ELSEVIER

Journal of Organometallic Chemistry 629 (2001) 1–6

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Disproportionation reactions of organohydrosilanes in the presence of base catalysts

Masayoshi Itoh [a,*], Koji Inoue [b], Jun-ichi Ishikawa [b], Kenji Iwata [b]

[a] *Chemistry and Biochemistry, Fukushima National College of Technology, 30 Aza Nagao, Taira Kamiarakawa, Iwaki-City, Fukushima 970-8034, Japan*

[b] *Material Science Laboratory, Mitsui Chemicals, Inc., Advanced Materials Group, 580-32 Nagaura, Sodegaura-City, Chiba 299-0265, Japan*

Received 26 October 2000; received in revised form 14 February 2001; accepted 23 February 2001

Abstract

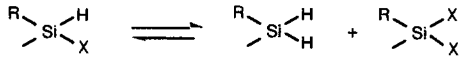
Alkoxides, alkyl compounds, amides and hydrides of alkali metals (M) and barium, such as MOR, $Ba(OR)_2$, *n*-BuM, PhM, $MN(SiMe_3)_2$ and $MAlH_4$ showed high catalytic activities versus the disproportionation reactions of $PhSiH_3$ to produce SiH_4, Ph_2SiH_2 and Ph_3SiH. A good correlation between the catalyst basicities and the catalytic activities was observed, and a reaction mechanism involving the metal hydride and alkyl metal was proposed. A considerable amount of SiH_4 was produced in the reduction of $PhSiCl_3$ with $LiAlH_4$ when over three moles of $LiAlH_4$ was used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Disproportionation reactions; Phenylsilane; Base catalysts

1. Introduction

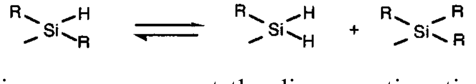
In reactions involving organometallic compounds such as organosilicon compounds, there have been many reports on catalytic reactions using transition metal compounds as catalysts [1,2]. On the other hand, there are few catalytic reactions reported using compounds of the main group elements as catalysts, which are generally ionic compounds, even though ionic catalysts have some industrial advantages, for example they can be easily prepared at low cost and can be separated from the reacted solution using ion-exchange resins or zeolites. We have been studying reaction systems involving organosilicon compounds such as hydrosilanes, using ionic compounds as the catalysts, and have found high catalytic activities of some compounds of alkali and alkaline-earth metals toward the hydrosilylation reactions of hydrosilanes with olefins [3] and dehydrogenative coupling reactions between hydrosilanes and alkynyl compounds [4–8]. In this paper, we report a new catalytic reaction system using ionic compounds as the catalyst.

Catalytic disproportionation reactions of alkoxy silanes and chlorosilanes have been studied by treating such silanes with a suitable catalyst under mild conditions shown as follows (Eq. (1)):


(1)

wherein R is a hydrocarbon group or hydrogen, and X is an alkoxy group or halogen [9]. Base catalysts such as alkali metal alkoxides have generally been employed.

There have been some reports on the disproportionation reactions of organohydrosilanes using Lewis acids such as $AlBr_3$ [10], solid acids such as $SiO_2–A1_2O_3$ [11], KH, $LiAlH_4$ [12], Red-Al [13] and transition metal complexes such as $(Ph_3P)_3RhC1$ [14], $Cp^*Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$ [15], $CP^*_2SmCH(SiMe_3)_2$ [16] or $RuCl_2[P(C_6H_4Me\text{-}p)_3]$ [17] (Eq. (2)).


(2)

In this paper, we report the disproportionation reactions of arylhydrosilanes in the presence of base catalysts such as alkoxides, alkyl compounds, amides or hydrides of alkali or alkaline earth metals (Eq. (3)).

$$RSiH_3 \xrightleftharpoons{\text{cat.}} SiH_4 + R_2SiH_2 + R_3SiH + R_4Si \qquad (3)$$

---

* Corresponding author. Tel.: +81-246-460810; fax: +81-246-460825.

