Journal of Organometallic Chemistry, 346 (1988) C11–C14
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Reactivity of hypervalent species of silicon: reduction of CO_2 to formaldehyde with formation of silanone

P. Arya, J. Boyer, R.J.P. Corriu *, G.F. Lanneau, M. Perrot

Unité Mixte CNRS/Rhône-Poulenc/USTL, Institut de Chimie Fine, Université des Sciences et Techniques du Languedoc, Place E. Bataillon, F-34060 Montpellier Cedex (France)

(Reçu le 24 février 1988)

Abstract

Carbon dioxide can be converted into formaldehyde by insertion into the Si–H bond of a pentacoordinated organosilane, followed by decomposition of the product under mild conditions. The transient formation of silanone in this decomposition has been demonstrated by trapping with $(Me_2SiO)_3$.

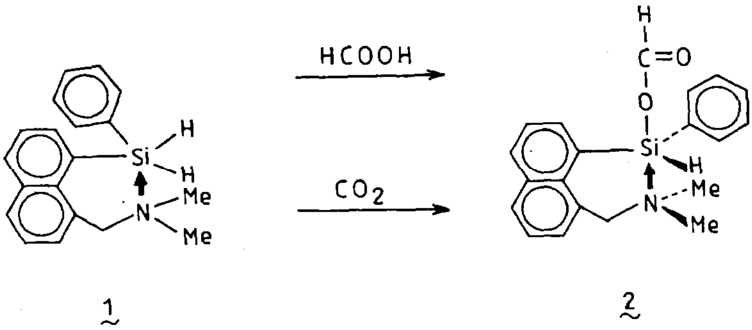
For almost 30 years, chemists have postulated that metaphosphates are intermediates in the hydrolysis of phosphorus esters [1–3*], but only recently have analogous silanones been considered as possible intermediates in the solvolysis of polyfunctional silyl derivatives [4]. Except for this solvolysis, the formation of transient silanones usually required drastic conditions, and such silanones have either been directly observed only by matrix isolation techniques or their participation inferred from trapping experiments [5,6*,7–16]. The present paper describes the formation of transient silanones during the thermal decomposition of a pentacoordinated silyl ester under mild conditions.

The reducing properties of silicon hydrides are enhanced by intramolecular pentacoordination. We have recently described the catalyzed exchange reaction of dihydrogenosilanes with carboxylic acids [17–19]. The addition process with carbonyl derivatives is much slower and gives mono addition [18]. We have now investigated the reaction of carbon dioxide with the highly reactive pentacoordinated silicon hydride **1** (Scheme 1).

---

* This and other references marked with asterisks indicate notes occurring in the list of references.

