Access to Stabilized Silyl Anions by Electroreduction of Chlorosilanes

C. Duprat, C. Biran,* M. Bordeau,* T. Constantieux, P. Gerval and J. Dunoguès

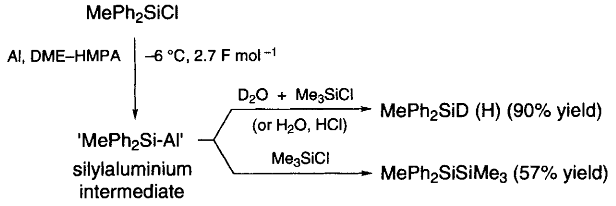
Laboratoire de Chimie Organique et Organométallique, URA, 35 CNRS, Université Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex, France

Using the sacrificial anode technique, the electroreduction of arylchlorosilanes into the corresponding arylhydrosilanes occurs *via* a silylaluminium intermediate characterized for the first time in such reactions.

The electrochemical reduction of chlorosilanes, particularly using the sacrificial anode technique, has been widely developed in recent years for the synthesis of polysilanes, which are important as new potential industrial raw material.[1] The general scheme proposed for the formation of the Si–Si bond involves the cathodic generation of a silyl anion which is subsequently trapped by excess of chlorosilane. Under these conditions, the formation of silyl organometallic intermediates has not previously been reported in the literature, although compounds having carbon–metal bonds were detected by ^{19}F NMR in the reduction of CF_3Br with copper, cadmium or zinc anodes.[2,3]

From methyldiphenylchlorosilane, chosen as a model, and using a special procedure (sacrificial Al anode, undivided cell, high dilution, continuous reactant addition, temperature under 0 °C), it was possible to avoid the coupling reaction leading to the symmetrical disilane, by trapping the silyl anion as a silylaluminium intermediate. The latter was obtained as an oily compound which was characterized by the formation of $MePh_2SiD$ upon deuteriolysis, and by the formation of the unsymmetrical disilane $MePh_2SiSiMe_3$, after reaction with Me_3SiCl.

In a typical procedure, the electrolysis of methyldiphenylchlorosilane (5.6 g, 0.024 mol) was carrfied out at −6 °C, under an inert atmosphere of argon or nitrogen, in 1,2-dimethoxyethane (DME) (88 ml) containing 10% of hexamethylphosphoramide (HMPA) (8 ml) as the complexing cosolvent and Et_4NBF_4 (5.10^{-3} mol dm^{-3}) as the supporting electrolyte. The undivided cylindrical glass cell (100 ml) was thermostated and fitted with an aluminium bar (1 cm diameter) as the anode and a concentric stainless steel grid (1.0 + 0.2 dm^2 surface area of the wires), as the cathode. A constant current (0.1 A, density 0.1 ± 0.05 A dm^{-2}) was provided by a SODILEC EDL 36-0.7 regulated DC power supply. DME was dried over sodium benzophenone ketyl. Residual traces of water in the electrolytic medium were removed by addition of a small amount of trimethylchlorosilane: the consumpton of Me_3SiCl by hydrolysis (giving $Me_3OSiOMe_3$) was monitored by ^{1}H NMR. Methyldiphenylchlorosilane, previously distilled and stored over magnesium powder, was then introduced into the cell through a septum with an automatic syringe. The flow of chlorosilane was adjusted to the current intensity (3.9×10^{-7} mol s^{-1}; i = 0.1 A). Under these conditions, the chlorosilane concentration remained low and constant during the whole electrolysis and the coupling reaction between the silyl anion and the chlorosilane was limited. After passing 2.7 F mol^{-1} (0.7 F mol^{-1} excess due to non quantitative faradaic yield), the solvent was evaporated and the organometallic intermediate was characterized by its deuteriolysis or hydrolysis products, $MePh_2SiD$ or $MePh_2SiH$, or by its reaction with trimethylchlorosilane (Scheme 1).



Scheme 1

The crude product can be stored for several weeks under an inert, dry atmosphere without decomposition. A preliminary study by ^{1}H NMR of this crude product was carried out after eliminating the salts by adding anhydrous pentane, filtering off and evaporating the solvent. ^{1}H NMR data in C_6D_6 showed a sharp methyl signal at δ 0.9. After hydrolysis of the sample with D_2O, the sole detected product was $MePh_2SiD$. Extensive ^{29}Si and ^{27}Al NMR studies are in progress. The titration of aluminium by iodine according to the method of Bartkiewicz and Robinson[4] and of chlorine (Volhard's method[5]) indicated the presence of Al (5%) and Cl (5%), in good agreement with the stoichiometry 2Al : $3SiMe_2Ph$: 2Cl for the main species.

When the electroreduction was performed with a stainless steel anode, the reduction of $MePh_2SiCl$ did not occur; the major part of the chlorosilane was recovered, after hydrolysis, as the corresponding silanol and siloxane. However, if a large excess of $AlCl_3$ was added before the electrolysis, the reduction occurred and led to 35% of $MePh_2SiH$ and 30% of $(MePh_2Si)_2$.

The electrolysis of Ph_3SiCl and $PhMe_2SiCl$ solutions was carried out according to the same procedure. The yields of the corresponding hydrosilanes Ph_3SiH and $PhMe_2SiH$ were 50% and 51.5% respectively.

C.N.R.S., Ministère de l'Education Nationale and Région Aquitaine are acknowledged for their financial assistance.

Received, 27th June 1995; Com. 5/04143K

References

1 M. Bordeau, C. Biran, M.-P. Léger-Lambert, F. Spirau and D. Deffieux, *ACS Symp. Ser., Inorganic and Organometallic Polymers II,* 1994, **572**, 18 and references cited therein.
2 J.-M. Paratian, E. Labbé, S. Sibille, J.-Y. Nédélec and J. Périchon, *J. Organomet. Chem.*, 1995, **487**, 61.
3 J.-M. Paratian, E. Labbé, S. Sibille and J. Périchon, *J. Organomet. Chem.*, 1995, **489**, 137.
4 S. A. Bartkiewicz and J. W. Robinson, *Anal. Chim. Acta*, 1959, **20**, 326.
5 G. Charlot, *Les méthodes de la chimie analytique quantitative minérale*, Masson et Cie, *Paris*, 1961, p. 683.