E-mail address: m-itoh@fukushima-nct.ac.jp (M. Itoh).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)00755-0

2. Experimental

2.1. Reaction procedures

$PhSiH_3$, Ph_2SiH_2, Ph_3SiH, $C_6H_{13}SiH_3$ (*n*-hexylsilane) and Et_3SiH were used as the hydrosilanes for the disproportionation reactions. These liquid reactants were dried over 3 Å molecular sieves prior to use. Alkali and alkaline-earth metal compounds were mainly used as the catalysts (see Table 1). The solvents of diglyme, 1,2-dimethoxyethane (DME), THF, 1,4-dioxane, hexane and toluene were dried over 3 Å molecular sieves. All experiments were carried out in a nitrogen atmosphere. A 50 mmol sample of the hydrosilane, 2.5 mmol of the catalyst and 10 ml of the solvent were typically charged into a glass flask which was connected with a condenser cooled to 15°C. The reactions were carried out at 50°C for 6 h. The gaseous products were trapped by reaction with a solution of LiOEt in ethanol (Li 0.5 wt.%). After the reaction, the amounts of liquid products in the reaction solution and the gaseous products trapped as alkoxides in the ethanol solution (the amounts of $Si(OEt)_4$ and $R_nSi(OR)_{4-n}$) were determined by GC measurement using *n*-tetradecane as the internal standard.

The reduction of $PhSiCl_3$ to $PhSiH_3$ was carried out in THF using $LiAlH_4$ with specific mole ratios of $PhSiCl_3$ to $LiAlH_4$ in a nitrogen atmosphere. Forty seven ml of THF and 10 mmol of $PhSiCl_3$ were charged into a 200 ml glass flask with a condenser cooled to 15°C. $LiAlH_4$ (solution of THF, 2.16 mol l^{-1}) of the specified quantity was then gradually added, while the temperature was maintained at 40°C or less by cooling. After 1 h, the reaction temperature was raised to ca. 65°C, and the reaction mixture was refluxed with stirring for an additional 2 h. The products were analyzed in a manner similar to the disproportionation reaction.

2.2. Product assignment

The liquid products ($PhSiH_3$, Ph_2SiH_2, Ph_3SiH, $Si(OEt)_4$) were identified by mass spectroscopy [18] and GC.

$PhSiH_3$; MS (m/z): (EI mode) 108 (100, M^+), 107 (100), 106 (98), 105 (73), 81 (20).

Ph_2SiH_2; MS (m/z): (EI mode) 106 (100), 105 (50), 184 (37, M^+), 78 (33), 53 (17).

Ph_3SiH; MS (m/z): (EI mode) 182 (100), 181 (59), 183 (29), 105 (23), 260 (18, M^+).

$Si(OEt)_4$; MS (m/z): (EI mode) 193 (100), 149 (86), 163 (70), 79 (57), 208 (11, M^+).

The gaseous product (SiH_4) was trapped directly in a cylinder and identified by mass spectroscopy.

SiH_4; MS (m/z): (EI mode) 30 (100), 31(86), 29 (15), 32 (11, M^+). The data coincided with those in the literature [18,19].

Table 1
Disproportionation reactions of $PhSiH_3$ [a]

Entry	$PhSiH_3$ (mmol)	Catalyst	Amount of catalyst (mmol)	Reaction temperature (°C)	Conversion of $PhSiH_3$	Product yield (%) [b]			
						SiH_4	Ph_2SiH_2	Ph_3SiH	Ph_4Si
1	49.9	LiOEt	2.5	50	32.0	9.8	10.3	0	0
2	50.6	LiO-*i*-Pr	2.5	50	58.7	17.0	17.4	0	0
3	50.2	LiOPh	2.5	50	0	0	0	0	0
4	50.5	NaOEt	2.5	50	99.3	44.7	2.9	28.0	0.8
5	49.7	KOEt	2.4	50	97.5	50.4	6.9	15.2	7.0
6	50.7	$Ba(OC_8H_{17})_2$ [c]	2.5	50	98.2	25.5	23.0	15.1	0.1
7	50.3	LiOCOPh	2.5	50	0	0	0	0	0
8	50.2	*n*-BuLi	2.5	50	96.5	43.7	41.3	2.7	0
9	49.8	PhLi	2.5	50	97.3	46.6	38.2	8.4	0
10	49.1	$LiN(SiMe_3)_2$	2.6	50	85.0	36.6	36.9	1.1	0
11	50.7	$LiN(SiMe_3)_2$	2.6	100	99.0	53.1	16.3	21.4	0
12	50.2	$NaN(SiMe_3)_2$	2.5	50	95.4	39.2	34.1	2.0	0.1
13	50.4	$KN(SiMe_3)_2$	2.5	50	96.3	39.7	36.7	1.5	Trace
14	50.4	$LiAlH_4$	2.5	50	94.2	47.6	25.8	13.2	0
15	49.4	$LiAlH_4$	2.6	100	98.1	57.2	9.3	23.8	0.1
16	50.8	$NaAlH_4$	2.5	50	91.0	41.3	30.3	8.5	Trace
17	49.6	MgO [d]	126	50	23.6	1.9	3.3	0	0

[a] Reactions were carried out for 6 h. 10 ml of diglyme was used as the solvent unless otherwise noted.

