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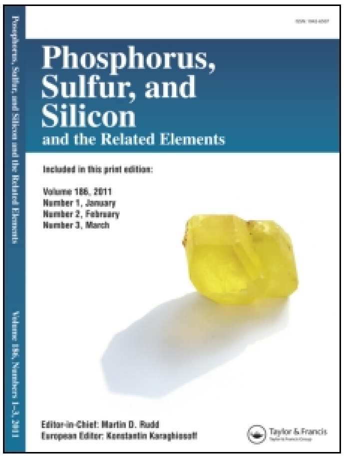

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Silylhydrazines Lithium-Derivatives, Isomerism, Rings

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SILYLHYDRAZINES
LITHIUM-DERIVATIVES, ISOMERISM, RINGS

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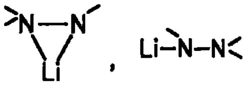
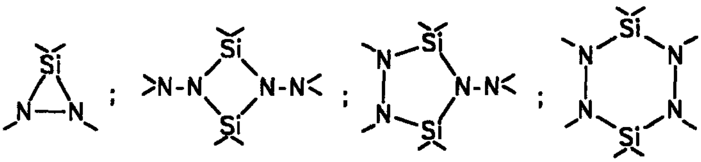
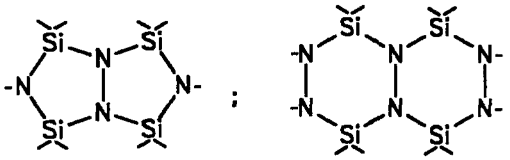
Abstract Lithium-derivatives of hydrazines are obtained by the reaction of BuLi with hydrazine. Lithium is bonded both, side-on and end-on in these silylhydrazines.



Depending on the reaction conditions, the molar ratio, and the bulkiness of the substituents, three-, four-, five-, and six-membered cyclic silylhydrazines are formed by the reaction of lithiated silylhydrazines with fluorosilanes.



Fluoro- and hydrogenfunctional rings are excellent presursors for bicyc lic systems.



Reactions and X-ray analyses are discussed.

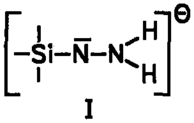
The syntheses of the first acyclic and cyclic silylhydrazines were reported by Aylett and Wannagat in 1956 - 1958.[1] Normally two isomers are formed, e.g. in the reaction of chlorotrimethylsilane and hydrazine the symmetric and asymmetric bis(trimethylsilyl)hydrazines

$(Me_3Si)_2N\text{-}NH_2$, $Me_3SiNHNHSiMe_3$

Primary silylhydrazines with R=Me, Et, or Pr cannot be isolated, as they immediately undergo further condensation to bis(silyl)hydrazines with elimination of hydrazine. For the isolated $Ph_3SiNHNH_2$, this condensation occurs under more drastic conditions at 90°C[1].

Recently we were able to show that primary and fluorofunctional silylhydrazines can be kinetically stabilized by the use of bulky tert-butyl groups. Lithium derivatives of these hydrazines allow a stepwise synthesis of cyclic silylhydrazines[2].

The lithium derivative of di-tert-butylmethylhydrazine crystallizes as a hexamer with Li^+ ions bound side-on and end-on. The crystal structure of this compound exhibits two tautomeric silylhydrazide units I and II[3].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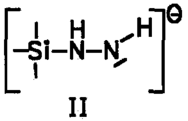
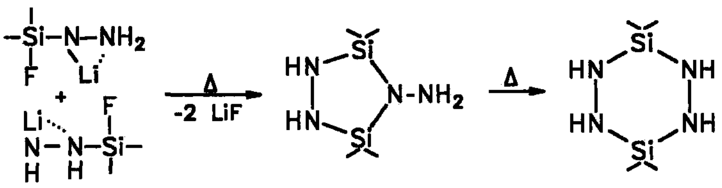
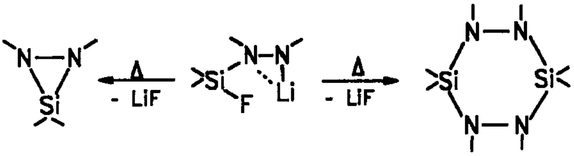

II

This phenomenon accounts for the isomerizations during secondary substitutions[4], and now it is understandable that lithium derivatives of fluorosilylhydrazines are excellent precursors of five-membered rings.

