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Preliminary communication

REACTION OF 2,4,6-TRI-t-BUTYLPHENYLLITHIUM WITH BROMOTRICHLOROSILANE. GENERATION OF TRICHLOROSILYLLITHIUM, $LiSiCl_3$

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Summary

Trichlorosilyllithium, $LiSiCl_3$, is formed by reaction of bromotrichlorosilane with 2,4,6-tri-t-butylphenyllithium or mesityllithium. It is detected as trichlorosilane which is obtained by protonation and characterized by a ^{29}Si NMR shift of 30.9 ppm. Its stability is evaluated.

Bromotrichlorosilane reacts with sterically sufficiently hindered organolithium derivatives in a metal halogen exchange reaction to give trichlorosilyllithium, $LiSiCl_3$.

We became involved with this problem when we tried to obtain 2,4,6-tri-t-butylphenylchlorosilanes by interaction of 2,4,6-tri-t-butylphenyllithium with silicon tetrachloride, the methylchlorosilanes or trichlorosilane. These reactions in no case led to the formation of a silicon–carbon bond. In accordance with the results of Weidenbruch and Kramer, who independently did the same experiments [1], we also observed the formation of 1,3,5-tri-t-butylbenzene as a main reaction product. Its formation is the result of the reaction of the highly reactive organolithium compound with the solvent, tetrahydrofuran. But ^1H NMR spectroscopic monitoring of the reaction of 2,4,6-tri-t-butylphenyllithium with silicon tetrachloride revealed that continually changing quantities of 2,4,6-tri-t-butylbromobenzene were formed. This was independent of the method of preparation of the organolithium compound, either made in the common way by reaction of 2,4,6-tri-t-butylbromobenzene with n-butyllithium in tetrahydrofuran [2], or for the first time, to our knowledge, by an ultrasonically induced direct interaction of 2,4,6-tri-t-butylbromobenzene with lithium at room temperature in ether/tetramethylethylenediamine. The formation of 2,4,6-tri-t-butylbromobenzene is understood on the basis of a metal-halogen exchange reaction between the organolithium derivative and bromotrichlorosilane, which is formed in a preceding equilibrium from silicon tetrachloride and ionic bromide.

The consequently expected formation of trichlorosilyllithium was confirmed by interaction of 2,4,6-tri-t-butylphenyllithium with bromotrichlorosilane (eq. 1). The

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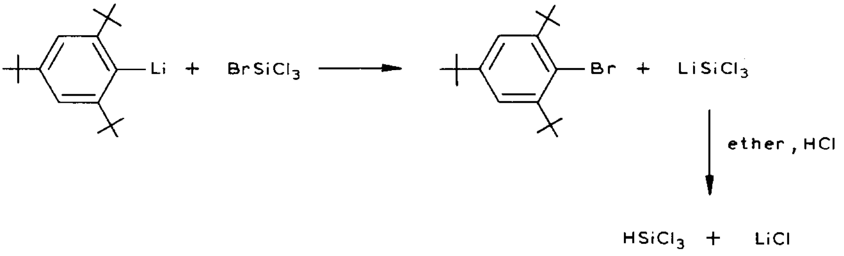


(1)

reaction proceeds to completion at −78°C in tetrahydrofuran within 30 min. The reaction path is monitored spectroscopically (^{1}H NMR) by way of the trichlorosilane proton appearing after protonation of $LiSiCl_3$ with ethereal hydrogen chloride. Furthermore, this way also allows the consumption of the organolithium compound and the production of 2,4,6-tri-t-butylbromobenzene to be followed (chemical shifts of the aromatic ring protons in THF/ether: 2,4,6-tri-t-butylphenyllithium δ 6.94 ppm; 2,4,6-tri-t-butylbromobenzene δ 7.37 ppm: 1,3,5-tri-t-butylbenzene δ 7.20 ppm). The yield of $LiSiCl_3$ determined from ^{1}H NMR spectroscopy is approx. 60%.

This technique of conversion of the $LiSiCl_3$ into trichlorosilane was also used for an evaluation of the thermal stability of trichlorosilyllithium, which was found to slowly decompose precipitating lithium chloride and presumably the formation of perchloropolysilanes. The half-life of $LiSiCl_3$ in THF/ether at room temperature was found in this way to be approx. 62 h.

