389 (1993). (c) W.D. Wulff, B.M. Bax, T.A. Brandvold, K.S. Chan, A.M. Gilbert, R.P. Hsung, J. Mitchell, J. Clardy, Organometallics 13 (1994) 102. (d) K. Fuchibe, N. Iwasawa, Org. Lett. 2 (2000) 3297.
[14] D.W. Macomber, P. Madhukar, R.D. Rogers, Organometallics 10 (1991) 2121.
[15] J.W. Herndon, P.P. Patel, J. Org. Chem. 61 (1996) 4500.

---

[6] We found that when chromium or tungsten phenyl–carbene complex was treated with silane in THF, reduction-insertion product was obtained in good yield. The corresponding reaction of molybdenum phenyl–carbene complex was not examined due to the instability of the complex. Full details of these results will be published in due course. The reason for the difference of reaction pathway between chromium phenyl–carbene and silyl–carbene is not clear.

[7] Facile CO insertion into a carbon–chromium bond is probably due to weaker bond energy of Cr–CO bond rather than Mo–CO or W–CO bond. See [13].