[b] Determined by GC.

[c] Barium-2-ethylhexoxide.

[d] 5.06 g of MgO was used.

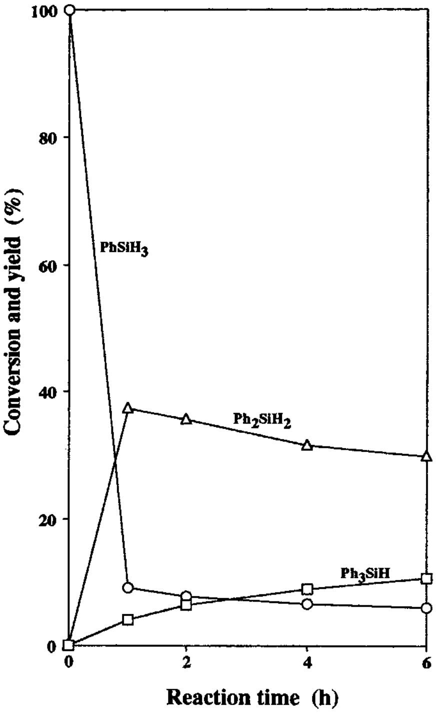


Fig. 1. Disproportionation reaction of PhSiH$_3$ in the presence of LiAlH$_4$ (entry no.1 in Table 1).

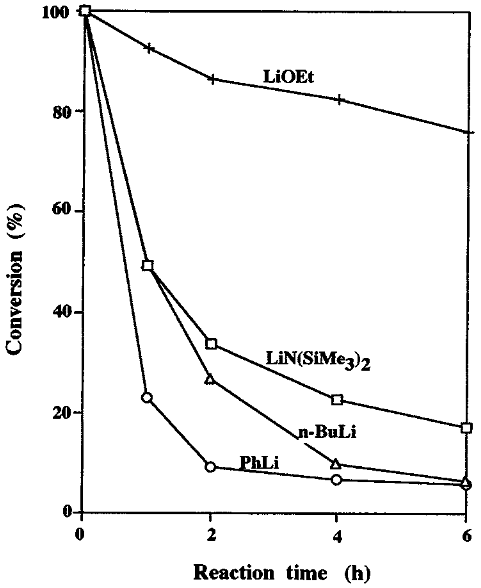


Fig. 2. Disproportionation reaction of PhSiH$_3$ in the presence of Li compounds.

3. Results and discussion

The reaction results are shown in Table 1. The disproportionation reactions of PhSiH$_3$ occurred to produce the monosilane (SiH$_4$), Ph$_2$SiH$_2$, Ph$_3$SiH, and Ph$_4$Si in the presence of alkoxides, alkyl compounds, amides or hydrides of alkali metals and barium alkoxides, which are strong bases. No other products were detected by GC. The first reaction of PhSiH$_3$ proceeded rapidly during the early stages of the reaction with the production of SiH$_4$, and Ph$_2$SiH$_2$, and then the reaction of Ph$_2$SiH$_2$ to produce Ph$_3$SiH gradually proceeded as shown in Fig. 1. Because SiH$_4$ was identified by conversion to Si(OEt)$_4$, some SiH$_4$ would be lost, especially during the early reaction stage. When we did not use the trap containing the ethanol solution of LiOEt, which was connected to the reaction vessel to convert SiH$_4$ into Si(OEt)$_4$ with hydrogen gas evolution, smoke or a flame was observed at the exit of the reaction vessel.

The alkoxides of the elements belonging to Groups 2 (alkaline earth metals), 11, 13 and 3 of the periodic table such as Mg(OEt)$_2$, Ca(OEt)$_2$, Sr(OEt)$_2$, Ba(OEt)$_2$, Cu(OEt)$_2$, Al(OEt)$_3$, Ga(OEt)$_2$ and La(O-*i*-Pr), which have higher ionization potential energies [20] and are weaker bases than the alkali metal alkoxides, were insoluble in the reaction solution and showed almost no catalytic activity. Ba(OC$_8$H$_{17}$)$_2$ (barium-2-ethylhexoxide), which is soluble in the solvent, showed a high catalytic activity.