0022-328X/88/$03.50

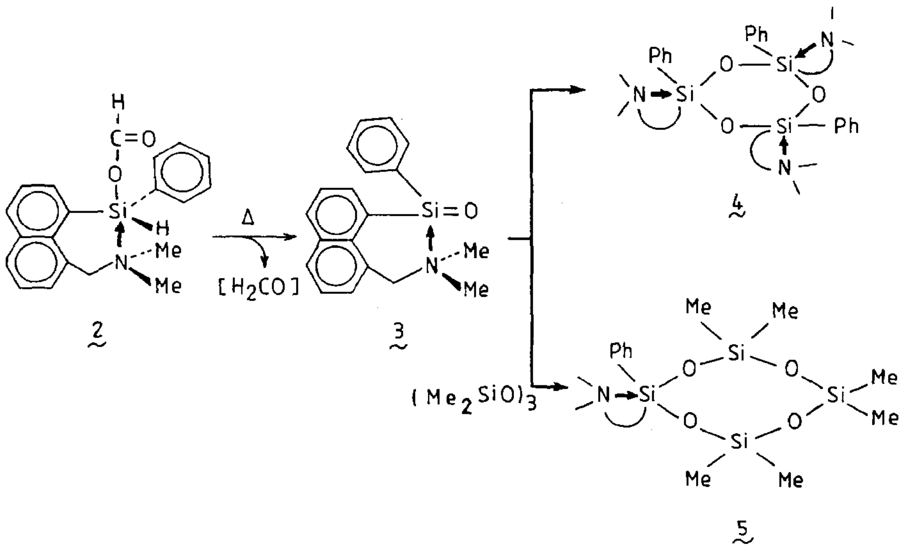


Scheme 1

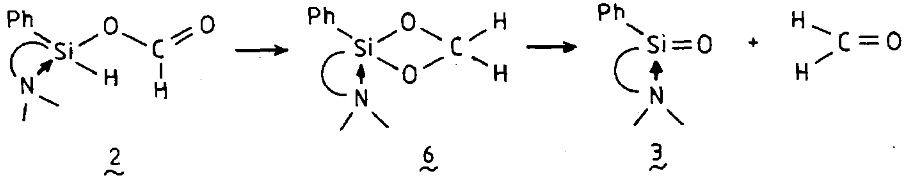
The reaction is fast, almost quantitative, and can be performed at low temperature. We obtain the same product **2** from either formic acid or CO_2. The silyl formate **2** is stable at room temperature for weeks [20*].

Heating the mixture at 65–85 °C for 2 h under argon results in the decomposition of the silyl ester with evolution of formaldehyde (which is immediately trapped with 2,4-dinitrophenylhydrazine). The residue consists solely of the trimer **4** [21*]. If the decomposition is performed in the presence of an excess of $(Me_2SiO)_3$ the major product corresponds to the insertion of the silanone **3** into the six-membered ring siloxane [22*] (Scheme 2).

A possible decomposition mechanism could involve the transient formation of a siladioxetane, which would be highly unstable and undergo fragmentation to silanone and formaldehyde [15,23].



Scheme 2



Scheme 3

Two factors which may account for the ease of decomposition of the silyl formate to silanone are as follows:

(1) Step 1 is favoured by increased reactivity of the Si–H bond arising from intramolecular coordination [24]; pentacoordination is indicated by the ^{1}H NMR data for **2**.

(2) The presence of an amino group stabilises the transient silanone, and lowers the energy barrier for the overall process. There is evidence that low valent silicon species (like their phosphorus analogues) are stabilized by external coordination with nucleophiles [25–29].

It should be noted that the cyclic oligomerization gives only the trimer; no formation of the tetramer was ever observed.

The one pot reaction described provides a very mild method of converting CO_2 into formaldehyde, through the silyl ester of formic acid. It emphasizes the potential of pentacoordinated hydrogenosilanes as reactive synthons in organometallic chemistry, since both steps of the addition-elimination process are facilitated by coordination of the nitrogen at the silicon center. (For comparison, the $[PPh_3]_3RuCl_2$ catalytic addition of CO_2 to Et_2MeSiH at 100 °C gives only 14% of diethylmethylsilylformate [30]. Such an ester is thermally stable and can be distilled.) In view of the case of reaction of carbon dioxide with the pentacoordinate organosilicon hydrides, we plan to extend our studies to insertions of other heterocumulenes.

References and notes

1 W.W. Butcher and F.H. Westheimer, J. Am. Chem. Soc., 77 (1955) 2420.

2 P.W.C. Barnard, C.A. Bunton, D.R. Llewellyn, K.G. Oldham, B.L. Silver and C.A. Vernon, Chem. Ind. London, (1955) 760.

3 For a general discussion, see: F.H. Westheimer, Chem. Rev., 81 (1981) 313.

4 Z.H. Aiube, J. Chojnowski, C. Eaborn and W.A. Stanczyk, J. Chem. Soc. Chem. Commun., (1983) 493. See also: J. Chojnowki and W. Stanczyk, Phosphorus and Sulfur, 27 (1986) 211; C. Eaborn, W.A. Stanczyk, J. Chem. Soc. Perkin Trans. II, (1984) 2099.

5 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdodin, Accounts Chem. Res., 8 (1975) 18 see also: L.E. Gusel'nikov and N.S. Nametkin, Chem. Rev., 79 (1979) 529. For a recent review of π bonded silicon see: G. Raabe and J. Michl, J. Chem. Rev., 85 (1985) 419.

6 For a theoretical study of H_2SiO see: M.J. Gordon and C. George, J. Am. Chem. Soc. 106 (1984) 609; T. Kudo and S. Nagase, J. Phys. Chem., 88 (1984) 2833. See also R. Withnall and L. Andrews, J. Am. Chem. Soc. 108 (1986) 8118; M.W. Schmidt, P.N. Truong and M.S. Gordon, ibid., 109 (1987) 5217.

