Silole and Its Anions

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Introduction

Silole (Figure 1) is the five-membered heterocyclic compound that contains a silicon atom and a butadiene unit. It is also named as silacyclopentadiene based on IUPAC rules. Silole has been of considerable interest, since its anion is considered to possess aromaticity and may be used as a 5η-silacyclopentadiene ligand.[1] This is especially reasonable if one realizes that the silole anion is an analog of the cyclopentadiene anion and the latter is a completely delocalized π-system and has the richness and diversity of chemistry of transition metal complexes.

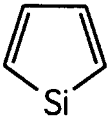


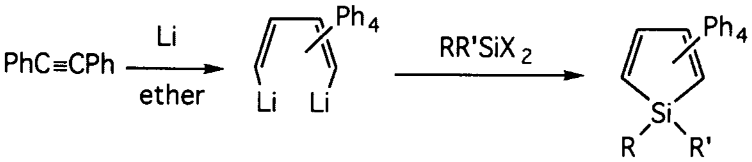
Figure 1

Since the synthesis of the first silole, 1,1,2,3,4,5-hexaphenylsilole,[2] was reported in 1959, the chemistry of silole has developed significantly. At the present time, several methods to such a compound are known and a series of silole derivatives have been synthesized.[3] The evidence of partial aromaticity of the silole monoanion,[4] X-ray structure of the silole dianion,[5] and the first transition-metal 5η-silacyclopentadienyl complex[6] have also been reported.

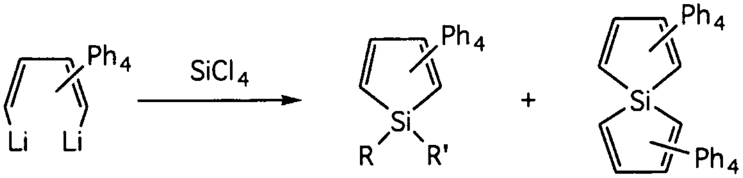
Synthetic Methods

1. C-Substituted Silole

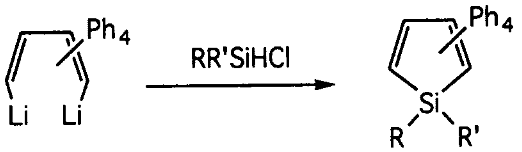
Cyclization of 1,4-dilithio-1,2,3,4,-tetraphenyl-1,3-butadiene (DLTPB)



This method allowed the preparation of the first silole and was applied to the synthesis of a series of other compounds with different substituents on the silicon. Usually, the corresponding siloles are formed in good yield when DLTPB reacts with di- or trihalogenosilanes. The use of $SiCl_4$, however, generates not only dichlorosilole, but also the spiro derivative.[7]

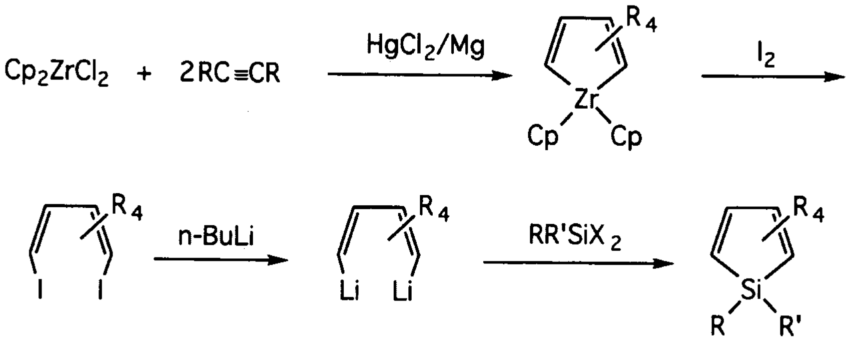


Even the hydride in functional silanes can be used as a leaving group in this type of reaction. Thus, treatment of DLTPB with an hydridochlorosilane also gives siloles in good yield.[8]



Cyclization of 1,4-dilithio-1,2,3,4,-tetraalkyl-1,3-butadiene (DLTAB)

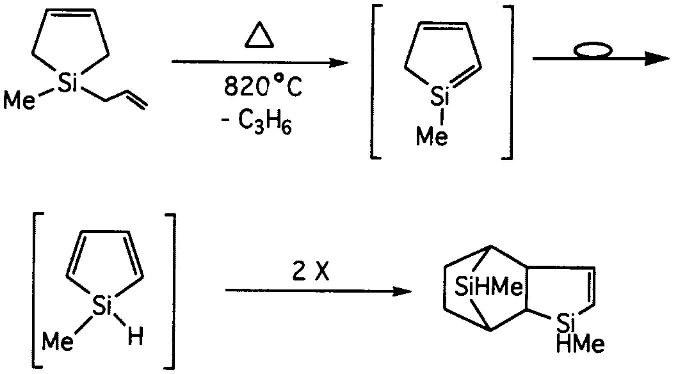
The above method is very successful for the preparation of the tetraphenyl derivatives. Other substituted siloles, however, can not be synthesized via this route, since the corresponding dilithium reagents can not be generated from the reaction of corresponding acetylene and lithium. Therefore, the following metal-halogen exchange approach offers a practical alternative.[9]