The order of the catalytic activities of Li compounds was PhLi > *n*-BuLi > LiN(SiMe$_3$)$_2$ > LiOEt ≫ LiOPh, LiOCOPh (not catalytically active) as shown in Fig. 2. The order coincides with that of the basicities of the conjugated acids [21]. Moreover, the catalytic activities of the alkali metal alkoxides (NaOEt ~ KOEt > UOEt) correlate with the ionization potentials of the metals (see Table 1, Fig. 3) [20]. Because the alkali compounds were soluble in the reaction solution, the basicity of the catalyst would be one of the factors which determines the catalytic activity. The addition of 10% of a more

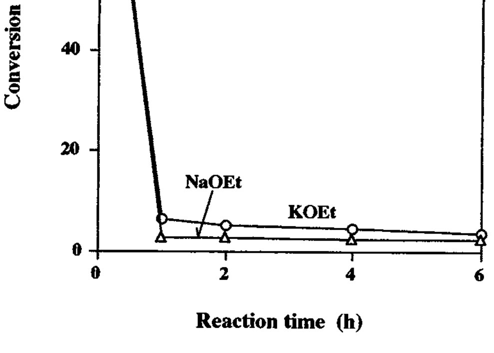


Fig. 3. Disproportionation reaction of PhSiH$_3$ in the presence of alkali metal alkoxide.

Table 2
Effects of solvent and catalyst amount on disproportionation reaction of $PhSiH_3$ in the presence of NaOEt [a]

Entry	$PhSiH_3$ (mmol)	NaOEt (mmol)	Solvent [b]	Conversion of $PhSiH_3$	Product yield (%) [c]			
					SiH_4	Ph_2SiH_2	Ph_3SiH	Ph_4Si
1	50.5	2.5	Diglyme	99.3	44.7	2.9	28.0	0.9
2	50.0	2.5	DME	99.6	53.7	2.4	28.5	1.2
3	50.6	1.3	DME	99.7	52.1	4.3	28.2	0.2
4	50.5	0.3	DME	50.0	17.2	20.9	0.1	0
5	50.5	2.5	THF	99.9	53.7	4.8	26.6	0.2
6	49.8	2.5	1,4-Dioxane	30.5	8.7	9.6	0	0
7	50.5	2.5	Hexane	0	0	0	0	0
8	50.5	2.5	Hexane–diglyme [d]	98.0	46.0	28.4	13.5	0
9	50.7	2.4	Toluene	0	0	0	0	0
10	50.0	2.5	Toluene–diglyme [e]	97.4	47.1	33.3	10.4	0

[a] Reactions were carried out at 50°C for 6 h.

[b] 10 ml of the solvent was used unless otherwise noted.

[c] Determined by GC.

[d] 10 ml of hexane and 1 ml of diglyme were used.

[e] 10 ml of toluene and 1 ml of diglyme were used.

polar solvent to a non-polar solvent yields results analogous to those in the polar solvent alone (Table 2). This might suggest that there is preferential solvation of the transition state with the more polar solvent.

The reaction mechanism in which the substituent moves from the silicon to the lithium is considered (Si···H···Li, see Fig. 4). When the substituent is a phenyl group, the activation energy would be low due to the resonance effect of the benzene ring and the reaction would proceed easily. $C_6H_{13}SiH_3$ was not disproportionated. There would be no resonance effect in alkyl substitution. The conversion of Et_3SiH was zero and that of Ph_3SiH was much lower than that of $PhSiH_3$, which would be caused by steric hindrances (Table 3).

As mentioned above, the strong basic catalysts showed high catalytic activities. We presumed that the reaction proceeded via an ionic transition state as shown in Fig. 4. It is well known that alkyl metals [22], metal amides [23] and metal alkoxides [23,24] react with $PhSiH_3$ to produce metal hydrides [22]. $PhSiH_3$ would be activated by the alkyl metal and metal hydride and a disproportionation reaction would occur. We proposed the four-center-type transition state as shown in Fig. 4. Five-coordinate silicon hydrides could also be considered as an intermediate [12,25]. More study must be done to clarify the reaction mechanism. The above results indicate that the Si–H bond would be more easily activated by an ionic catalyst than the C–H bond, because the C–H bond cannot generally be activated by base catalysts such as alkoxides, alkyl compounds, amides or hydrides of alkali metals.

