

## Preliminary communication

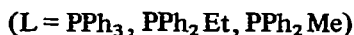
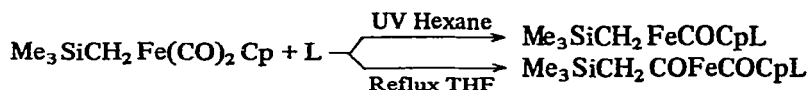
### Rearrangements of silylmethyl- and silylacetyl-iron complexes

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We recently described some stereochemical features of  $\sigma$ -silylmethyl and  $\sigma$ -silylacetyl complexes of the asymmetric  $\pi$ -cyclopentadienylironcarbonylphosphine system<sup>1</sup> and now present a preliminary account of reactions of such complexes involving novel rearrangements. The trimethylsilyl compounds are prepared by treating  $\sigma$ -trimethylsilylmethyl- $\pi$ -cyclopentadienyliron dicarbonyl (made from  $\text{Fe}(\text{CO})_2 \text{Cp}^-$  and  $\text{Me}_3\text{SiCH}_2\text{Cl}$  - see ref. 2) with the appropriate phosphine either in refluxing tetrahydrofuran or under ultraviolet irradiation in hexane:

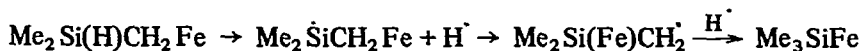


The interaction of  $\text{Fe}(\text{CO})_2 \text{Cp}^-$  and  $\text{Me}_2\text{HSiCH}_2\text{Cl}$  leads to a very unstable red liquid [ $\nu(\text{C}\equiv\text{O})$  1999, 1950  $\text{cm}^{-1}$ ,  $\nu(\text{SiH})$  2081  $\text{cm}^{-1}$ ], which when treated with triphenylphosphine in hexane under UV irradiation gives  $\sigma$ -trimethylsilyl- $\pi$ -cyclopentadienyliron-carbonylphosphine<sup>3</sup>,  $\text{Me}_3\text{SiFeCOCpPPh}_3$ , in good yield. The mechanism of the rearrangement involved is still uncertain, but it is noteworthy that the hydrosilyl iron complex contains a reactive Si-H bond (*cf.* ref. 4)  $\beta$  to the iron atom, and hence an alkene elimination, such as that which occurs with  $\sigma$ -ethyl transition metal complexes, might be expected<sup>5</sup>, and this could be followed by an iron hydride addition to the unsaturated species<sup>5</sup> to produce the observed product:



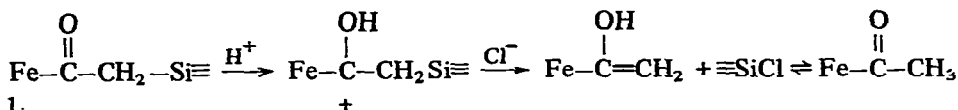
That an intermediate containing the Si=C linkage is involved does not detract from this mechanism, since the intermediate need never leave the coordination sphere of the iron atom and might thus be stabilized in a manner similar to cyclobutadiene in  $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$ <sup>6</sup>. It is noteworthy that the products isolated from the decomposition of  $\text{Me}_2\text{Si}(\text{H})\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}$  are  $\text{HFe}(\text{CO})_2\text{Cp}$  and  $\text{Me}_3\text{SiFe}(\text{CO})_2\text{Cp}$ .

Another possible mechanism involves the formation of a silyl radical followed by a novel 1,2-iron migration and radical recombination:



No rearrangements of the corresponding trimethylsilylmethyl iron complexes have been observed during this work.

The silylacetyl complexes are the first transition metal substituted  $\beta$ -ketosilanes<sup>7</sup> and exhibit characteristically lower ketonic carbonyl stretching frequencies than related carbon complexes, e.g.  $\text{Me}_3\text{SiCH}_2\text{COFeCOCpPPh}_3$ ,  $1555\text{ cm}^{-1}$ ;  $\text{MeCOFeCOCpPPh}_3$ ,  $1594\text{ cm}^{-1}$ ;  $\Delta\nu(\text{CHCl}_3)$ ,  $43\text{ cm}^{-1}$ ; cf.  $\text{Me}_3\text{SiCH}_2\text{COCH}_3$ :  $\text{CH}_3\text{COCH}_3$ ,  $\Delta\nu(\text{CCl}_4)$ ,  $24\text{ cm}^{-1}$ . Treatment of these silylacetyl complexes with HCl leads to quantitative production of the corresponding  $\sigma$ -acetyl complexes, (e.g.  $\text{Me}_3\text{SiCH}_2\text{COFeCOCpPPh}_3 \rightarrow \text{MeCOFeCOCpPPh}_3$ ), probably via the mechanism outlined in Scheme 1. The initial protonation would be similar to that suggested by Green and Hurley<sup>8</sup> for the reaction of  $\text{MeCOFeCOCpL}$  ( $\text{L} = \text{CO}, \text{PPh}_3$ ) with hydrogen chloride. The  $\beta$ -silylcarbonium ion would readily lose the silyl group to form an alkene<sup>9</sup>, which in this reaction would be a tautomer of the recovered product.



Scheme 1.

#### ACKNOWLEDGEMENT

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