Research Article

Air-Stable Emissive Disilenes Protected by Fused-Ring Bulky “Rind” Groups

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1. Introduction

The design and improvement of substituents or ligands that play supporting roles in both fundamental and applied chemistry has been a key research theme for many years. In 1981, West and Yoshifuji introduced the concept of kinetic stabilization of the highly reactive Si=Si and P=P double bonds by bulky 2,4,6-trimethlphenyl (mesityl) and 2,4,6-tri-*tert*-butylphenyl (supermesityl) groups, as shown in Figure 1.[1,2] Thereafter, a large variety of unsaturated compounds of the heavier main group elements have been synthesized using the sterically bulky protecting groups.[3] For example, in organosilicon chemistry, silaaromatics (silabenzene),[4] trisilaallenes ($R_2Si{=}Si{=}SiR_2$),[5] and disilynes ($RSi{\equiv}SiR$)[6] have been successfully isolated by taking advantage of the steric protection with the appropriate bulky substituents. In 2011, we reported the synthesis and characterization of a cyclobutadiene silicon analog (tetrasilacyclobutadiene) with a planar rhombic charge-separated structure.[7]

Recent efforts have been directed toward investigating the incorporation of unsaturated bonds of the heavier main group elements into carbon π-conjugated systems, because of their potentially useful properties and unique functions, which might offer a way to new elemento-organic hybrid materials.[8] However, this chemistry always suffers from a dilemma. While the steric protection by the bulky groups is essential to stabilize the highly reactive heavier unsaturated bonds, it causes the π-conjugated framework to twist, which reduces the extension of the π-conjugation. A key for the further evolution of this chemistry is to certainly attain a well-defined substituent that can maintain the highly planar π-conjugated framework, as well as providing sufficient steric protection of the heavier unsaturated bonds. This manuscript describes newly developed bulky groups based on a fused-ring octa-R-substituted s-hydrindacene skeleton (Rind groups) and their application to the synthesis of novel air-stable emissive disilenes.

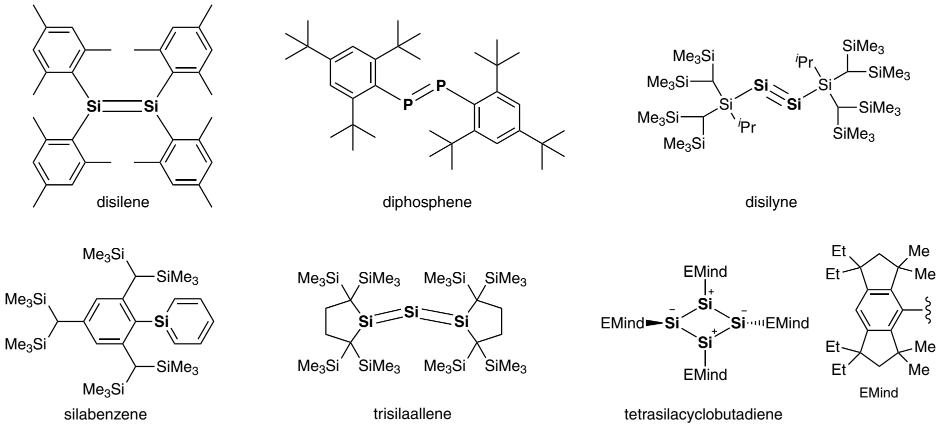

Figure 1. Examples of stable unsaturated compounds of the heavier main group elements.

2. Development of Rind groups

As shown in Figure 2, we have recently focused on the development of a new family of 1,1,3,3,5,5,7,7-octa-R-substituted *s*-hydrindacen-4-yl groups, called the "Rind" groups, where R stands for the initial of the substituents on the four benzylic positions.[9] Significant characteristics of the Rind groups are summarized as follows: (1) The Rind groups can be easily synthesized by the intramolecular Friedel-Crafts reaction. (2) A variety of R-substituents (R^1, R^2, R^3, and R^4) can be introduced at the benzylic positions of the *s*-hydrindacenyl skeleton. (3) The steric effects, and the size and shape variations of the Rind groups can be controlled by the proximate R^3 and R^4 substituents. (4) The physical properties, such as crystallinity or solubility, may be primarily attributable to the peripheral R^1 and R^2 substituents. (5) The Rind groups have a high chemical stability due to the full substitution at all the benzylic positions. (6) The Rind groups can offer an adequate space for the element (E) center; this space is only slightly restricted by the benzylic substituents as a consequence of the *freeze-rotation* fixed in the five-membered fused rings. (7) As another unique feature, the Rind groups have the unsubstituted *para*-position open for further functionalization, thus providing potentially useful *para*-phenylene types of difunctional compounds.

