

Deoxygenation Reactions Enabled by Cyclic Bis(silyl)iron Skeletons as Key Fragments

(¹Graduate School of Engineering and ²Institute of Industrial Science, The University of Tokyo)

○Yuto Suga¹, Yusuke Sunada^{1,2}

Keywords: Iron, Silicon, Deoxygenation, Carbene

Organosilyl ligands attached to the transition-metal centers exhibit unique reactivities, especially toward oxygen-containing substrates owing to their electropositivities. For instance, when a carbonyl compound reacts with a transition-metal-silyl complex, a siloxyalkyl complex is formed via insertion of the C=O double bond to the metal–silicon bond (Scheme 1-a).^[1] Furthermore, it was reported by several research groups that transition-metal-disilyl complex could give rise to the formation of a transition-metal-carbene intermediate by treatment with a carbonyl compound via intramolecular deoxygenation from the siloxyalkyl complex formed as stated above (Scheme 1-b).^[2] Although this type of reaction is expected as a new synthetic route of transition-metal-carbene complexes, the isolation of the transition-metal-carbene intermediates has not been reported, instead, the formation of them was confirmed by trapping experiments in the previous reports. Inspired by these precedented works, we decided to elucidate the mechanism of the deoxygenation reaction to obtain better understandings of the reactivity of organosilicon-based ligands attached to the transition metal centers, as well as to establish a new synthetic method of transition-metal-carbene complexes.

We found that iron complexes **1** and **2** bearing chelating disilyl ligands (Chart 1) reacted with aryl aldehydes to afford corresponding stilbene derivatives in a deoxygenative manner. Moreover, when **1** was reacted with cyclopropanone derivatives, iron-cyclopropenylidene complexes were formed, which are the first examples of structurally determined transition-metal-carbene complexes generated via deoxygenation reaction induced by transition-metal-disilyl complexes. The proposed mechanism of the deoxygenation reaction will be presented based on the isolation of various iron complexes formed in the deoxygenation reaction.

Scheme 1.

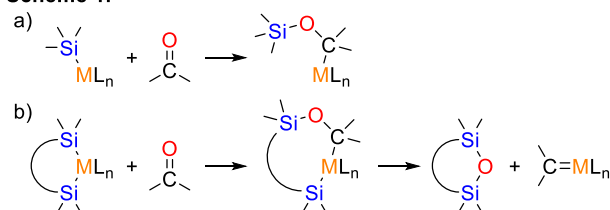
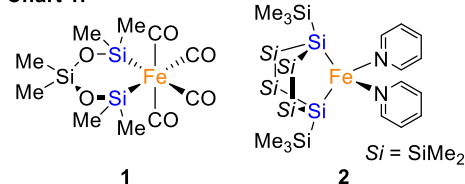


Chart 1.



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