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PRELIMINARY COMMUNICATION

N-DILITHIOPENTAFLUOROANILINE AND SOME SILICON AND GERMANIUM ORGANODERIVATIVES

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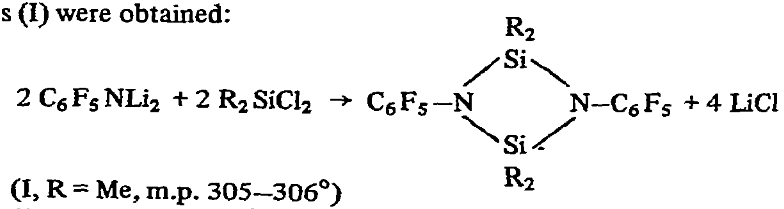
In recent years the chemistry of silicon–nitrogen compounds, particularly cyclosilazanes, has been a subject of considerable interest and was intensively investigated (see refs. 1–3 for review), mainly in connection with the search for thermostable polymers. Promising results have been achieved by linking cyclodisilazane rings through aromatic bridges attached to nitrogen[4]. In general, nitrogen substitution in organosilazanes is a feature known to contribute to increased thermal and hydrolytic stability of this type of compound.

We report now the preparation of some model compounds, containing pentafluorophenyl groups attached to nitrogen in some silazanes and a germazane. Since our attempts to prepare such compounds by the direct reaction of some chloroorganosilanes with pentafluoroaniline failed, we adopted another approach: namely, the metalation of pentafluoroaniline at nitrogen sites, followed by the reaction with the appropriate chlorosilane or -germane. Pentafluoroaniline can be readily metalated★★ with n-butyllithium in tetrahydrofuran, at –70°:

$$C_6F_5NH_2 + 2\ \text{n-BuLi} \rightarrow C_6F_5NLi_2 + 2\ \text{n-BuH}$$

At a low temperature *N*-dilithiopentafluoroaniline is a crystalline precipitate, but it was derivatized *in situ*, without isolation, with various chloroorganosilanes. Monofunctional chloroorganosilanes gave *N*-pentafluorophenyl disilazanes, *e.g.*, $C_6F_5N(SiMe_3)_2$, b.p. 60°/0.5 mm Hg, whereas with difunctional chloroorganosilanes, good yields of cyclodisilazanes (I) were obtained:



(I, R = Me, m.p. 305–306°)
(I, R = Ph, m.p. 296°)

(I)

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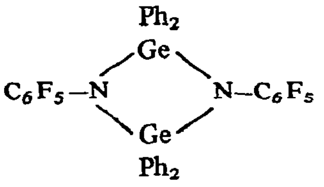
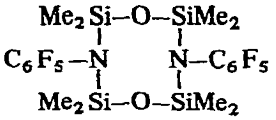
★★For metalation with sodium hydride, see ref. 5.

In a similar way, with diphenyldichlorogermane a cyclodigermazane (II), m.p. 331–332° was prepared which, according to our best knowledge, is the first four-membered germanium–nitrogen ring to be reported.

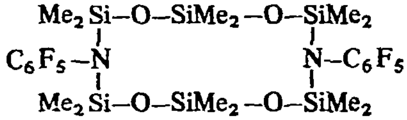


(II)

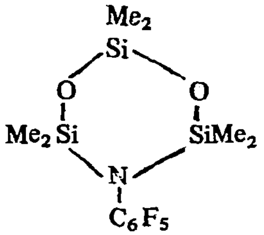
Related reactions with oligomeric α,ω-dichlorodimethylsiloxanes were used to prepare several *N*-pentafluorophenylcyclosilazoxanes, (III–V), and the cyclosilazane (VI).



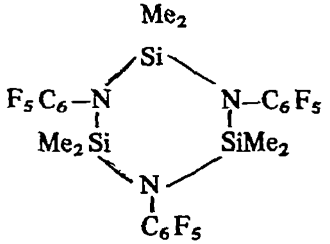
(III, m.p. 107–108°)



(IV, m.p. 117–118°)



(V, m.p. 42°)



(VI, m.p. 168°)

All compounds reported had satisfactory elemental analyses and the molecular weights were determined by mass spectrometry. The cyclosilazanes and cyclosilazoxanes melt without decomposition and show no sign of hydrolysis after prolonged exposure to atmospheric moisture. Decomposition temperatures were found to lie in the range 400–450°.

In comparative experiments we found that aniline can also be dimetalated at nitrogen when treated with two equivalents of n-BuLi in THF or hexane, and $PhNLi_2$ thus formed reacted with dimethyldichlorosilane, to give the known *N,N'*-diphenyltetramethylcyclodisilazane[6]. Monolithiation of aniline, to give PhNHLi was used recently in the preparation of some silicon and germanium derivatives[7].

The results of this work suggest that *N*-dilithiopentafluoroaniline is a versatile reagent which can be successfully used in the synthesis of cyclic and linear C_6F_5–N derivatives of silicon, germanium, and possibly other elements, such as boron, phosphorus, arsenic or sulphur.

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