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Reactivity of hypervalent silicon derivatives. One step synthesis of mono- and di-hydrogenosilanes

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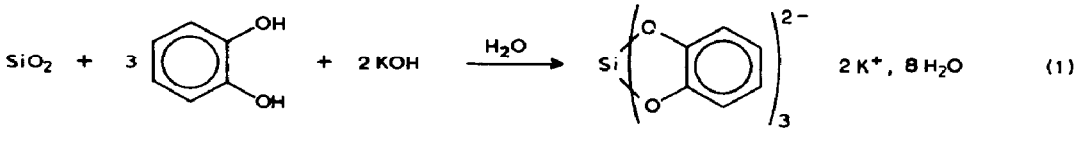
Abstract

A study has been made of the reactivity of the anionic hexacoordinate silicon complex $Si(o\text{-}O_2C_6H_4)_3]^{2-}2Na^+$ (**1**) and some pentacoordinate complexes $[RSi(o\text{-}O_2C_6H_4)_2]^-M^+$ (**2**) towards reducing alkyl Grignard reagents activated by Cp_2TiCl_2. The reaction products depend on the nature of the Grignard reagent; with the primary alkyl reagents the main product is the monohydrogenosilane, but with secondary and tertiary alkyl reagents it is the dihydrogenosilane. The results are interpreted in term of a competition between replacement of Si–O bonds by Si–alkyl bonds on the one hand and reduction on the other.

Introduction

The depolymerisation of silica to monomeric salts has been known for a long time; in 1931 Rosenheim [1] observed that silica was converted into hexacoordinated complexes in water by catechol (eq. 1).



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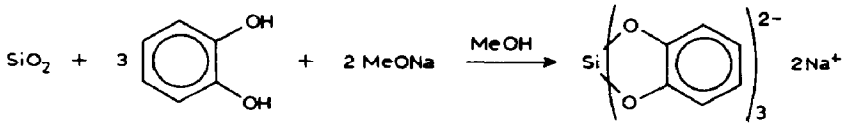
We have been interested in the reactions of these dianionic silicon complexes with a view to finding new routes to organosilicon compounds. At present organosilicon compounds are almost always prepared from reagents made from elemental silicon [2,3]. It represents an interesting challenge to find a route to organosilicon compounds from silica without having to convert it into elemental silicon. Some attempts have been made to use silica as a starting material [4] but seem not to have been successful.

Recently we reported the reactions of the dianionic hexacoordinated silicon complex **1** [5] with nucleophiles (Grignard and organolithium reagents and metal hydrides). Complex **1** is prepared in methanol by the reaction shown in eq. 2. This



(2)

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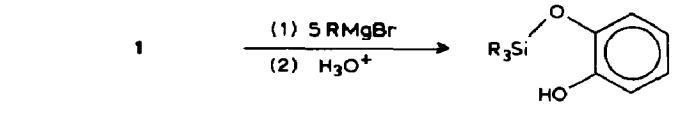
study was extended to the anionic pentacoordinated silicon complexes **2** [6]. Although anionic, both complexes **1** and **2** can undergo nucleophilic attack at silicon. Examples of their reactions are given in eqs. 3, 4, and 5.



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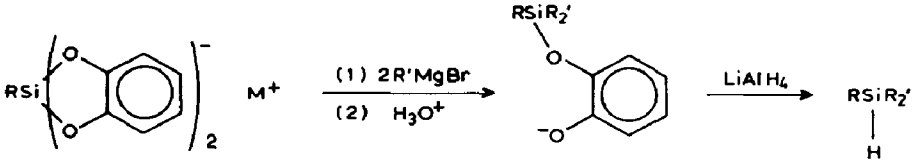


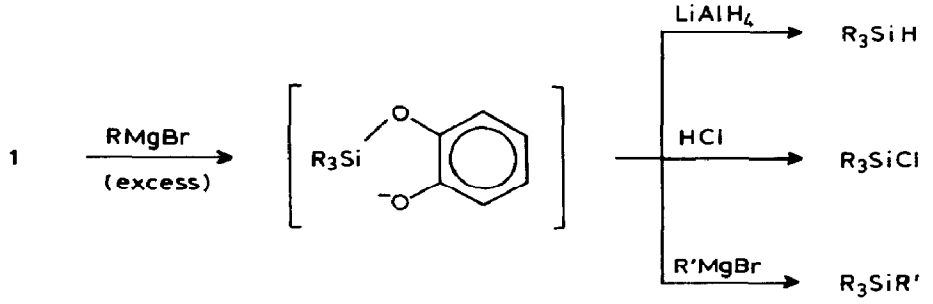
(4)

