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STRUCTURAL CHARACTERIZATION OF A PENTACOORDINATE MONOHYDROSILANE WITH THE APICAL Si–H BOND*

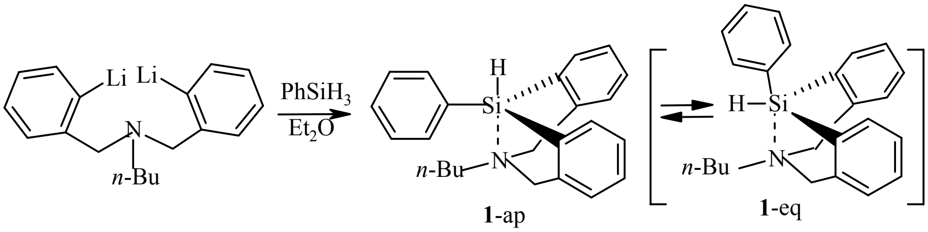
K. Saruhashi, K. Goto, T. Kawashima

A pentacoordinate phenyldibenzosilazocine containing the apical Si–H bond has been prepared and characterized by ^1H and ^{29}Si NMR spectra and X-ray analysis.

Keywords: hydrosilane, apicophilicity, intramolecular N–Si coordination.

Recently, much attention has been paid to the structural features of highly coordinate organosilicon compounds and there have been a number of reports on the structures of penta- and hexacoordinate hydrosilanes [1]. As for a highly coordinate monohydrosilane with a hydrogen atom at the apical position, however, only one example bearing a silatrane framework has been known so far [2]. Recently, Corriu et al. reported the synthesis and structures of the eight-membered silicon-containing heterocycles of the dibenzosilazocine series with the intramolecular N–Si coordination [3]. We report here the synthesis and structural characterization of the title compound.

Hydrosilane **1** was prepared by dilithiation of dibenzylbutylamine followed by reaction with trihydrophenylsilane (Scheme 1). In the ^{1}H and ^{29}Si NMR spectra ($CDCl_3$) of **1** at -60°C, the H-apical form **1**-ap and the H-equatorial form **1**-eq were observed independently in the ratio of 5:3 (**1**-ap:**1**-eq).



1-ap **1**-eq

X-ray crystallographic analysis revealed that **1** has a distorted TBP structure as shown in Fig. 1. It is notable that the hydrogen atom occupies the apical site in spite of its apicophilicity being lower than that of a phenyl group. This is consistent with the predominance of **1**-ap over **1**-eq in solution observed in the NMR spectra. Probably the steric repulsion among three aryl rings resulted in the occupation of the apical site by the hydrogen atom.

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* Dedicated to Prof. E. Lukevics in honor of his 65th birthday.

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-0033, Japan; e-mail: takayuki@chem.s.u-tokyo.ac.jp. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1524-1525, November, 2001. Original article submitted October 22, 2001.

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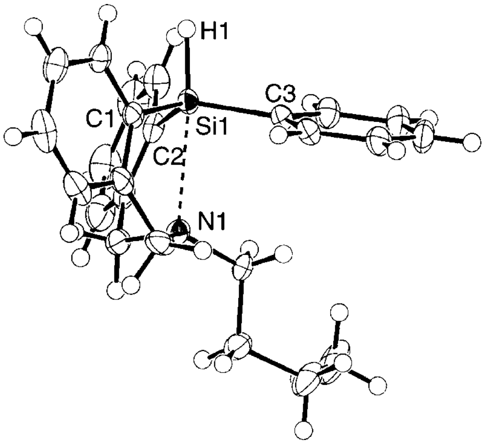

Fig. 1. ORTEP drawing of 1 (50% probability). Selected bond lengths (Å) and angles (°): Si1···N1, 2.516(2); Si1–H1, 1.42(2); C1–Si1–C2, 119.37(11); C2–Si1–C3, 115.43(11); C1–Si1–C3, 114.73(11); N1···Si1–H1, 174.5(10).

EXPERIMENTAL

Monohydrosilane 1. To prepare the monohydrosilane **1**, Corriu's methods were used [3, 4]. A solution of *n*-BuLi in hexane (1.7 M, 2.50 ml, 4.00 mmol) was added dropwise to a solution of N,N-bis(2-bromobenzyl)butylamine (822 mg, 2.00 mmol) in ether (10 ml) at -45°C. The solution was stirred at -30~25°C for 3 h and then allowed to warm to room temperature. After stirring for an additional 1 h, ether (20 ml) was added to the mixture. Then the mixture was cooled to -30°C, and phenylsilane (0.25 ml, 2.0 mmol) was added dropwise. The mixture was stirred for 5 h, during which time it was warmed to room temperature and a white precipitate was formed. The white suspension was stirred for an additional 12 h at room temperature. Then 0.1 ml of water was added to hydrolyze LiH. After removal of the solvent, hexane was added to the residue and then filtered to remove LiOH. The solvent was removed and the residue was purified by gel permeation liquid chromatography and silica-gel chromatography to give a viscous oil, which was recrystallized from $CHCl_3$ to afford hydrosilane **1** as colorless crystals (392 mg, 55%); mp 48-51°C ($CHCl_3$). ^{1}H NMR ($CDCl_3$), δ: 0.73 (br, 3H, CH_3); 1.11 (br, 2H, $CH_3C\underline{H}_2$); 1.35 (br, 2H, $CH_2C\underline{H}_2CH_2$); 1.86 (br, 2H, $NC\underline{H}_2CH_2$); 3.76 (s, 4H, $NC\underline{H}_2Ph$); 5.50 (s, $^1J_{SiH}$ = 178 Hz, 1H, SiH); 7.23 (d, $^3J_{HH}$ = 7.3 Hz, 2H); 7.29-7.49 (m, 9H); 7.90 (br, 2H). ^{29}Si NMR ($CDCl_3$), δ: -26.6(br); IR ($CDCl_3$) $\nu_{Si\text{–}H}$ 2032 cm^{-1}; Found, %: C 74.48; H 7.03; N 3.28. $C_{24}H_{27}NSi$ (0.3 $CHCl_3$). Calculated, %: C 74.73; H 7.05; N 3.59.

Crystallographic data for **1**: $C_{24}H_{28}NSi{\cdot}0.5CHCl_3$, trigonal, space group *P*-3, $a = b = 22.989(9)$, $c = 22.264(8)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $U = 10190(7)$ Å^3, $Z = 16$, $d_{calc} = 1.244$ g·cm^{-3}, μ(MoKα) = 0.419 mm^{-1}. The structure was solved by the direct method and refined by full-matrix least squares on F^2 for all 3963 unique reflections using SHELXL 97. $R_1 = 0.0347$ ($I > 2\sigma(I)$), $wR_2 = 0.1356$ (all data).

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