Coordination Chemistry Reviews 377 (2018) 1–43

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

N-heterocyclic carbene supported halosilylenes: New frontiers in an emerging field

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ARTICLE INFO

Article history:
Received 28 October 2017
Accepted 23 August 2018

Dedicated to Prof. Dr. Dr. h.c. mult. Herbert W. Roesky.

Keywords:
Group-14 elements
Halosilylene
Low valent silicon
Main group chemistry
N-heterocyclic carbene
Silicon(II)
Transition metal chemistry

ABSTRACT

The isolation of a rare and highly unstable silicon(II) dihalide using N-heterocyclic carbene (NHC) proved to be a landmark achievement in the field of silicon chemistry. The first stable NHC stabilized halosilylene was isolated and structurally characterized in 2009. Subsequently the study of NHC stabilized halosilylenes over the past nine years has opened-up a new dimension in the field of organosilicon chemistry. NHC stabilized halosilylene compounds have been extensively used as starting materials for the synthesis of rare organosilicon compounds like small ring systems with high ring-strain energy containing silicon (silaoxirane), C4-silyl substituted NHC, Si–Si multiple bond, molecule with rare Si–M bond (M = main group or transition metals), dichlorosilamines (Si═N), silaisontriles, trisilaallenes (silicon analogue of allene) etc. These studies clearly demonstrated the potential applications of NHC stabilized halosilylenes in various fields of organosilicon chemistry. The present review summarizes the progress and scope of NHC-halosilylene chemistry. In particular, an overview of synthetic strategies, spectral properties, key structural features and available bonding analysis are discussed.

Contents

Abbreviations: Ar, aryl; Et, ethyl; cAAC, cyclic alkyl(amino) carbene; Cp, η-cyclopentadienyl; Cp*, η-pentamethyl cyclopentadienyl; DFT, density functional theory; diip, 2,6-diisopropylphenyl; EI-MS, electron ionization mass spectrometry; HOMO, highest occupied molecular orbital; h, hours; Im, imidazol-2-ylidene; Idipp, N,N′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IR, infrared; IMe_4, 1,3,4,5-tetramethylimidazolin-2-ylidene; IiPr, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; LUMO, lowest unoccupied molecular orbital; NBO, natural bond orbital; NHC, N heterocyclic carbene; NMR, nuclear magnetic resonance; *i*Pr, isopropyl; Me, methyl; Mes, mesityl; Mes*, 2,4,6-tritertiarybutylphenyl; Ph, phenyl; RT, room temperature; SIdipp, 1,3-bis[2,6-bis(isopropyl)phenyl]imidazolidin-2-ylidene; *t*Bu, *tert*-butyl; Tbb, 2,6-$(CH(SiMe_3)_2)_2$-4-*t*Bu phenyl or 4-*t*butyl-2,6-bis(bis(trimethylsilyl)methyl)phenyl; THF, tetrahydrofuran; TMS, trimethylsilane; Tp^{Me}, κ3-N,N′,N″-hydridotris(3,5-dimethyl-1-pyrazolyl)-borate; Triip, 2,6-bis(2,6-diisopropylphenyl)phenyl; Trip, 2,4,6-triisopropylphenyl; UV–vis, ultraviolet visible.

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https://doi.org/10.1016/j.ccr.2018.08.021
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1. Introduction

Highly reactive low valent silicon species are rare and such type of molecules are in high demand for the technological development. At this juncture, low-valent silicon chemistry has witnessed a renaissance area of research, experiencing continuous diversification. For example, two decades ago silylene was thought to be unstable at room temperature; however, today silylenes are "bottleable". Numerous properties and characteristics of silylene have been measured and calculated (Chart 1). Silylenes are molecules that have a divalent neutral silicon(II) atom having lone pair of electrons (R_2Si:). Silylenes are key intermediates in various photochemical, thermal, and metal reduction reactions of organosilicon compounds [1]. Silylenes and its derivatives are generally highly reactive and were observed only in the gas-phase, in diluted solutions, and in frozen rare-gas matrices at low temperatures [2–4]. However, most of the silylenes are extremely unstable, decomposes or polymerizes rapidly above 77 K or reacts rapidly with solvents [5,6]. The realm of silylene chemistry has been expanded dramatically, and the investigation of reactivity of NHC stabilized silylene has had a profound influence in advancing modern inorganic chemistry.

The analogues of silylenes viz., carbenes, stannylenes and germylenes are well-known 'di-coordinate divalent' species [7–9]. With the advent in the field of carbene chemistry, in 1991, Arduengo and co-workers reported the synthesis and isolation of the first room-temperature stable crystalline carbene, imidazol-2-ylidene 1 (E = C, R = 1-adamantyl) [10]. Since this benchmark discovery, the chemistry of stable carbenes began its journey through a new way of developing the metallylenes to a large figure, and nowadays they are routinely used in synthesis, catalysis, and to stabilize unusual molecules [11–16]. More recently, stannylenes and germylenes were synthesized and characterized [7–9]. The preparation of these surprising compounds left silicon as the only element of group 14 with no di-coordinate divalent compound stable under ambient temperature. In fact, the isolation of related silicon compound is one of the most challenging task in organosilicon chemistry. Specific electronic and steric requirements are essential to stabilize these elusive and often ephemeral species. This situation has been changed when West *et al.* reported the first N-heterocyclic silylene that is stable at room temperature using N-donor ligand in 1994 [17], which is comparable to the NHC [10]. Since then, stable silylenes have emerged as versatile building blocks for the synthesis of novel organosilicon compounds.