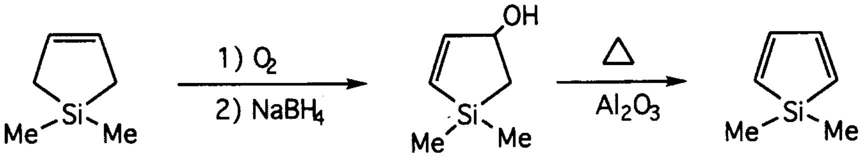
R = Me and Et

2. C-Unsubstituted Silole

The synthesis of C-unsubstituted silole has been pursued by a number of research groups and has proven to be one of the most interesting challenges. The first C-unsubstituted silole, 1-methylsilole, was prepared by Barton et al in 1979. It was generated by flash vacuum pyrolysis of 1-allyl-1-methyl-1-silacyclopenta-3-ene and could only be identified as its dimer.[10]



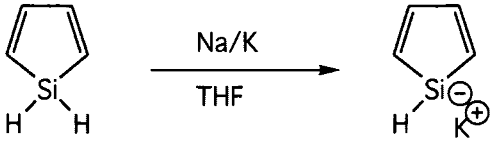
The monomeric C-unsubstituted silole, 1,1-dimethylsilole, was obtained simultaneously by Barton[11] and Laporterie[12] in 1981. It was produced by dehydration of 1,1-dimethyl-1-silacyclopent-4-n-3-ol in the gas or liquid phase at elevated temperatures. The C-unsubstituted silole remains difficult to synthesize and no important chemistry of this interesting system has been reported.



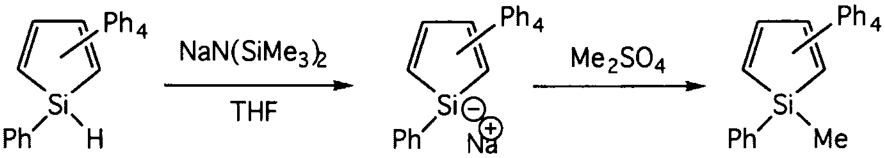
Monoanions and Dianions.

1. Monoanions

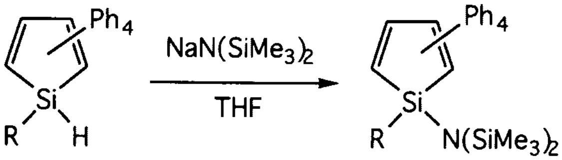
Benkeser and co-workers claimed to have prepared the first silole anion by treating the silole with potassium in THF,[13] but later reported that this experiment could not be repeated.[14]



Rühlmann described that 1,2,3,4,5-pentaphenylsilole, when reacted with the bases sodium hexamethyldisilazide or phenyllithium, undergoes deprotonation to give the silole anion.[15] He also reported the isolation of the methyl derivative from the reaction of the silole anion with methyl sulfate.[16]

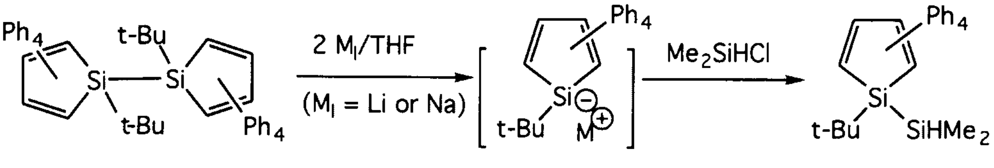


Pan and Boudjouk, et. al. examined the same reaction finding no evidence for the deprotonated species, but observed the substituted products instead.[17]



Reaction of 1-chloro-1,2,3,4,5-pentaphenylsilole with lithium leads to unstable species that react with chlorotrimethylsilane in the manner expected for 1-chloro-1,2,3,4,5-pentaphenylsilole anion.[18]

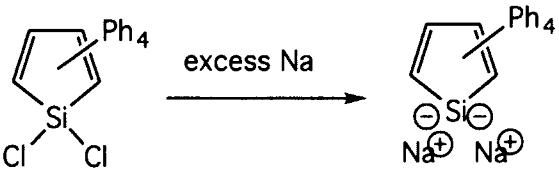
The noncontroversial synthesis and characterization of silole anions was finally accomplished by Hong and Boudjouk in 1993.[19] I was generated by cleavage of an Si-Si bond in bis(1-tert-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene) with alkali metals. NMR studies suggest delocalization of the negative charge in I onto the butadiene moiety and indicate I possessing significant aromaticity.



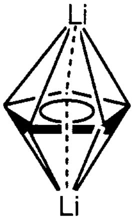
I

2. Dianions

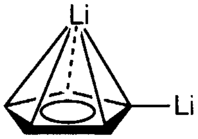
Although the studies on silole dianions began in recent years, their synthesis and characterization are now well established. The preparation of first silole dianion was reported by Joo et. al. in 1990.[20] It was generated from the reaction of 1,1-dichloro-2,3,4,5-tetraphenylsilole with excess sodium in THF and isolated as a purple solid.



Recently two isomers of silole dianions have been prepared and characterized by X-ray crystal structure determination. One isomer is an η^5-η^5 binding model **II** and the other is η^5-η^1 binding species **III**.[21,22] NMR and X-ray studies show that both types of silole dianions are aromatic and the negative charges are more delocalized than those of the monanions.



II



III

Summary

This brief review introduces synthetic aspects of siloles, including silole monoanions and dianions. Not covered in this review of silole is its unique electronic structure and the lower LUMO energy level. These properties provide siloles with opportunities to become the useful materials. Recent research shows that silole derivatives can be used as efficient electron transporting materials[23]. Silole-containing polysilane[24] is a new type of material. Significant developments in this area can be expected soon.

References

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