The fact that $LiMH_4$ catalyzed the disproportionation reaction of organohydrosilane to produce SiH_4 is very important, because almost all organohydrosilanes are usually synthesized by the reduction of the corresponding organochlorosilanes [26], which are easily obtained by Rochow's direct process via the reaction of RCl with silicon metal.

$$Si + RCl \rightarrow R_nSiCl_{4-n} \xrightarrow{LiAlH_4} R_nSiH_{4-n} \qquad (4)$$

Fig. 5 shows the amount of SiH_4 produced during the reduction of $PhSiCl_3$ with $LiAlH_4$ for various ratios of $LiAlH_4$ to $PhSiCl_3$. A considerable amount of SiH_4 was produced when over 3 mol of $LiAlH_4$ was used.

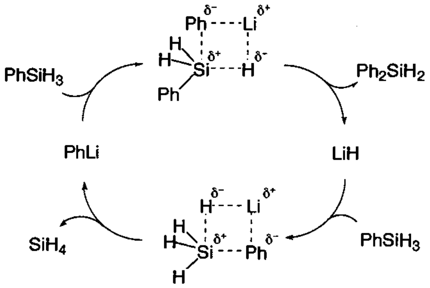


Fig. 4. Presumed mechanism of the disproportionation reaction of hydrosilane in the presence of alkali metal compound.

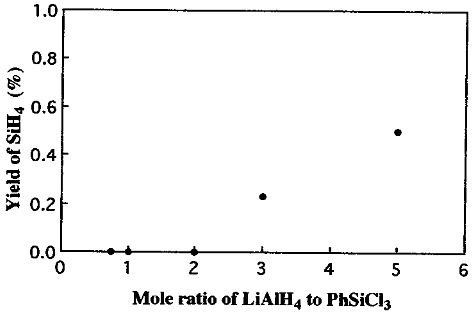


Fig. 5. The amount of SiH_4 produced in the reduction of $PhSiH_3$ by $LiAlH_4$.

Table 3
Disproportionation reaction of hydrosilanes in the presence of NaOEt [a]

Entry	Hydrosilane	Amount of hydrosilane (mmol)	NaOEt (mmol)	Solvent [b]	Conversion of hydrosilane (%)	Product yield (%) [c]				
						SiH_4	$RSiH_3$	R_2SiH_2	R_3SiH	R_4Si
1	$PhSiH_3$	50.1	0.5	DME	97.8	47.5		27.1	13.0	0
2	Ph_2SiH_2	50.0	0.50	DME	82.9	20.2	0.6		51.7	0.1
3	Ph_3SiH	50.0	0.49	DME	7.9	0.2	0	0		1.0
4	$C_6H_{13}SiH_3$	48.9	0.50	DME	0	0		0	0	0
5	$PhSiH_3$	50.5	2.5	Diglyme	99.3	44.7	0.7	2.9	28.0	0.9
6	$C_6H_{13}SiH_3$	49.1	2.39	Diglyme	0	0		0	0	0
7	Et_3SiH	49.4	2.82	Diglyme	0	0	0	0		0

[a] Reactions were carried out at 50°C for 6 h.
[b] 10 ml of the solvent was used unless otherwise noted.
[c] Determined by GC.

The mole ratio of $LiAlH_4/PhSiCl_3$, which gave SiH_4, suggests that the partially chlorinated aluminum hydrides such as $LiAlH_3Cl$ or $LiAlH_2Cl_2$ would not be as active as $LiAlH_4$ for the disproportionation reaction of $PhSiH_3$.

$$PhSiCl_3 + 3LiAlH_4 \rightarrow PhSiH_3 + 3LiAlH_3Cl \quad (5)$$

These results caution us that there is the possibility of the generation of SiH_4 (self-burning gas in air, minimum explosion limit is 0.8 vol%) during the reduction of $PhSiCl_3$ by $LiAlH_4$. Because the reaction solution is not always homogeneous, we must take sufficient care, especially when we use an amount of $LiAlH_4$ larger than the equivalent amount of an organochlorosilane.

