

学位論文の要約

題目 Synthetic Studies towards Unexplored Multiple Bonds to Silicon
Utilizing Kinetic Stabilization
(速度論的安定化を利用した未踏ケイ素多重結合化学種の合成研究)

氏名 Julius Adrie Aguirre Garcia

序論

The chemistry of multiply bonded compounds between heavier group 14 elements has considerably developed to date. However, highly reactive silicon compounds such as silynes and several silenes purely stabilized by taking advantage of steric protection remain difficult to obtain due to the synthetic limitations in accessing possible precursors. In this study, the author presented the challenges and possible solutions in obtaining these elusive compounds by using a combination of Tbt and terphenyl groups as protecting groups to the reactive centers. In chapter 2, the author described the newly found 1,4-silyl group migration from carbon to carbon which arises from the attempts to synthesize benzylic silanes bearing TbtCH₂ group. In chapter 3, the author described the attempted synthesis of a dihalogenated silane bearing a bulky terphenyl group which should be an excellent precursor for the target silyne as well as other novel highly reactive silicon compounds. In chapter 4, the author described the synthesis and structure of a novel, kinetically stabilized 2,2-dihydrosilenes.

A Unique Silyl Group Migration from Carbon to Carbon.

Organosilicon compounds bearing a reactive site such as Si-X (X = Halogen atom) are very important precursors for various type of low-coordinated organosilicon compounds such as silynes. In order to synthesize a silyne, a 1,1,2,2-tetrahalogenated silane should be a good precursor. The author expected that the reaction of a 1,1,2,2-tetrahalogenated silane with various reducing agents will help him to obtain the desired silyne. In order to obtain a 1,1,2,2-tetrahalogenated silane, a proper benzylic silane precursor must be synthesized. However, in attempts to synthesize a benzylic silane, a unique silyl group migration occurred. This study described an unexpected but novel 1,4-silyl group migration from carbon to carbon which arises from the attempts to synthesize a 1,1,2,2-tetrahalogenated silane bearing Tbt group. This rearrangement is made possible by the intermediacy of a 5-membered silicate.

Studies Towards Attempted Synthesis of Novel Highly Reactive Silicon Compounds Bearing Terph^{t-Bu}CH₂ and 2,6-Diisopropyl groups.

Terphenyl groups are known to be effective in stabilizing homonuclear triply bonded compounds containing heavier group 14 elements. However, these ligands have never been used in the stabilization of heteronuclear triply bonded compounds containing a silicon atom. With this, the author decided to use this ligand but with minor alterations in order to synthesize a universal precursor which can be used for various types of highly reactive silicon compounds. Guided by the previous results reported by the laboratory to which the author belongs, the same synthetic approach might be useful in order to obtain a proper benzylic silane precursor which is necessary to acquire a 1,1-dihalogenated silane containing a terphenyl ligand. In this study, attempts to functionalize Terph^{t-Bu}CH₂ group were described by using a unique terphenyl ligand in which it can arrest both the head-to-tail coupling products as well as the head-to-head coupling products. Furthermore, the author described the attempts to synthesize a 1,1-dihalogenated silane bearing a Terph^{t-Bu}CH₂ group which can be used as a universal precursor for a wide array of highly reactive silicon compounds.

Synthetic Studies towards Kinetically Stabilized 2,2-Dihydrosilenes Bearing Tbt and 2,6-Diisopropyl groups.

In this study, the author presented the synthetic challenges towards a stable 2,2-dihydrosilene by utilizing the very own kinetically stabilized dilithiosilane, TbtDipSiLi₂, developed in Tokitoh's group. Since 2,2-dihydrosilenes are expected to be highly reactive due to less steric hindrance around the sp²-carbon atom, no stable example has been reported so far except for its generation on the basis of the products of trapping reactions.

In this chapter, a stable 2,2-dihydrosilene was successfully synthesized by the reaction of the corresponding dilithiosilane, TbtDipSiLi₂, with CH₂Cl₂. The formed 2,2-dihydrosilene was reasonably characterized by multinuclear NMR studies and X-ray crystallographic analysis. The silene was found to be stable in solution and in the solid state at room temperature for a long period of time and does not undergo usual dimerization upon recrystallization, suggesting that the steric protection used was sufficient enough. The observed values for spectroscopic analysis and certain parameters were further reinforced with proper level of theoretical calculations.