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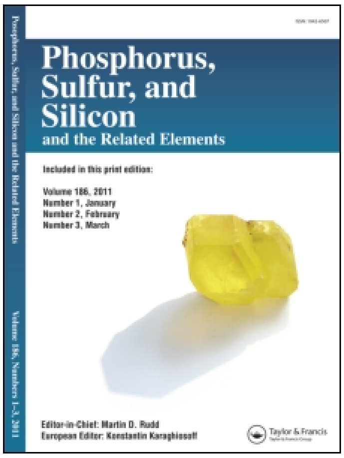

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Reactions of Organosiloxanes and Silicon Monoxide

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Lithium salts of primary amines react readily with organosiloxanes, cleaving the Si-O bonds to produce amidosiloxanes of the form $[\{RN(H)\}Si(Me)_2O]^-$ as lithium salts. These amidosiloxanes aggregate forming large cage complexes, several of which are described herein.

Keywords: siloxanes; lithium amides; silicon monoxide

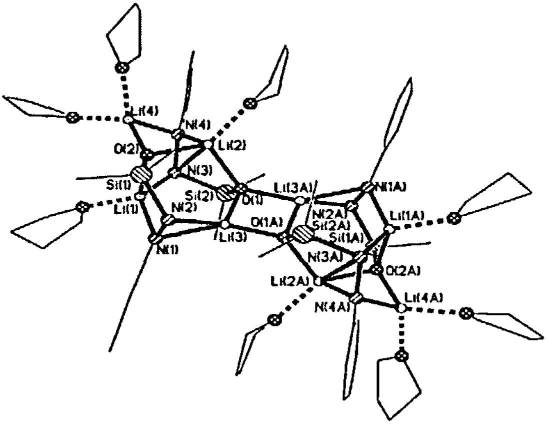
Lithium reagents have commonly been prepared *in situ* for organic synthesis for many years. More recently isolation and characterisation of the intermediate species has been achieved and structural principles determined. This important area has been the subject of several review articles.[1]

In 1994 Herberich *et al.* reported the cleavage of siloxanes of vacuum greases by lithium amides.[2]

$$2(Me_2SiO)_3 + 6LiNMe_2 \xrightarrow{THF} [LiOSiMe_2(NMe_2)]_6$$

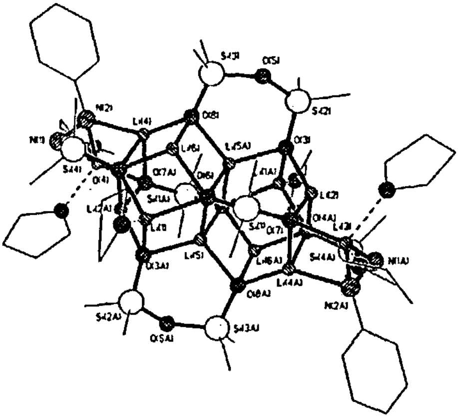
This observation is surprising given the strength of the Si-O bond within a siloxane. We have seen similar reactivity but have observed additional twists which indicate that the chemistry is far more intricate than may appear at face value.

Dilithiated phenylhydrazine reacts with $(Me_2SiO)_3$ in a 3:1 ratio producing two novel crystalline complexes **(1)** and **(2)**. Complex **(1)** formed in the stoichiometry of the reactants, the lithium amide has cleaved the siloxane into (Me_2SiO) units forming the amidosiloxane $[Me_2Si(O)N(H)\text{-}N(Ph)]_2^{2-}$ prior to aggregation. The product consists of two identical cages bound electrostatically by the lithium atoms and sharing a Li_2O_2 ring between the cages.



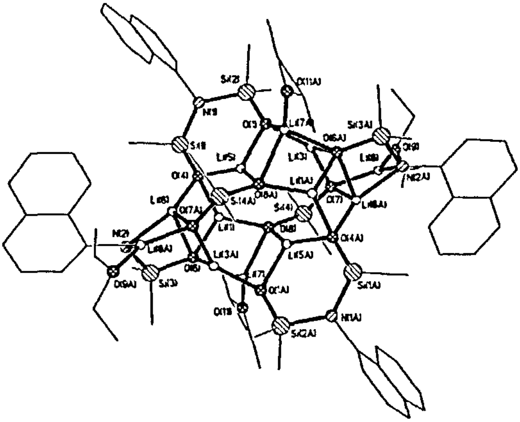
Complex **(1)**

Complex **(2)** consists of two hexagonal prisms linked through a shared Li_2O_2 face and capped by a lithium atom. Unlike complex **(1)** complex **(2)** bears little resemblance to the stoichiometry of reactants. The different outcome of the same reaction leading to either complex **(1)** or **(2)** suggests there may be many different species present in solution.



Complex (2)

$(Me_2SiO)_3$ reacts with dilithiated α-napthylamine, crystallisation from a THF hexane mixture (5:1) yielded complex (3) a large open cage structure, with 2 SiO species per Li_2NR unit, stabilised by ten lithium atoms.



Complex (3)

Currently research into the reaction of silicon monoxide with lithium amides is being undertaken. Commercial SiO is an intimate mixture of silica and silicon[3]; using a rotating cryostat[4] we produce SiO in the vapour phase as a high temperature highly reactive silylene. Little is reported in the literature regarding silicon monoxide.[5] Reactions to date have yielded small quantities of crystalline products, the chemistry of which are currently under investigation.

In conclusion, several interesting and complex structures result from this work. However, it is evident that in solution there are many complex units resulting from nucleophilic cleavage of the cyclotrisiloxane. Identifying and rationalising the precise nature of the products remains the biggest challenge of this work.

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