(**2a** : R = Ph , M = Na ;
2b : R = Me , M = K ;
2c : R = 1-Np , M = Na)

In this paper we describe a useful new route to organosilanes from the hexa- and penta-coordinate silicon complexes **1** and **2** involving reactions with Grignard reagents activated by a catalytic amount of Cp_2TiCl_2 ($Cp = \eta^5$-C_5H_5).

In the light of reports of the activation of Grignard reagents by transition metal compounds by Felkin et al. [7] (later extended by others [8,9]) we devised new methods of forming Si–C bonds from Si–H bonds and reducing Si–X bonds (X = OCH_3, F, Cl) by use of Grignard reagents in the presence of certain transition metal compounds [10–14].

The Cp_2TiCl_2-Grignard reagent combination in which the Grignard component contains a hydrogen atom in the β position proved as powerful a reducing agent as



(5)

$LiAlH_4$ towards Si–X bonds [14]. We therefore decided to examine the reactivity of this system towards complexes **1** and **2**.

Results and discussion

Treatment of complexes **1** and **2** with an excess of a reducing Grignard reagent in the presence of Cp_2TiCl_2 (1 to 2 mol% with respect to the Grignard reagent) gave hydrogenosilanes in one step. As shown in Tables 1 and 2, the products depend on the nature of the alkyl Grignard reagent:

(a) With primary alkyl Grignard reagents the main product is a monohydrogenosilane; R_3SiH form complex **1** (Table 1) and RR'_2SiH from complexes **2** (Table 2).

(b) With secondary and tertiary alkyl Grignard reagents, the main product is the dihydrogenosilane: R_2SiH_2 form complex **1**, (Table 1) and $RR'SiH_2$ from complexes **2** (Table 2).

In considering an explanation of these results, it is relevant to recall that the efficiency of RMgX in presence of Cp_2TiCl_2 as reducing agent is assumed to be due to the in situ formation of Cp_2TiH [15]:

$$Cp_2TiCl_2 + 2\ R^1R^2CHCR^3R^4MgBr \rightarrow Cp_2TiCR^3R^4CHR^1R^2$$

$$Cp_2TiCR^3R^4CHR^1R^2 \rightarrow Cp_2TiH + R^1R^2C{=}CR^3R^4$$

Several possible routes could lead to the formation of hydrogenosilanes by the reaction of Grignard reagents activated by Cp_2TiCl_2 with complexes **1** and **2** and these are summarized in Scheme 1. The routes a,a′ and b,b′ involve initial substitution of the Si–O bonds followed by reduction, whereas the routes c and c′ involve an initial complete reduction of the Si–O bonds followed by substitution of the Si–H bond. The choice of route must depend on the nature of the Grignard reagent. The results are consistent with the reaction of primary Grignard reagents by route a or a′ and of tertiary Grignard reagents by route c or c′, while secondary Grignard reagents can react via both routes b,c or b′,c′.