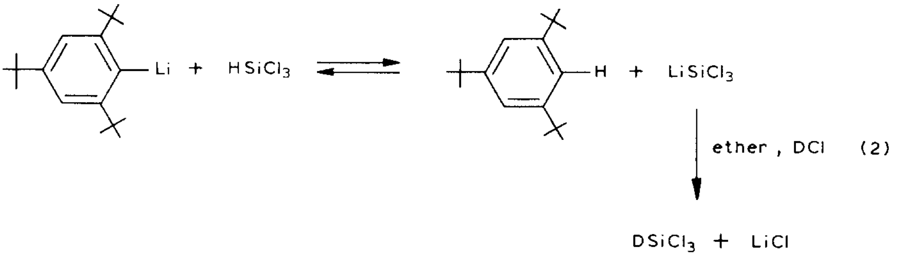
^{29}Si NMR studies of the $LiSiCl_3$-THF/ether solution showed one signal at δ 30.9 ppm (standard TMS). This value roughly fits the expectations from the U-shaped dependence of silicon-29 chemical shifts on the sum of the electronegativities of the four substituents reported by Spialter et al. [3]. But owing to the dilution of the reaction mixture investigated and the general problems in performing ^{29}Si NMR studies we consider this to be a tentative assignment. Decomposition products could not be detected.

Metal-halogen exchange reactions are principially known in organosilicon chemistry and were observed occasionally as side reactions in interactions of organolithium metal derivatives with organic halides [4]. The factors governing this exchange are obviously similar to those which apply to conventional organolithium compounds [5]. So it is easily understood that only the bromine atom of bromotrichlorosilane is exchanged, whereas silicon tetrachloride does not give the reaction. Moreover, the fact that in the reaction discussed above the exchange was observed only in case of the reaction of the organolithium reagent with bromotrichlorosilane, i.e. when silicon tetrachloride had been applied, however, that methylchlorosilanes behave indifferently, can be due to the relatively high stability of the trichlorosilyl anion.

These observations and discussions are in complete agreement with results obtained by Benkeser et al., who in 1970 reported that trichlorosilane $HSiCl_3$ is completely deprotonated by t-amines in acetonitrile to give salts containing the trichlorosilyl anion, whereas methylchlorohydridosilanes could not be converted into their corresponding bases [6]. In these cases the stability of the $SiCl_3$ anion is obviously also decisive for the course of the reaction.

Attempts to use less complex and more conveniently available organolithium derivatives for the preparation of trichlorosilyllithium gave the following results; isopropyllithium, n-butyllithium and phenyllithium react with bromotrichlorosilane only by nucleophilic substitution at the silicon centre. t-Butyllithium, even at −110°C in THF/pentane, did not undergo the exchange, i.e. after protonation with ether/HCl no chlorosilane could be detected. Beside 2,4,6-tri-t-butylphenyllithium, only mesityllithium gave satisfactory yields of trichlorosilyllithium.

From a preparative point of view direct metallation of trichlorosilane by metal-hydrogen exchange would be particularly interesting. But here one encounters the same problems which have already become apparent in the metal-halogen exchange reactions studied. Experiments with trichlorosilane and n-butyllithium, t-butyllithium and mesityllithium showed that in the competition between nucleophilic substitution at the highly electrophilic trichlorosilane and deprotonation of the acidic $HSiCl_3$ substitution reactions generally dominate. Only 2,4,6-tri-t-butylphenyllithium with trichlorosilane at −78°C in THF gives at least a partial metal-hydrogen exchange. This was shown by decomposition of the $LiSiCl_3$ in ethereal deuterium chloride and infrared investigation of the mixture of $HSiCl_3$ and $DSiCl_3$ distilled off (eq. 2). The intensities of the Si-H and Si-D absorptions, respectively, refer to an approx. 50% lithium-hydrogen exchange. In all the other cases no $DSiCl_3$ could be detected. In the ^1H NMR spectrum the disappearance of the $HSiCl_3$ proton signal after addition of 2,4,6-tri-t-butylphenyllithium to the trichlorosilane solution and reappearance of the signal after addition of ethereal HCl proved that metal-hydrogen exchange and formation of trichlorosilyllithium had occurred.



These results are understood to be a consequence of the extreme steric shielding of the 2,4,6-tri-t-butylphenyl substituent which obviously avoids nucleophilic attack of the organolithium reagent at the silicon atom of trichlorosilane and allows the 2,4,6-tri-t-butylphenyllithium to show only its basic properties.

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