Among silylenes, halosilylenes were generated in the gas phase through thermolysis reactions and recognized with the aid of trapping reactions [18–20] or detected spectroscopically as transient species [21]. Compared to monochlorosilylene [22], the isolation of dihalosilylenes are most challenging. Schmeisser [23] and Schenk [24] studied the condensation of dichlorosilylene to polymeric $(SiCl_2)_n$ at room temperature. Occasionally halosilylenes exist as intermediates in condensed phases [25]. Since the first report of the stable divalent silicon species, Cp^*_2Si: (Cp^* = Me_5C_5, silicocene), by Jutzi and co-workers [26–28], a remarkable class of stable silylenes such as dialkyl silylene [29] and cyclic silylenes were synthesized and characterized [17,30–32]. In 2009, the research groups of Roesky [33] and Filippou [34a] showed that the NHC can stabilize dihalosilylenes [NHC(SiX_2)] (X = Cl, Br) to form stable NHC:→SiX_2 complexes (Chart 1). The carbene center donates its lone pair of electron and binds strongly with silicon in low oxidation state [35]. As shown in the Chart 1, [Si(:)X_2] species is electronically stabilized by NHC group and sterically protected by the attached bulky group. However, under specific reaction conditions the bond formed is facile enough to break for the use of free [Si(:)X_2] specious [36]. The thermal stability and the crystalline nature of the NHC-dihalosilylene adduct depends on the NHC and silicon halide used. Interestingly, [NHC(SiX_2)] can act as electron donor to transition metals and main group elements [37a]. In particular, the Si(II) compounds [(Idipp)SiX_2] (Idipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and Si(Cl)R(IMe_4) (IMe_4 = 1,3,4,5-tetramethylimidazolin-2-ylidene) proved to be promising building blocks, which enabled the synthesis of new classes of unsaturated silicon compounds, including zwitterionic silylidene complexes, silylidyne complexes, metallosilylenes, and metallosilanones [38]. Besides, the chemistry of other low valent silicon NHC adducts, such as Si_2 [39] silanones [40] and [Si(Cl)R] [41] are under developing stage.

In the singlet ground state, silylenes are divalent neutral silicon species with the lone pair of electrons as the HOMO and a vacant *p* orbital as the LUMO. Hence, depending on the substituents these molecules can behave as Lewis acids as well as Lewis bases (Chart 2). The silicon-carbon bond in [NHC(SiX_2)] considered to be a strong C → Si donor-acceptor single bond through donation of the carbene carbon lone pair into the vacant silicon p orbital of SiX_2 [34,35]. Therefore the Si–C bond is shorter than that of the silylene-carbene adduct [L″SiCL″)] (Si–C = 2.162(5) Å; L″ = 1,2-$(NCH_2tBu)_2C_6H_4$) [37b], but longer than the Si═C bonds of the

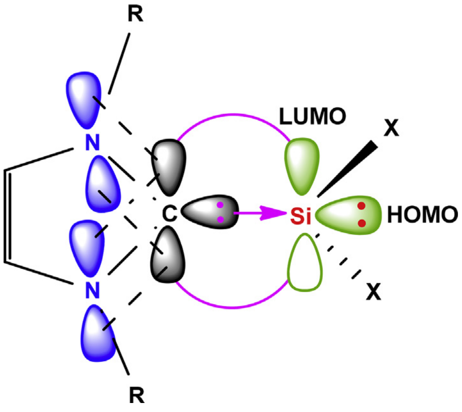

Chart 2. Bonding picture in NHC stabilized halosilylenes.

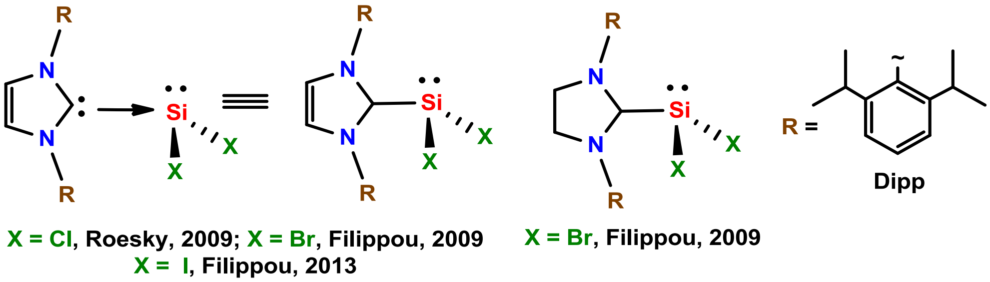

Chart 1. NHC stabilized halosilylenes.