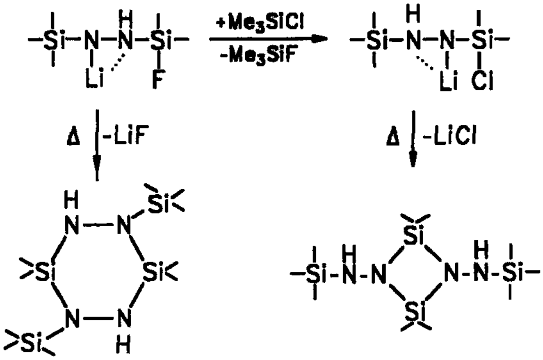


The lithium derivative of bis(tert-butyldimethylsilyl)hydrazine crystallizes as a dimer with two LiN_2-three- and one $(LiN)_2$-four-membered ring.

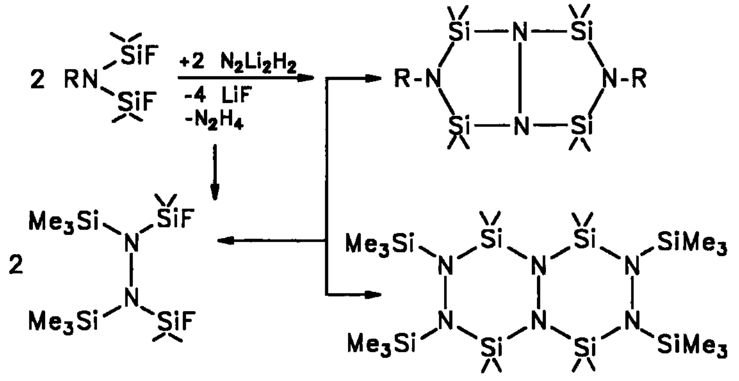
Theoretically salt elimination from lithiated N-silyl-N'-fluorosilylhydrazines should lead to the formation of three-, four-, or six-membered rings. We examined the LiF elimination of fluorofunctional lithium-N,N'-bis(silyl)hydrazines and isolated, depending on the bulkiness of the substituents three- and six-membered rings.



A cyclisation with formation of a four-membered ring has not been achieved via LiF elimination from lithiated N(silyl)-N'-fluorosilylhydrazines. A quantitative fluorine-chlorine exchange occurs in the reaction of some of these lithium derivatives with $ClSiMe_3$ and LiCl-elimination leads to the formation of isomeric four-membered cyclic silylhydrazines.

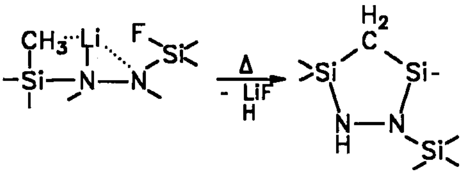


Like bis(fluorosilyl)amines, which are excellent precursors for five-membered mono- and bicyclic rings, bis(fluorosilyl)hydrazines are excellent precursors for mono- and bicyclic six-membered rings.



The lithium derivative of tris(trimethylsilyl)hydrazine crystallizes as dimer, too. It forms a four-membered Li-N ring. Lithium is both side-on and end-on coordinated. The coordination sphere of lithium is saturated with very short CH_3-Li-contacts.

Once again there are several possibilities for ring closure reactions of fluorofunctional tris(silyl)hydrazines. If the substituents are too bulky to be bonded on three-, five-, or six-membered rings, LiF-elimination leads to the formation of a carbon-silicon bond, and a five-membered N_2Si_2C ring is formed.



This mechanism of cyclisation was previously unknown in silicon-hydrazine chemistry.

REFERENCES

1. U. Wannagat, Adv. of Inorg. Radiochem., 6, 225 (1964).
2. C. Drost and U. Klingebiel, Chem. Ber., 126, 1413 (1993).
3. S. Dielkus, C. Drost, R. Herbst-Irmer, and U. Klingebiel, Angew. Chem. Int. Ed. Engl., 32, 1625 (1993).
4. R. West, Adv. Organomet. Chem., 16, 1 (1977).