(1) Primary alkyl Grignard reagents

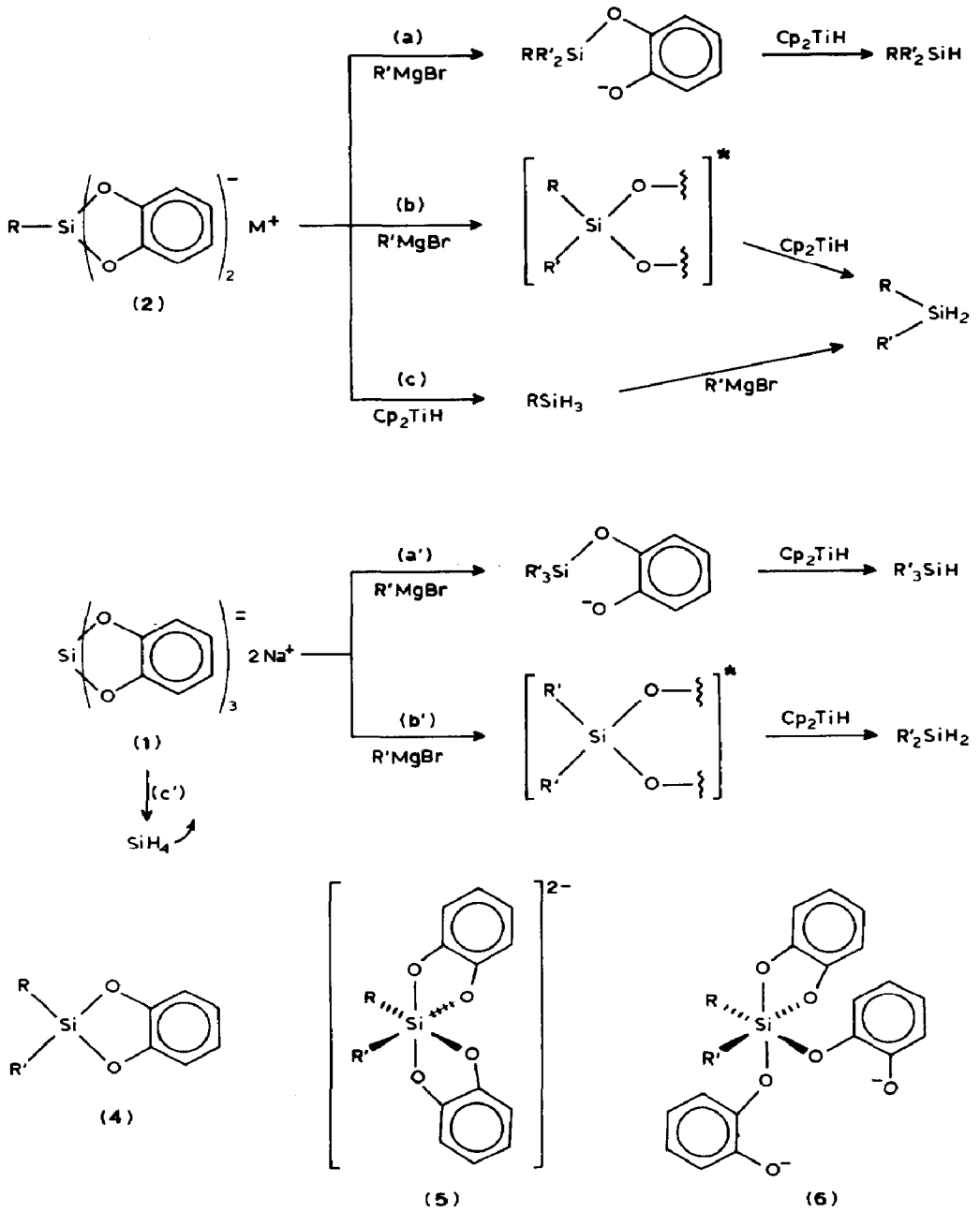
Complexes **1** and **2** react rapidly with an excess of primary alkyl Grignard reagents (5 molar equivalents) activated by Cp_2TiCl_2 (1 to 2 mol%). (The reaction is complete after one hour at 35 °C in ether.) The product is the same monohydro-

Table 1

Reactions of complex **1** with 5 molar equival. of a Grignard reagent in the presence of 1 to 2 mol% of Cp_2TiCl_2 in ether

Entry	Grignard reagent	Reaction conditions		Products, yield(%)
		T(°C)	t(h)	
1	EtMgBr	35	3	Et_3SiH, 49
2	n-BuMgBr	35	3	n-Bu_3SiH, 71
3	i-BuMgBr	35	3	i-Bu_3SiH, 54
4	s-BuMgBr	35	5	s-Bu_2SiH_2, 41
5	t-BuMgBr	35	18	no product