A series of octa-R-substituted bromo-*s*-hydrindacenes, (Rind)Br, can be prepared by a sequence of the Lewis acid catalyzed intramolecular Friedel-Crafts reaction, bromination and vice versa.[9] All the bulky aryl bromides, (Rind)Br, can be transformed into the corresponding bulky aryllithiums, (Rind)Li, as a key reagent for the introduction into various main group elements and transition metals. The abbreviation "Rind" in English demotes the thick outer skin of some types of fruit for protection of the inside fruity flesh. This is totally in accordance with our research concept. In fact, the bulky Rind groups enable us to isolate some new unsaturated compounds of the heavier main group elements, as represented by the π-conjugated disilenes as described below.

3. Air-Stable Emissive Disilenes

We have recently demonstrated a novel class of Si=Si and Si=P compounds, i.e., π-conjugated disilenes and phosphasilenes, by taking advantage of the steric protection with the bulky Rind groups.[8d,8f,10,11] The Rind groups successfully encapsulate the reactive Si=Si and Si=P double bonds and produce the highly coplanar arrangement of the π-frameworks by their perpendicular orientation to and the interlocking proximate R^3 and R^4 substituents above and below the π-frameworks, which are suitable for studying the inherent conjugation properties.

As for the typical examples of the π-conjugated disilenes, Figure 3 shows the two regioisomers, i.e., (*E*)-1,2-di(1-naphthyl)-disilene and (*E*)-1,2-di(2-naphthyl)disilene, protected by the bulky Eind groups (Eind: $R^1 = R^2 = R^3 = R^4 =$ Et). These disilene compounds have been synthesized by the reductive coupling of the corresponding dibromosilanes, (Eind)ArSiBr$_2$ (Ar = 1-naphthyl and 2-naphthyl), with lithium naphthalenide (LiNaph) in THF.[10b,10d] The disilenes have been isolated as red crystals and found to be quite air-stable in the solid state for more than several years with no detectable change, as confirmed by the ^{1}H NMR spectra. They decompose in a dilute hexane solution (*ca.* 10^{-5} mol L^{-1}) upon exposure to air, but slowly with a half-lifetime of *ca.* 2–4 h, much longer than that observed in Tip$_2$Si=SiTip$_2$ (17 min; Tip = 2,4,6-triisopropylphenyl),[12] as estimated by the UV-vis spectroscopy, indicative of the outstanding protection ability of the Eind group. Both the 1,2-di(1-naphthyl)disilene and the 1,2-di(2-naphthyl)disilene exhibit strong π–π* absorptions and distinct emissions at room temperature, both in solution and in the solid state, as shown in Figure 4. The DFT calculations at the B3LYP/6-31G(d,p) level indicate the substantial contribution of the $3p_\pi^*$(Si–Si)–$2p_\pi^*$(naphthyl) conjugation.

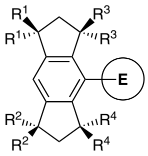

Figure 2. Rind groups.

The X-ray crystallographic analysis of the 1-naphthyl counterpart shows a highly coplanar (*E*)-1,2-di(1-naphthyl)-disilene skeleton, which is favorable for the efficient π-conjugation containing the Si=Si unit, along with a distinct CH/π interaction between the *peri*-H atom of the 1-naphthyl groups and the benzene ring of the perpendicularly-oriented Eind groups.[10d] In the 2-naphthyl counterpart, the Si atoms and the 2-naphthyl groups are disordered over the two positions in the crystal, corresponding to a mixture of two rotational isomers, *s-cis*, *s-cis* and *s-trans*, *s-trans*, in the ratio of *ca*. 6:4.[10b] Each conformer has an essentially coplanar (*E*)-di(2-naphthyl)-disilene framework; thus, only the structure of the *s-trans*, *s-trans* conformer is presented in Figure 3.

The 1,2-dinaphthyldisilenes have a high thermal stability with a decomposition temperature of 245–248 °C for the 1-naphthyl counterpart and 282–285 °C for the 2-naphthyl counterpart under an argon atmosphere. The excellent stability would provide new opportunities for application in a range of organic electronic devices, since the Si=Si units have a smaller HOMO–LUMO energy gap compared to the C=C units. We have demonstrated that the 1,2-di(2-naphthyl)disilene can emit light in an organic light-emitting diode (OLED), as shown in Figure 4.[13] To the best of our knowledge, this is the first experimental observation of electroluminescence (EL) from the heavier group 14 unsaturated compounds, which has opened a new platform for the development of functional elemento-organic materials and devices.

