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Coordination Chemistry Reviews 249 (2005) 781–798

COORDINATION CHEMISTRY REVIEWS

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Review

Silicon derivatives of group 1, 2, 11 and 12 elements

Hans-Wolfram Lerner*

Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität Frankfurt am Main, Marie-Curie-Straße 11, 60439 Frankfurt am Main, Germany

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Abstract

Silyl anions and especially silicon derivatives of group 1, 2, 11 and 12 elements are important and versatile organometallic reagents in synthesis. The best-studied class of silyl anions are the alkali metal silanides that feature monomeric, dimeric and polymeric arrangements as molecular units. Alkali metal silanides have not only become interesting for their molecular structures but have also attracted recent attention due to their synthetic abilities. Recently, alkali metal tri-*tert*-butylsilanides (supersilanides, MSi*t*Bu_3) have been used for the synthesis of new main group element clusters and compounds with elements in low coordination states. In contrast to the well-established silanides with alkali metals, few alkaline-earth metal silanides are known. Information regarding the structure and reactivity of these molecules is thus still rather limited. Silyl derivatives of the zinc group are conveniently accessible by metathesis reaction of MX_2 and alkali metal silanides. X-ray

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Abbreviations: Ar, aryl; DME, dimethoxyethane; hmpa, hexamethylphosphoramide; Mes, mesityl; Np, neopentyl; Ph, phenyl; *i*Pr, isopropyl; THF, tetrahydrofuran; TMDAP, tetrametyldiaminopropane; TMEDA, tetramethylethylenediamine; Tip, 2,4,6-*i*$Pr_3C_6H_2$

* Tel.: +49 69 798 29151; fax: +49 69 798 29260.
E-mail address: lerner@chemie.uni-frankfurt.de.

0010-8545/$ – see front matter
doi:10.1016/j.ccr.2004.08.020

crystal structure analyses show that the silanides of zinc, cadmium and mercury (tBu$_3$SiMSitBu$_3$; M = Zn, Cd, Hg) are monomeric, wheras tBu$_3$SiZnBr and tBu$_3$SiHgCl are tetrameric, the former with a regular, the latter with a pronounced irregular cubic M_4X_4 framework. The compound $(Me_3SiMe_2Si)_3Si{-}Hg{-}Hg{-}Si(SiMe_2SiMe_3)_3$ represents the first molecular two-coordinated dinuclear mercury(I) silyl derivative. Contrary to the well-known cuprates with organic ligands, few compounds are known with a Si−Cu bond. In contrast to homoleptic transition metal silanides, a huge number of heteroleptic complexes of transition metals with silyl ligands have been synthesized and structurally characterized. Most of them are prepared by addition of silanes, R_3SiH, to reactive transition metal species.

Keywords: Silyl anion; Alkali metals; Alkaline-earth metals; Transition metals

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1. Introduction

Compounds with carbanion character such as lithium alkyls represent an important class of reagents in synthesis. Over the past decade, their heavier homologues, the alkali metal silanides, have also gained a wide area of application. Papers regarding the synthesis and reactivity of silanides $MSiR_3$ were published by Gilman et al. in the 1950s and 1960s [1,2]. The first silanides studied in detail were the triphenylsilanides $MSiPh_3$ (M = Li, Na, K, Rb, Cs) [3]. Early syntheses used hexaphenyldisilane $Ph_3Si{-}SiPh_3$ as a starting material, which was treated with the respective alkali metal in ammonia solution in the presence of pyridine. However, the amount of by-products such as silazanes and silylated 1,4-dihydropyridine was considerably high with this method [4].

In addition to the well-established tri-*tert*-butylsilyl group (“supersilyl”, tBu$_3$Si−) [5] and the tris(trimethylsilyl)-silyl group (“hypersilyl”, $(Me_3Si)_3Si$−) [7], this paper presents the di-*tert*-butylphenylsilyl group (tBu$_2$PhSi−) as a new sterically demanding substituent [8,9]. An advantage of the bulky silyl ligands is the good space-filling property, which enables the kinetic stabilization of elements with rare oxidation and coordination numbers. Sterically demanding silyl anions have a strong basicity on account of their electron-donor capacity; metal–metal bonds are thus strengthened. Metathesis reactions can easily be carried out due to the strong nucleophilic power. Bulky silanides are especially suited for cluster synthesis owing to their basicity as well as their nucleophilicity [5].

2. Alkali metal silanides

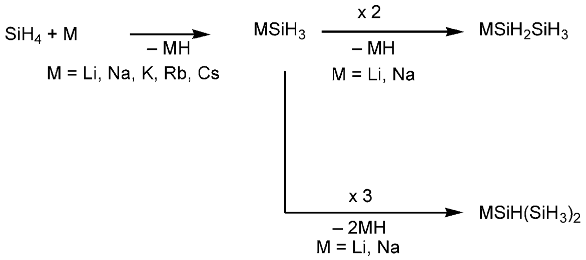
The best-studied class of compounds containing silyl anions are the alkali metal silanides that feature single (monomeric) [5–7,10–14], cyclic (dimeric) [5,7,8] and chain (polymeric) [9] arrangements of molecular units. In addition to the reaction of halosilanes with alkali metals, silanides can be prepared as follows: (i) by transforming a Si−H bond with MH or alkali metals [15,16]; (ii) by cleaving a Si−Si bond using alkali metals, alkoxides ROM (M = Na, K, Cs), alkali metal hydrides MH or lithium alkyls [13,14]; (iii) by methathesis reaction [15,16]; (iv) by metal–metal exchange [7,10].

Alkali metal silanides have not only become interesting on account of their molecular structures but have also attracted recent attention due to their synthetic abilities. However, alkali metal tri-*tert*-butylsilanides (supersilanides), MSitBu$_3$ and tris(trimethylsilyl)silanides (hypersilanides), $MSi(SiMe_3)_3$, have been used in the synthesis of new main group element clusters and compounds with elements in low coordination states. Accordingly, the reaction of sodium supersilanide with thallium(III) chloride produces the supersilylated thallium clusters, (tBu$_3$Si)$_6$Tl$_6$Cl$_2$ and (tBu$_3$Si)$_4$Tl$_3$Cl [17], and with $[(Me_3Si)_2N]_2Sn$ leads to the tristannaallene, (tBu$_3$Si)$_2$Sn=Sn=Sn(tBu$_3$Si)$_2$ [18].

2.1. Synthesis of alkali metal silanides

2.1.1. Synthesis of silanides by transforming a Si−H bond with alkali metals or MH into a Si−M bond

The hydrogen substituted silanides $MSiH_3$ (M = K, Rb, Cs) are synthesized by the reaction of SiH_4 with alkali metals or alloys of alkali metals such as KNa in monoglyme or diglyme [19–26]. In contrast to $MSiH_3$ (M = K, Rb, Cs), the silanides $MSiH_3$ (M = Li, Na) are formed together with by-products [e.g. $NaSiH_2(SiH_3)$] by the same procedure.



(1)

Another synthetic route is the reaction of silanes $HSiR_3$ with alkali metal hydride MH at elevated temperatures to give the appropriate silanides $MSiR_3$ and hydrogen, as shown in Eq. (2):

$$HSiR_3 + MH \underset{M=Na,K}{\xrightarrow[-H_2]{}} MSiR_3 \qquad (2)$$

The metalation of silanes with MH is a general reaction and has been applied to many silanes with hydrogen, alkyl and aryl substituents [27–29]. Examples of alkali metal silanides synthesized by cleaving a Si−H bond are listed in Table 1.