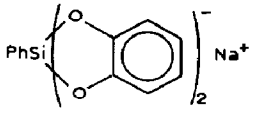
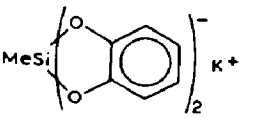
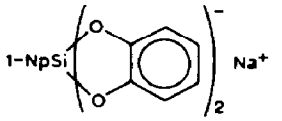
genosilane as is obtained in two steps by reaction of a primary Grignard reagent on complexes **1** and **2** followed by reduction with $LiAlH_4$ (eq. 6). Moreover the reaction of complex **1** with only 2 molar equivalents of n-BuMgBr in the presence of Cp_2TiCl_2 gives a mixture of tributylsilane (34%) and tributyl(2-hydroxy-



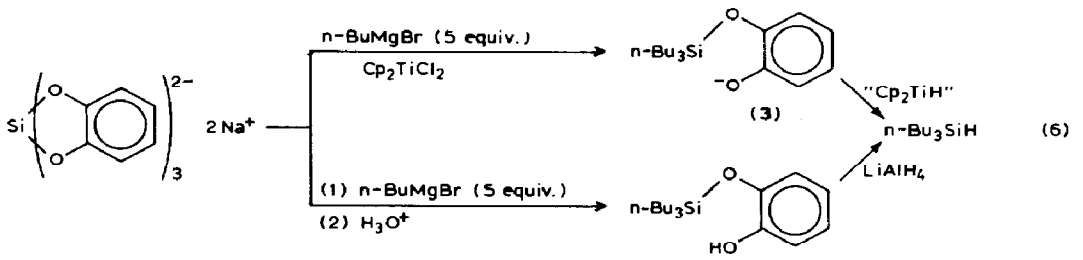
Scheme 1. * The exact structures of these two intermediates have not been established. Some recent results [16] indicate that silane **4** (R = R′ or R ≠ R′) is not involved. Intermediates such as **5** or **6** are possible.

Table 2

Reactions of complexes **2** with 4 molar equiv. of a Grignard reagent in the presence of 1 to 2 mol% of Cp_2TiCl_2 in ether.

Entry	Complex **2**	Grignard reagent	Reaction conditions		Products, yield(%)
			T(°C)	t(h)	
1		n-BuMgBr	35	3	Ph-n-Bu_2SiH, 50 n-Bu_3SiH, 16 Ph_2-n-BuSiH, 12
2		i-BuMgBr	35	3	i-Bu_3SiH, 6 Ph-i-Bu_2SiH, 38 Ph_2-i-BuSiH, 10.5
3		s-BuMgBr	35	4	Ph-s-$BuSiH_2$, 80
4		t-BuMgBr	35	7	Ph-t-$BuSiH_2$, 61
5		n-BuMgBr	35	3	Me-n-Bu_2SiH, 62
6		i-BuMgBr			Me-i-Bu_2SiH, 39
7		cyclo-$C_6H_{11}MgBr$	35	4	cyclo-$C_6H_{11}SiH_2Me$, 61
8		t-BuMgBr	35	7	1-Np-t-$BuSiH_2$, 62

phenoxy)silane (25%). These results indicate that **3** (eq. 6) is an intermediate in the reaction.



(6)

The hydrogenosilane by-products obtained from complex **2a** (Table 2, entries 1 and 2) are significant. A disproportionation reaction promoted by Cp_2TiCl_2 apparently occurs, since in the absence of this catalyst no redistribution takes place. A similar disproportionation is observed in the presence of $(PPh_3)_2NiCl_2$, a catalyst which does not bring about reduction [16]. It follows that the redistribution reaction takes place before the reduction.

(2) Tertiary Grignard reagent (t-BuMgBr)

The results with tertiary Grignard reagents are as follows:

(a) Neither any reaction product nor silica (resulting from the hydrolysis of the starting material) was obtained from the reaction of t-BuMgBr with complex **1**.

(b) Reaction between complex **2c** and t-BuMgBr gave a 62% yield of 1-Np(t-Bu)SiH_2 (Table 2).

In the case of the reaction of complex **1** with t-BuMgBr we suggest that there is formation and subsequent loss of the very volatile SiH_4. This suggestion is supported by the observation that 1-$NpSiH_3$ is formed (21% isolated yield) by reaction of complex **2c** with t-BuMgBr (3 molar equiv.) in the presence of 1.5 molar equiv. of Cp_2TiCl_2. 1-Naphthylsilane reacts with t-BuMgBr in the presence of Cp_2TiCl_2 (5%) to give 1-naphthyl(t-butyl)silane (40%).