7 C.M. Golino, R.D. Bush and L.H. Sommer, J. Amer. Chem. Soc, 96 (1974) 614; 97 (1975) 7371.

8 P.V. Valkovich and W.P. Weber, J. Organomet. Chem., 99 (1975) 231.

9 I.M.T. Davidson and J.F. Thomson, J. Chem. Soc. Faraday Trans. I, (1975) 2260.

10 H.S. Soysa, H. Okinoshima and W.P. Weber, J. Organomet. Chem., 133 (1977) C17.

11 W. Ando and A. Sekiguchi, J. Organomet. Chem., 133 (1977) 219.

12 T.J. Barton and J.A. Kilgour, J. Am. Chem. Soc., 96 (1974) 2278; 98 (1976) 7231. See also, T.J. Barton and G. Hussmann, Organometallics, 2 (1983) 692.

13 A.V. Tomadze, N.V. Yablokonva, V.A. Yablokov and G.A. Razuvaev, J. Organomet. Chem., 212 (1981) 43.

14 G. Manuel, G. Bertrand, W.P. Weber and S. Kazoura, Organometallics, 3 (1984) 1340.

15 I.M.T. Davidson and A. Fenton, Organometallics, 4 (1985) 2060; I.M.T. Davidson, A. Fenton, G. Manuel and G. Bertrand, ibid., 4 (1985) 1324.

16 T.J. Barton and B.L. Groh, J. Am. Chem. Soc., 107 (1985) 7221.

17 A. De Saxce, Thesis Montpellier, 1979.

18 J. Boyer, C. Breliere, R.J.P. Corriu, A. Kopton, M. Poirier and G. Royo, J. Organomet. Chem., 311 (1986) C39.

19 R.J.P. Corriu, G.F. Lanneau and M. Perrot, Tetrahedron Lett., 28 (1987) 3941.

20 Silylformyl ester **2**: ^{1}H NMR (CCl_4) 1.7 (m, 6H, $N(CH_3)_2$, 3.2 and 4.6 (dd, *J* 14 Hz, 2H, $N(CH_2Ar)$, 5.25 (s, 1H, Si–H), 7–8 (m, 11H, Ar–H); ^{29}Si NMR ($CDCl_3$): −69.12 ppm; ^{13}C NMR ($CDCl_3$): 44 (m, $N(CH_3)_2$, 63.6 (s, CH_2N) 163.7 (s, H–C(0)).

21 Trimer **4**: ^{1}H NMR ($CDCl_3$) 1.7 (m, 6H, $N(CH_3)_2$, 3.9 (m, 2H, NCH_2Ar), 6.9–8.6 (m, 11H, (Ar)–H); ^{29}Si NMR ($CDCl_3$) −45.43, broad s; −46.75, broad s; −47.48m. Mass spectrum, *m/e* (% rel. int.) 915 (18), 872 (30), 855 (40), 812 (15), 715 (40), 672 (50), 550 (30), 425 (50), 343 (60), 306 (100), 215 (40), 184 (70), 141 (62), 91 (55), 76 (48), 58 (65).

22 Thermolysis of **2** with D_3: cyclotetrasiloxane **5**: ^{1}H NMR ($CDCl_3$) 0.05, broad s (18H); 1.95, broad s (6H); 4.30, broad s (2H); 7.2–8.25, m (10 H); 8.6, m (1H). ^{29}Si NMR ($CDCl_3$) −47.94, −46.82, −21.77, −21.33, −19.41, −17.2. Mass spectrum *m/e* (% rel. int.): 527 (7), 512 (10), 434 (100), 343 (60), 327 (15), 249 (16), 215 (10), 184 (40), 141 (20), 91 (20), 73 (35), 58 (65), 44 (15).

23 A.G. Brook, W.J. Chatterton, J.F. Sawyer, D.W. Hughes and K. Vorspohl, Organometallics, 6 (1987) 1246.

24 C. Brelière, F. Carré, R.J.P. Corriu, M. Poirier and G. Royo, Organometallics, 5 (1986) 388.

25 N. Wiberg, G. Wagner, G. Muller and J. Riede, J. Organomet. Chem. 271 (1984) 381.

26 N. Wiberg, G. Wagner, G. Reber, J. Riede and G. Muller, Organometallics, 6 (1987) 35.

27 N. Wiberg, K. Schurz, G. Reber and G. Muller, J. Chem. Soc. Chem. Commun., (1986) 591.

28 N. Wiberg and H. Köpf, J. Organomet. Chem., 315 (1986) 9.

29 N. Wiberg, K. Schurz and G. Fisher, Angew. Chem., 97 (1985) 1085.

30 H. Koinuma, F. Kawakami, H. Kato and H. Hirai, J. Chem. Soc. Chem. Commun., (1981) 213.