New Aspects of Electrochemical Synthesis in Organosilicon Chemistry

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In organosilicon chemistry, one big challenge is the development of alternative routes for the synthesis of Si-Si and Si-Element bonds. Standard techniques very often involve the handling of hazardous alkali metals or highly toxic organometallic mercury compounds. Thus, the electrochemical formation of Si-Si and Si-C bonds has been investigated as an alternative pathway in the last several years, most of the publications dealing with the synthesis of peralkylated or perarylated silanes [1].

The present study is aimed at the development of electrochemical methods to form functionalized silanes of the general formula $X(SiR_2)_nR'$, that means mono- or oligosilanes with at least one substituent different from an alkyl or aryl group.

1. Synthesis of organofunctional silanes

Organofunctional silanes of the general formula $X–Si(R_2)–R'Y$ are of great interest for various industrial applications. Looking for new and general routes for their synthesis we followed two different pathways, the first one involving the anionic cleavage of electrochemically generated disilanes:

$$\text{X-SiR}_2\text{Cl} \xrightarrow{\text{electrolysis}} \text{X-SiR}_2\text{SiR}_2\text{-X} \xrightarrow{\text{NaOMe}} [\text{X-SiR}_2^-]$$

$$[\text{X-SiR}_2^-] \xrightarrow{\text{ClR'Y}} \text{X-SiR}_2\text{R'Y}$$

The second, even more general route implies the electrolysis of organic halides in the presence of chloro- or alkoxysilanes in an organic solvent:

$$\text{R2SiX'X} + \text{X-R'Y} \xrightarrow{\text{electrolysis}} \xrightarrow{\text{workup}} \text{X-SiR}_2\text{R'Y}$$

(e.g. X, X´= Cl, Br, OR, H; Y = OH, OR, NR_2; R, R´ = H, alkyl, aryl)

Thus, with the right choice of solvent, supporting salt and electrolysis parameters the products have been obtained in a one step process with yields up to 90%.

2. Electrochemical silicon-iron bond formation

Electrochemical reduction is a very simple and elegant route to iron substituted silyl substrates. Using an undivided cell under controlled current conditions reduction of the iron complex and subsequent iron-silicon bond formation is afforded in a convenient one pot synthesis. Based on a work by *Ruiz et al.*, who showed that it is possible to generate silicon iron bonds electrochemically when using Fp_2 ($[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$) and Me_3SiCl as substrates [2], we extended this method to different mono- and oligosilanes, thus yielding a variety of iron substituted silyl compounds (Tab. 1):

$$2\ R_3SiCl\ + Fp_2 \xrightarrow{\text{i, Mg}} 2\ \text{Fp-SiR}_3\ + MgCl_2$$

Tab. 1: Results of electrolyses with Fp_2

silane	product	Yield [%]
Me_3SiCl	Fp-SiMe_3	66
Me_2SiCl_2	$\text{Fp-SiMe}_2\text{Cl}$	57
$MePhSiCl_2$	Fp-SiMePhCl	54
Ph_2SiCl_2	$\text{Fp-SiPh}_2\text{Cl}$	49
$ClMe_2SiSiMe_2Cl$	$\text{Fp-Me}_2\text{SiSiMe}_2\text{Cl}$	60
$ClMe_2SiSiMe_2Cl$	$\text{Fp-Me}_2\text{SiSiMe}_2\text{-Fp}$	62
$PhMe_2SiSiMe_2Cl$	$\text{Fp-Me}_2\text{SiSiMe}_2\text{Ph}$	62
$(Me_3Si)_3SiCl$	$\text{Fp-Si(SiMe}_3)_3$	65

Upon upscaling of the reaction in order to get isolable amounts of products, however, we observed, that far less than the stoichiometric amount of electrons (2 $Fmol^{-1}$) is needed to achieve complete conversion. Obviously, the reaction is catalyzed by the electrochemically induced activation of Mg.

References:

[1] see for example and references therein: a) C. Moreau, F. Serein-Spireau, M. Bordeau, C. Biran, *Organomet.* (2001) **20**, 1910; b) T.Shono, H. Ohmizu, S. Kawakami, H. Sugiyama, *Tetrahedron Lett.* (1980) **21**, 5029; c) A. Kunai, T. Kawakami, E. Toyoda, T. Sakurai, M. Ishikawa, *Chem.Lett.* (1993) 1945
[2] J.Ruiz, F.Serein-Spireau, P.Atkins, D.Astruc, *C.R.Acad.Sci., Ser. IIb: Mec., Phys., Chim., Astron.* (1996) **323(12),** 851