

Synthesis, Structure, and Reactivity of Transition Metal Silylenes

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Ever since the discovery of transition metal carbenes, chemists have attempted to synthesize complexes having double bonds to other group IV elements. A large number of transition metal complexes with double bonds to Ge, Sn, and Pb have already been synthesized, but Si complexes are somewhat more elusive [1]. Because of silicon's similarities to carbon, metal silylenes should behave similarly to their carbene counterparts. In fact, shortly after the discovery of carbenes, silylenes were proposed as intermediates in a variety of polymerization and redistribution reactions. Reactions of silylene precursors with trapping reagents gave products that supported the existence of these intermediates [2, 3, 4].

Some differences between carbenes and silylenes can be expected. Silicon is known to form weak double bonds to other elements. The diffuse π orbitals and instability of the triplet state on Si are responsible for this behavior [5]. The singlet state favors the formation of metal-silicon double bonds through donor-acceptor interactions like those in Fischer carbenes. The presence of π -donating substituents on the silylenes also aids in the stabilization of the metal-silicon double bond.

Early attempts to synthesize metal silylenes used methods similar to those for the synthesis of carbene complexes. Unfortunately, many of these methods require precursors that have no silicon analogues: addition of RLi to M-CO, addition of ROH to isocyanide complexes, and cleavage of the double bonds of electron-rich olefins [6]. However, other carbene syntheses can be modified to afford silylene analogues, such as the reaction of $[M(CO)_n]^-$ with geminal dichlorides [7] and trapping free carbenes [8]. An important synthesis for silylene complexes which has no carbene analogue is the displacement of a good leaving group on silicon by a very weakly coordinated base [9]. The first structurally characterized metal silylene complex was prepared by this method:

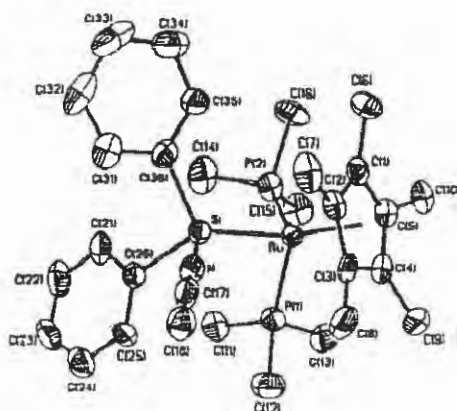


Figure 1: ORTEP of $[Cp^*L_2Ru=SiPh_2(NCMe)]^+$

The slight pyramidalization around Si, the shortening of the M-Si bond, and the very long Si-donor bond found in this structure are typical for other base-stabilized metal silylenes as well [10, 11].

Few non-base-stabilized metal silylenes have been isolated. ^1H NMR spectra of the first complex of this type, $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{Si}(\text{SR})_2][\text{BPh}_4]$, indicated that the trifluoromethanesulfonate groups used in the synthesis coordinate reversibly to the silicon atom in solution [12]. The planarity of the Si atom and the slight shortening of bonds around Si indicate that there may be π -delocalization among the Si substituents that stabilizes this and other non-base stabilized silylene complexes such as $(\text{CO})_4\text{OsSi}(\text{STol-p})[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2]$ [13].

Even though metal silylenes have only recently been characterized and their reactivities are not well understood, they have been proposed as intermediates in silane polymerization and redistribution reactions involving Rh and Pt catalysts [2, 4, 14, 15]. Harrod [14] and Corey [17] proposed that the dehydropolymerization of silanes may proceed through metal silylene intermediates. Tilley proposed that the isolation of intermediates in certain reactions supports an oxidative addition and reductive elimination mechanism. In other reactions, Tilley proposes that the precedented σ -bond metathesis mechanism is more likely [16]. Finally, several groups in the early 1990's found spectroscopic evidence and isolated intermediates that suggested that $\text{Cp}(\text{CO})_2\text{FeSi}_2\text{R}_5$ polymerizes silanes through a metal silylene species [15, 17, 18]. Once the metal silylene is formed, photolysis releases the singlet silylene fragments, which either polymerize directly or form polysilane precursors as they are being ejected which then quickly polymerize. These reactions are not catalytic, however. The Fe systems mentioned above, besides giving small amounts of polysilanes, also redistribute the substituents on Si.

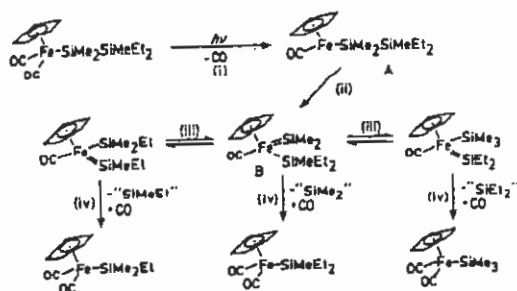


Figure 2: Redistribution of Silanes

Spectroscopic evidence suggests that metal silylenes react with oxygen-containing functional groups [19]. Alcohol, carboxylic acids, and ketones can coordinate to the Lewis acidic Si center and then react to form silicon-containing organic products. Similarly, the carbonyl oxygen of dimethylcarbonate coordinates to Si, activating it towards a sila-Wittig reaction [18].

The challenges of synthesizing transition metal silylene complexes have prevented any extensive studies of their structure and reactivity. With the recent isolation of various stable silylenes, the chemistry of these systems will become better understood and their potential more fully realized.

References

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