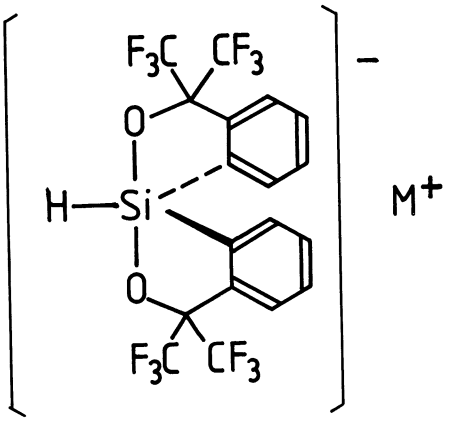
CHEMISTRY LETTERS, pp. 2243-2246, 1987.

Pentacoordinate Hydridosiliconates with Bidentate Ligands Derived from Hexafluorocumyl Alcohol. Characterization and Reduction of Carbonyl Compounds[1)]

Mitsuo KIRA,* Kazuhiko SATO, and Hideki SAKURAI*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

Pentacoordinate hydridosiliconates were prepared via the reaction of trichlorosilane with dilithiated hexafluorocumyl alcohol and characterized spectroscopically. The facile reduction of carbonyl compounds with the siliconates is indicative of the highly activated Si-H bond in the anionic hydridosiliconates.

Pentacoordinate hydridosiliconates have often been postulated as reactive species of reduction of carbonyl compounds with hydrosilanes promoted by fluoride[2,3)] or alkoxide[4,5)] ions. With our recent findings,[4)] it became very evident that the anionic pentacoordinate hydridosiliconates were responsible for the active species of the facile reduction of carbonyl compounds: bis(o-arenediolato)hydridosiliconates have been found to reduce various carbonyl compounds smoothly to give the corresponding alcohols in high yields. A Hammett relationship for the relative reactivity to substituted benzaldehydes showed that the hydride transfer was involved in the rate-determining step. However, anionic hydridosiliconates have been never characterized until now. Many attempts to isolate the bis(1,2-benzenediolato)hydridosiliconates have failed by our hands also. Whereas the lithium salt of the hydridosiliconate (**1**) with bidentate ligands derived from hexafluorocumyl alcohol was reported previously by Perozzi and Martin[6)] as a hygroscopic high-melting solid, the structural characterization seems to be questionable. We have reinvestigated the similar experiments but



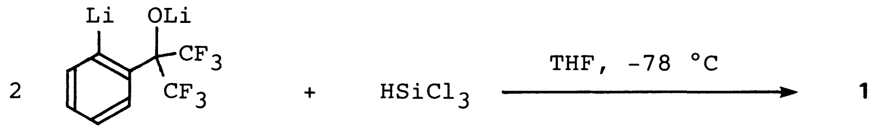
1, M= Li

2, M= PPN

($PPN^+ = Ph_3P{=}\overset{+}{N}{=}PPh_3$)

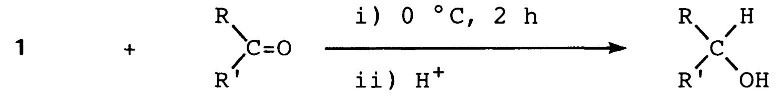
could not obtain reliable evidence for the existence at room temperature. We wish here to report the isolation of the bis(triphenylphosporanylidene)ammonium (PPN) salt of the hydridosiliconates (**2**) by low temperature manipulation. We also report the high ability of **1** and **2** as reducing reagents of carbonyl compounds.

A dilithio derivative (**3**, 4 mmol) of hexafluorocumyl alcohol was prepared from the alcohol and butyllithium in the presence of tetramethylethylenediamine in THF according to the reported procedure by Martin et al.[7] Trichlorosilane (2 mmol) was added to the solution of **3** at -78 °C and the mixture was stirred for 3 h. After addition of a pertinent carbonyl compound (2 mmol) in THF, stirring for 2 h at 0 °C, and usual work-up, the corresponding alcohol was obtained in high yields (Eqs. 1 and 2). The results are summarized in Table 1. Usual aldehydes and ketones were reduced very smoothly under mild conditions. The reactivity of **1** did not appear to be lower than that of bis(1,2-benzenediolato)hydridosiliconates.[4] Whereas Corriu et al. have recently reported the high reactivity of a neutral pentacoordinate hydrosilane towards carbonyl compounds,[8] the anionic hydridosiliconates are suggested to be much more activated as reducing reagents than the neutral analogs.



3

(1)

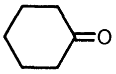
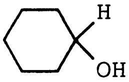
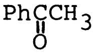
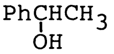


$$\mathbf{1} + \mathrm{RR'C{=}O} \xrightarrow[\text{ii) } H^+]{\text{i) } 0\ ^\circ\mathrm{C},\ 2\ \mathrm{h}} \mathrm{RR'CH(OH)} \qquad (2)$$