It follows that in the case of tertiary Grignard reagents reduction of Si–O bonds takes place because of the low reactivity of t-BuMgBr towards complexes **1** and **2** [6b] (route c,c′, Scheme 1). Likewise, from complex **1**, SiH_4 must be formed, and is immediately vaporised.

(3) Secondary Grignard reagents

The results with secondary Grignard reagents are as follows:

(a) Reaction between complex **1** and s-BuMgBr gives a 41% yield of s-Bu_2SiH_2 (Table 1, entry 4).

(b) Reaction between complex **2a** and s-BuMgBr gives a good yield of PhsBu-SiH_2 (80%) (Table 2, entry 3).

(c) Reaction between complex **2b** and cyclo-$C_6H_{11}MgBr$ gives a fairly good yield of cyclo-$C_6H_{11}MeSiH_2$ (61%) (Table 2, entry 7) when the reaction is performed in a flask with a dry ice condenser, but the yield is lower (37%) if a water condenser is used.

These results are consistent with a mechanism involving competition between routes b and c or b′ and c′. The low yields of s-Bu_2SiH_2 (41%) and cyclo-$C_6H_{11}MeSiH_2$ (37%) can be attributed to the partial formation and elimination of SiH_4 and $MeSiH_3$, respectively. The improvement in the yield of cyclo-$C_6H_{11}MeSiH_2$ when the escape of $MeSiH_3$ is prevented means that some of the cyclo-$C_6H_{11}MeSiH_2$ results from reaction of the volatile $MeSiH_3$ with cyclo-$C_6H_{11}MgBr$ activated by Cp_2TiCl_2 (route c), the remainder coming from the reduction of the intermediate cyclo-$C_6H_{11}MeSi(O^-)_2$ (route b). The good yield of $PhsBuSiH_2$ from complex **2a** (Table 2) is consistent with the formation of the involatile $PhSiH_3$ and Ph-s-BuSi$(O^-)_2$ as intermediates, the first being substituted by s-BuMgBr/Cp_2TiCl_2 and the second reduced. It is significant that no dihydrogenosilanes are obtained by reaction of secondary Grignard reagents with complexes **1** and **2** followed by reduction with $LiAlH_4$; under these conditions the main product is always the monohydrogenosilane [5b,6b].

We conclude that the new route represents an especially convenient way of making hydrogenosilanes. Particularly interesting is the formation of hydrogenosilanes from hexacoordinated complex **1**, since this complex can be prepared directly from silica. The preparation of hydrogenosilane in one step from the sodium bis(benzene-1,2 diolato)methylsilicate **2b** is also of interest since the latter can be prepared from polymethylhydrogenosiloxane (PMHS), a by-product in the manufacture of silicones.

Experimental

All experiments were carried out under nitrogen. Complexes **1** [5b] and **2** [6b] were prepared by published procedures. IR spectra were recorded with a

Perkin–Elmer 298 spectrophotometer and ^1H NMR spectra with a Varian EM 360 or Brucker WP 200 SY spectrometer. All compounds prepared were identified by the usual techniques or compared with authentic samples. The purity of the products was checked by GC (SE 30 column), and was better than 95% except for the two compounds mentioned below.

General procedure

A solution of 5 molar equiv. of Grignard reagent (75 mmol) in ether was added dropwise to a suspension of a mixture of complex **1** or **2** (15 mmol) and Cp_2TiCl_2 (0.8 mmol) in ether (80 ml) at room temperature but in the case of the reaction of primary Grignard reagents with complexes **2**, only 4 molar equiv. of the Grignard reagent were used. The mixture was refluxed for 2 to 7 h depending on the nature of Grignard reagent (cf. Tables 1 and 2). After hydrolysis with aqueous 25% H_2SO_4 solution, the mixture was extracted with ether (3 × 80 ml). The combined ethereal extracts were washed once with water, then with 2 × 50 ml of aqueous 1 *M* NaOH solution (to remove catechol), twice with water, then with brine, and dried over $MgSO_4$. After evaporation of ether the organosilicon residue was purified by distillation or by column chromatography. The following organosilanes were obtained:

From complex **1**. Triethylsilane (49%): b.p. 102–108°C/760 mmHg (lit. [17] b.p. 108.7°C/760 mmHg); Tributylsilane (71%): b.p. 112–114°C/16 mmHg (lit. [18] b.p. 104–106°C/12 mmHg). Triisobutylsilane (54%): b.p. 90–95°C/15 mmHg (lit. [18] b.p. 205,2°C/760 mmHg). Di-2-butylsilane (41%): b.p. 45–47°C/16 mmHg (purity 85%).

