

“Tetramethylsilanoviologen”: Synthesis, characterization, and hydrolysis of a Silolodipyridinium ion



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ABSTRACT

A silicon-bridged viologen has been synthesized by methylation of 4,4'-dipyridinodimethylsilole, and represents a new addition to the growing family of heteroatom bridged viologens. The dicationic species emits at 360 nm and exhibits two chemically reversible one electron reduction waves in acetonitrile at $E_{1/2}(2+/1+) = -0.829$ V and $E_{1/2}(1+/0) = -1.307$ V (versus Fc/Fc⁺). The UV–Vis spectrum for each of the three charge states is similar to the corresponding unbridged methyl viologen species. The silanoviologen is susceptible to ring-opening hydrolysis.

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1. Introduction

The N-alkylated 4,4'-bipyridinium salts (viologens) have been widely adopted as redox active components in a diverse array of applications such as electron mediators for hydrogen generation [1], electrochemical capacitors [2], and electrochromic displays [3]. The 4,4'-bipyridinium di-cations can be readily reduced to form relatively stable radical cation species [4] with intense colors that vary with the N-substituent. Likewise, metalloles including siloles and dibenzosiloles constitute an important class of materials with extensive academic interest and practical applications, including luminescent devices [5], photovoltaics [6], and sensors for explosives [7]. Siloles are electron acceptors due to contribution of the silicon σ^* orbitals to the LUMO of the sila-cyclopentadiene ring, and there has been extensive interest in incorporating fused siloles and other metalloles into polymers and extended conjugated systems [8]. Ohshita and coworkers synthesized the first 4,4'-dipyridinisolole and explored its solid state luminescence [9], but N-alkylation to make the silicon bridged viologen has not yet been reported.

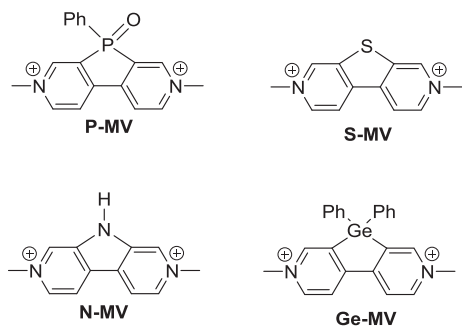
Synthetic modification at the C3 position of 4,4'-bipyridinium salts is usually undesirable since it prevents planarity and destabilizes the reduced species. C3–C3' bridging substituents on the other

hand enforce planarity and are an attractive synthetic target for tailoring the chemical, electrochemical, and optical properties of the viologens. Heteroatom bridged methyl viologen analogs have appeared in the literature with N, P, S, and Ge bridges (Scheme 1), with various effects attributed to the heteroatom incorporation. The 9-oxide-9H-phospholodipyridinium salts, e.g. **P-MV**, exhibit significantly lowered reduction potentials thanks to the phosphine oxide bridge [10]. This could enable sensing or catalytic applications involving electron transfer from weaker electron donors. Phosphaviologens have also been explored as tunable electrochromic materials [11]. The 2,7-dimethylthieno[2,3-c:5,4-c'] dipyridinium ion, **S-MV**, was shown to act as an electron shuttle and a photosensitizer for the photoreduction of water [12]. By comparison, unbridged methyl viologen can only act as an electron shuttle for the photoreduction of water in the presence of a photosensitizer such as Ru(bpy)₃²⁺. Pyrrolodipyridinium salts such as **N-MV** were developed for potential cytostatic activity [13]. A germanium bridged analog, **Ge-MV**, was recently synthesized, and it was shown that the germanium bridge slightly increased the electron affinity of the viologen with a slight shift of +0.08 V relative to methyl viologen's first reduction potential [14].

Silicon bridged viologens would be an attractive addition to this family combining benefits of siloles and viologens, and the silicon bridge could also enforce planarity while providing a useful site for subsequent functionalization or immobilization. Immobilization of viologens [15] on surfaces has proven beneficial, for example, in

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Scheme 1. Previously reported heteroatom bridged methyl viologen analogs, P-MV, S-MV, N-MV, and Ge-MV.

electrochromic device applications [16] and renewable carbohydrate fuel cells [17]. In this manuscript, we report the synthesis and structural characterization of a silanoviologen and explore its electrochemical, electrochromic, and hydrolytic stability.

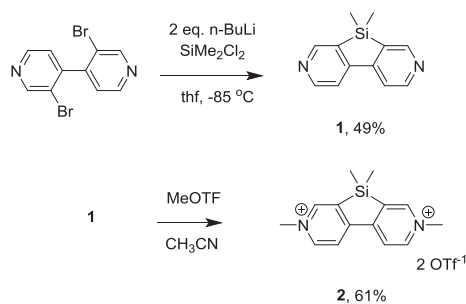
2. Results and discussion

The precursor, 4,4'-dipyridinodimethylsilole, **1**, was synthesized by allowing dichlorodimethylsilane to react with Li₂bipy at 85 °C following the method of Ohshita (Scheme 2). Subsequent chromatography and recrystallization from hexane provided a colorless crystalline material in 49% yield. Single crystals suitable for X-ray analysis were obtained via slow evaporation from hexane. The crystal structure of **1** is shown in Fig. 1.

Crystals of **1** were subsequently dissolved in acetonitrile and methylated with methyl triflate to produce the tetramethylsilanoviologen, **2**. Colorless crystals of **2** were recovered from the reaction mixture in 61% yield by diffusion of ether into the solution. The crystal structure of **2** is shown in Fig. 2 with anions and solvent omitted for clarity. Both structures exhibit a nearly planar bipyridinium framework with a small value for the C1–Si–C10 bond angle of 90.09(8)° for **1** and 88.55(11)° for **2**.