We have isolated the PPN salt of the hydridosiliconate (**2**) as follows. After the reaction of **3** (4 mmol) and trichlorosilane (2 mmol) in THF at -78 °C for 2 h followed by evaporation of the solvent at -50 °C in vacuo, a CH_2Cl_2 (10 ml) solution of PPNCl (2 mmol) was added at -30 °C and the mixture was stirred for 3 h (Eq. 3). Removal of the precipitated LiCl by filtration and evaporation of the solvent under argon at ambient temperature gave **2** as white crystals. Whereas further purification was unsuccessful because of the lability in air and moisture, the crude crystals gave the satisfactory spectroscopic data: ^{1}H NMR ($CDCl_3$) δ 8.3-8.0 (2H, m), 7.7-7.0 (36H, m), 5.63 (1H, brs); ^{29}Si NMR ($CDCl_3$) δ -77.7 (d, $|J_{Si-H}|$=253.5 Hz); IR ($CHCl_3$ soln) ν(Si-H) 2100 cm^{-1}. The ^{29}Si NMR chemical shift was in the range of the usual organosiliconates with the same ligands.[9] Although the ^{29}Si-H coupling constants for anionic pentacoordinate hydridosiliconates have never been reported, the value is quite reasonable in comparison with the value reported for the (tetrafluoroethyl)silane-trimethylamine complex (246 Hz),[10]

$$\mathbf{1} + \mathrm{PPNCl} \xrightarrow{\mathrm{CH_2Cl_2},\ -30\ ^\circ\mathrm{C}} \mathbf{2} + \mathrm{LiCl} \qquad (3)$$

Table 1. Reduction of Carbonyl Compounds by Pentacoordinate Hydridosiliconates **1** and **2** [a)]

Carbonyl compound	Hydrido-siliconate	Product	Yield[b)]/%
	**1**		80
 $PhC(=O)CH_3$	**1**	 $PhCH(OH)CH_3$	88
PhCHO	**1**	$PhCH_2OH$	95
$CH_3(CH_2)_7CHO$	**1**	$CH_3(CH_2)_8OH$	81
PhCHO	**2**	$PhCH_2OH$	61[c)]
PhCHO	**2**	$PhCH_2OH$	69[c,d)]

a) The reaction was carried out in THF at 0 °C for 2 h.
b) Yield determined by GLC analysis.
c) See in text for the detailed reaction conditions.
d) 4 equiv. of LiCl was used as an additive.

indicative of the equatorial location of the hydrido ligand which is bonded to the sp^2 hybridized orbital on silicon.

The isolated hydridosiliconate **2** was found also to reduce carbonyl compounds effectively. Thus, when benzaldehyde (1 equiv. for the starting trichlorosilane) was added to a THF solution of **2** isolated as above mentioned and the mixture was stirred at 0 °C for 2 h, the corresponding alcohol was obtained in 61% yield. The reaction was not accelerated apparently by the use of 4 equiv. of LiCl as an additive. The results indicate not only that the pentacoordinate hydridosiliconate should be the actual reactive species of the carbonyl reduction even in the one-pot reaction shown in Eqs. 1 and 2 but also that the activation of the carbonyl by the complexation of lithium cation may be unimportant in the present facile reduction.[11)] The lowering of the yields of alcohol may be attributed to the partial decomposition of the hydridosiliconate during the isolation procedure.

In conclusion, the present results should be taken as the first decisive evidence for the inherent activity of the Si-H bond in the anionic pentacoordinate hydridosiliconates, which are much more reactive towards carbonyl compounds than the neutral analogs as reported by Corriu et al.[8)]

References

1) Chemistry of Organosilicon Compounds 241.

2) J. Boyer, R. J. P. Corriu, R. Perz, and C. Reye, Tetrahedron, 37, 2165 (1981); J. Boyer, R. J. P. Corriu, R. Perz, M. Poirier, and C. Reye, Synthesis, 1981 558; C. Chuit, R. J. P. Corriu, R. Perz, and C. Reye, *ibid.*, 1982, 981.

3) a) M. Fujita and T. Hiyama, J. Am. Chem. Soc., 106, 4629 (1984); b) M. Fujita and T. Hiyama, *ibid.*, 107, 8294 (1985); c) M. Fujita and T. Hiyama, Tetrahedron Lett., 28, 2263 (1987).

4) M. Kira, K. Sato, and H. Sakurai, J. Org. Chem., 52, 948 (1987).

5) A. Hosomi, H. Hayashida, S. Kohra, and Y. Tominaga, J. Chem. Soc., Chem. Commun., 1986, 1411.

6) E. F. Perozzi and J. C. Martin, J. Am. Chem. Soc., 101, 1591 (1979).

7) E. F. Perozzi, R. S. Michalak, G. D. Figuly, W. H. Stevenson III, D. B. Dess, M. R. Ross, and J. C. Martin, J. Org. Chem., 46, 1049 (1981).

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

9) W. H. Stevenson III, S. Wilson, J. C. Martin, and W. B. Fahnham, J. Am. Chem. Soc., 107, 6340 (1985).

10) D. I. Cook, R. Fields, M. Green, R. N. Haszeldine, B. R. Iles, A. Jones, and M. J. Newlands, J. Chem. Soc., A, 1966, 887.

11) On the mechanism of the fluoride ion catalyzed reduction of carbonyl compounds with hydrosilane in HMPA, Hiyama et al. have recently proposed a hexavalent siliconate $[HSiR_3F(HMPA)]^-$ as the active hydride species.3c) In our cases, the coordination of the carbonyl oxygen to silicon may be involved in the transition state, because the Lewis acidity of the pentacoordinate siliconates remains still in a significant extent.12) The more detailed study should be required for the elucidation of the detailed transition state structure.

12) I. Wharf and M. Onyszchuk, Can. J. Chem., 50, 3450 (1972); R. Marat and A. F. Janzen, *ibid.*, 55, 3845 (1977).

(Received September 10, 1987)