4. Summary

We have described our recent and ongoing work concerning the newly developed fused-ring bulky protecting groups (Rind groups) and their application to the air-stable, room-temperature emissive disilenes. The sterically bulky Rind groups successfully protect the highly reactive Si=Si double bonds, thus providing extraordinarily air-stable disilene derivatives with the highly coplanar arrangement of the π-framework. For example, the (*E*)-1,2-di(1-naphthyl)disilene and the (*E*)-1,2-di(2-naphthyl)disilene demonstrate the strong π–π* absorptions and distinct emission at room temperature, originating from the π-conjugation between the Si=Si double bond and the carbon π-electron system. The unique electronic properties of the π-conjugated disilenes have been determined by spectroscopic methods as well as computational studies. The chemistry of the π-conjugated disilenes has just begun and further investigations are needed for a deeper understanding of their properties and functionalities.

The unique protection ability of the bulky Rind groups also enable us to isolate some other new unsaturated compounds containing the main group elements,[7,14–19] as represented by tetrasilacyclobutadiene, $Si_4(Rind)_4$,[7] germanone, $(Rind)_2Ge{=}O$,[14] and hydro-diboron compounds (Figure 5).[15] The bulky Rind groups have also proven to stabilize some low-coordinate species of transition metals,[20–24] such as mixed diorganocuprates[20] and diorganoiron(II) complexes.[24]

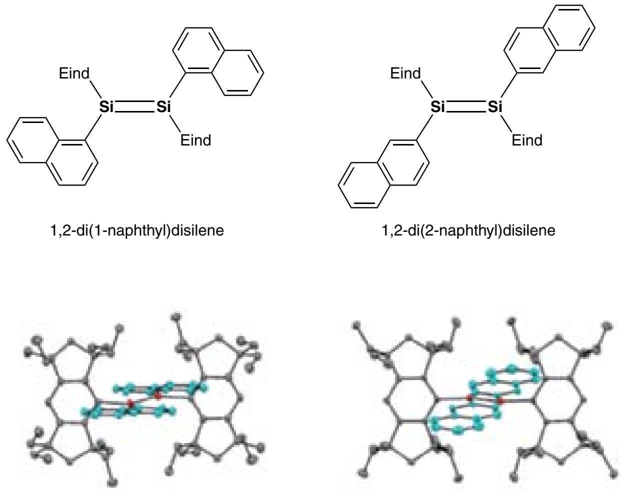

Figure 3. Molecular structures of (*E*)-1,2-di(1-naphthyl)disilene (left) and (*E*)-1,2-di(2-naphthyl)disilene (right).

Figure 4. Solid-state emission of (*E*)-1,2-di(1-naphthyl)disilene (left) and (*E*)-1,2-di(2-naphthyl)disilene (center) at room temperature in the open air. EL of (*E*)-1,2-di(2-naphthyl)disilene (right).

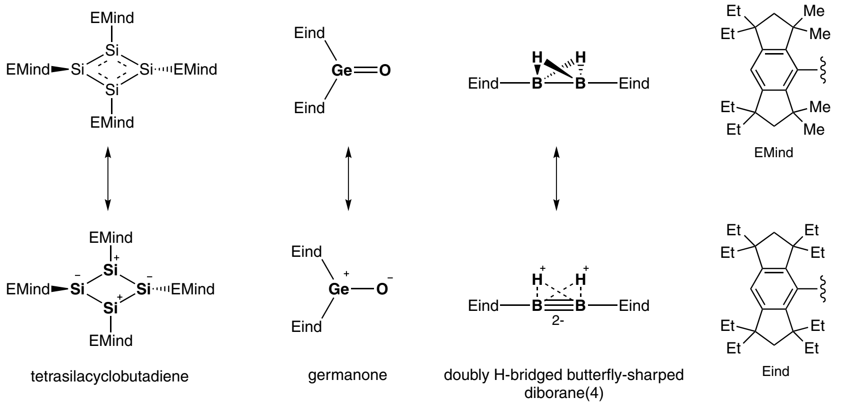

Figure 5. Examples of new unsaturated compounds of the main group elements stabilized by the bulky Rind groups.

The availability of stable low-coordinated species provides a new clue to the full understanding of the bonding nature of the heavier unsaturated compounds, as well as to various reactivities under ambient conditions, which would open a new facet to the chemistry of the main group elements.[25]

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