4. Conclusions

Alkoxides, alkyl compounds, amides and hydrides of alkali metals (M) and barium, such as MOEt, MO-*i*-Pr, $Ba(OC_8H_{17})_2$, *n*-BuM, PhM, $MN(SiMe_3)_2$ and $MAlH_4$ (M; Li, Na, K) showed high catalytic activities for the disproportionation reactions of $PhSiH_3$ to produce SiH_4, Ph_2SiH_2 and Ph_3SiH. Hydrosilanes having alkyl substitutions, such as $C_6H_{13}SiH_3$ (*n*-hexylsilane) and Et_3SiH were not disproportionated. The catalytic activities have good correlation with the ionization potentials of the metals and the pK_a of the conjugated acids of the catalysts. An ionic reaction mechanism involving the metal hydride and alkyl metal was proposed. A considerable amount of SiH_4 was produced in the reduction of $PhSiCl_3$ with $LiAlH_4$ when over 3 mol of $LiAlH_4$ were used.

Acknowledgements

This work was performed by Mitsui Chemicals, Inc., under the management of the Japan Chemical Innovation Institute as part of the Industrial Science and Technology Frontier Program supported by the New Energy and Industrial Technology Development Organization.

References

[1] B. Marciniec, J. Gulinski, W. Urbaniak, Z.W. Kornetka, in: B. Marciniec (Ed.), Comprehensive Handbook on Hydrosilylation, Pergamon, Tokyo, 1992.
[2] A. Norbert, W. Johann (Eds.), Organosilicon Chemistry III, Wiley-VCH, Weinheim, 1997.
[3] M. Kobayashi, M. Itoh, Chem. Lett. (1996) 1013.
[4] M. Itoh, M. Mitsuzuka, K. Iwata, K. Inoue, Macromolecules 27 (1994) 7917.
[5] M. Itoh, M. Mitsuzuka, T. Utsumi, K. Iwata, J. Organomet. Chem. 476 (1994) C30.
[6] M. Itoh, M. Kobayashi, J. Ishikawa, Organometallics 16 (1997) 3068.
[7] J. Ishikawa, K. Inoue, M. Itoh, J. Organomet. Chem. 552 (1998) 303.
[8] J. Ishikawa, M. Itoh, J. Catal. 185 (1999) 454.
[9] D.L. Bailey, N.Y. Buffalo, U.S. Patent 2723983 (1983); 2745860 (1957); 2723984 (1955).
[10] G.E. Russel, J. Am. Chem. Soc. 81 (1959) 4825.
[11] H. Fujisawa, T. Yamaguchi, Catal. Lett. 17 (1993) 319.
[12] B. Becker, R.J.P. Corriu, C. Guerin, B.J.L. Henner, J. Organomet. Chem. 369 (1989) 147.
[13] H.G. Woo, S.J. Song, E.J. Cho, I.N. Jung, Bull. Korean Chem. Soc. 17 (1996) 123.
[14] I. Ojima, S. Inaba, T. Kogure, Y. Nagai, J. Organomet. Chem. 55 (1973) C7.
[15] H. Hashimoto, H. Tobita, H. Ogino, J. Organomet. Chem. 499 (1995) 205.
[16] N.S. Radu, F.J. Hollander, T.D. Tilley, A.L. Rheingold, J. Chem. Soc. Chem. Commun. (1996) 2459.
[17] T. Sakakura, O. Kumberger, R.P. Tan, M.P. Arther, M. Tanaka, J. Chem. Soc. Chem. Commun. (1995) 193.
[18] F.W. McLafferty, D.B. Stauffer, The Wiley/NBS Registry of Mass Spectral Data, Wiley, 1988.
[19] F.E. Saalfeld, H.J. Svec, Inorg. Chem. 2 (1963) 46.
[20] First ionization potential (IP): K (4.34), Na (5.14), Ba (5.21), Li (5.39), La (5.58), Sr (5.70), Al (5.99), Ga (6.00), Ca (6.11), Mg (7.65), Cu (7.73).
[21] pK_a of the conjugate acids of the lithium compounds: *n*-BuH (51), PhH (43), $HN(SiMe_3)_2$ (35), EtOH (16), PhOH (10), PhCOOH (4).
[22] W.H. Nebergall, J. Am. Chem. Soc. 72 (1950) 4702.
[23] R.N. Meals, J. Am. Chem. Soc. 68 (1946) 1880.
[24] H. Gilman, G.N.R. Smart, J. Org. Chem. 19 (1954) 441.
[25] M. Fujita, T. Hiyama, J. Am. Chem. Soc. 106 (1984) 4629.
[26] S. Tannenbaum, S. Kaye, G.F. Lewenz, J. Am. Chem. Soc. 75 (1953) 3753.