The dimethylsilylene bridge has a subtle effect on the spectroscopic properties of the methyl viologen analog. A deoxygenated acetonitrile solution of compound **2** absorbs in the UV with a λ_{max} = 270 nm and emits with a broad emission band centered at 360 nm (Fig. 3). Both values are only slightly lower in energy than those reported for methyl viologen 260 nm [18] and 350 nm [19], respectively.

The effect of the dimethylsilylene bridge on the reduction potentials is also subtle. The standard reduction potentials of **2** were determined via cyclic voltammetry in acetonitrile solution with tetra-*n*-butylammonium hexafluorophosphate (0.10 M) as the electrolyte (Fig. 4). A platinum disk working electrode was used along with a Ag/AgCl reference electrode and the ferrocene/ferrocenium couple was used as an internal standard. The silanoviolo-



Scheme 2. Synthesis of **1** and **2**.

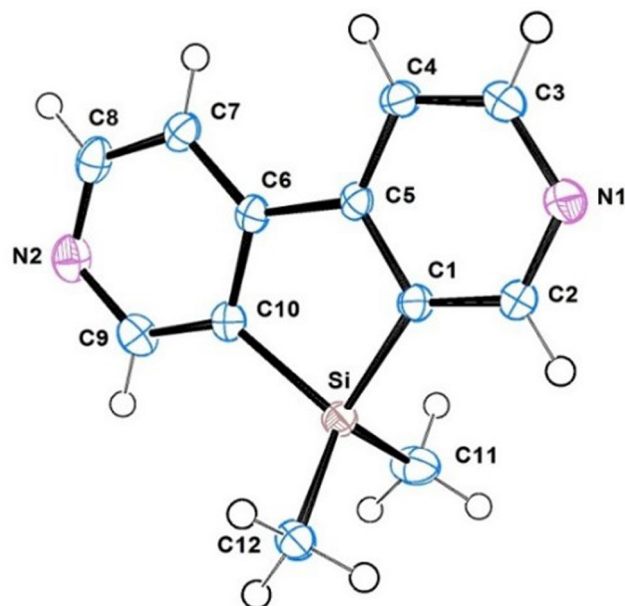


Fig. 1. Crystal structure of **1**. Selected bond distances (Å) and angles (°): Si–C1 1.8801(18), C1–C5 1.408(2), C5–C6 1.485(2), C6–C10 1.411(2), C10–Si 1.8858(18), C1–Si–C10 90.09(8), Si–C1–C5 110.27(13), C1–C5–C6 114.78(15), C5–C6–C10 114.71(15), C6–C10–Si 110.04(13). Torsion angles (°): C1–C5–C6–C10 0.2(2), Si–C1–C2–N1 –178.12(15).

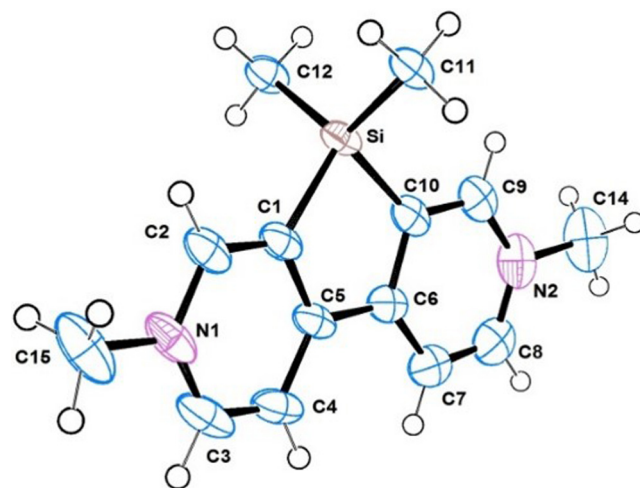


Fig. 2. Crystal structure of **2**. Counterions (two triflate ions) and solvent molecules omitted for clarity. Selected bond distances (Å) and angles (°): Si–C1 1.889(2), C1–C5 1.402(4), C5–C6 1.484(4), C6–C10 1.406(4), C10–Si 1.889(2), C1–Si–C10 88.55(11), Si–C1–C5 111.30(18), C1–C5–C6 114.5(2), C5–C6–C10 113.8(2), C6–C10–Si 111.74(19). Torsion angles (°): C1–C5–C6–C10 –1.2(3), Si–C1–C2–N1 –179.74(18).

gen dication exhibits two chemically reversible one electron reduction waves at $E_{1/2}(2+/1+) = -0.829$ V and $E_{1/2}(1+/0) = -1.307$ V (versus Fc/Fc⁺), very similar to values reported for Ge-MV of $E_{1/2}(2+/1+) = -0.80$ V and $E_{1/2}(1+/0) = -1.25$ [14].

The UV–Vis spectra of the 1+ and neutral reduced states of **2** were obtained using an argon flushed spectroelectrochemical cell with a 1.0 mm pathlength and a printed gold honeycomb working electrode (Pine Instruments), a gold counter electrode, and a Ag/AgCl reference electrode standardized to the ferrocene/ferrocenium couple. Dilute samples of **2** were prepared in anhydrous acetonitrile with tetra-*n*-butylammonium hexafluorophosphate (0.1 M). Figs. 5 and 6 contain the spectra of the 2+ species (red),

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