From complex **2b**. Dibutyl(methyl)silane (62%): b.p. 75–78°C/28 mmHg (lit. [19] b.p. 52–54°C/8 mmHg); diisobutyl(methyl)silane (39%); b.p. 67–70°C/35 mmHg (lit. [18] b.p. 159.8°C/760 mmHg); cyclohexyl(methyl)silane (61%): b.p. 55–60°C/45 mmHg. The yield was achieved by use of a dry-ice condenser to trap the initially formed $MeSiH_3$ (b.p. −57.5°C/760 mmHg); When the same procedure was performed with a water condenser, only a 37% yield of cyclohexylmethylsilane was obtained.

From complex **2a**. Dibutyl(phenyl)silane (50%); a mixture of dibutyl(phenyl) silane, butyldiphenylsilane (12%), and tributylsilane (16%) was obtained, and was separated by chromatography on acid alumina (eluant pentane). Diisobutylphenylsilane (38%). A mixture of diisobutylphenylsilane, isobutyldiphenylsilane (10.5%), and triisobutylsilane (6%) was obtained, and these were separated by chromatography on acid alumina (eluant pentane). 2-Butyl(phenyl)silane (80%): b.p. 84–88°C/18 mmHg. Phenyl(tertiobutyl)silane (61%): b.p. 89–94°C/32 mmHg (lit. [20] b.p. 186–188°C/760 mmHg).

From complex **2c**. 1-Naphthyl(tertiobutyl)silane (62%): b.p. 85–95/0.1 mmHg (purity 85%).

Reaction of complex 1 with 2 equiv. of n-BuMgBr

A solution of 33 ml (54.5 mmol) of n-BuMgBr in ether was added dropwise at room temperature to a suspension of 10 g (25 mmol) of complex **1** and 160 mg (0.64 mmol) of Cp_2TiCl_2 in 100 ml of ether. After 2 h reflux the mixture was hydrolyzed with aqueous 25% H_2SO_4 solution. After the usual work-up 1.7 g (34%) of

tributylsilane (b.p. 100–110°C/16 mmHg) and 1.95 g (25%) of tributyl(2-hydroxyphenoxy)silane (b.p. 120–125°C/0.5 mmHg) were obtained.

Formation of 1-naphthylsilane by reaction of complex 2c with t-BuMgBr in presence of Cp_2TiCl_2

A solution of 40 ml (35.2 mmol) of t-BuMgBr in ether was added at room temperature to a suspension of 3.7 g (9.4 mmol) of complex **2c** and 3.7 g (14.9 mmol) of Cp_2TiCl_2 in 100 ml of ether. After 1 h reflux the mixture was hydrolysed with 50 ml of a saturated NH_4Cl solution, and 25% aqueous H_2SO_4 solution was added until the mixture was neutral. After filtration the products were worked up in the the usual way to give 320 mg (21%) of impure 1-naphthylsilane (b.p. 120–130°C/25 mmHg), which was identified by comparison of its IR spectrum with that of an authentic sample.

1-Naphthyl(t-butyl)silane from 1-naphthylsilane

A solution of 20 ml (11 mmol) of t-BuMgBr in ether was added to a mixture of 1.5 g (9.5 mmol) of 1-naphthylsilane and 150 mg (0.6 mmol) of Cp_2TiCl_2. The mixture was refluxed for 20 h, then hydrolysed with aqueous saturated NH_4Cl solution. Extraction with ether followed by the usual work-up gave 600 mg (40%) of 1-naphthyl-t-butylsilane, b.p. 95–97°C/0.6 mmHg.

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