

Synthesis and Reactivity of Germylene and Stannylene Bridged Diiron Complexes

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論 文 内 容 要 旨

In this study, I used primary and secondary germanes and stannanes for the preparation of either diiron complexes with M-H-E 3-center 2-electron bonds (E=Ge, Sn) or germylene and stannylene bridged diiron complexes. The thermal and photochemical isomerization between the geometric isomers of mono and bis(germylene)-bridged diiron complexes were also studied.

In Chapter II, I studied the photochemical reaction of $Cp^*Fe(CO)_2SiMe_3$ ($Cp^* = \eta^5-C_5Me_5$) with the primary germane *p*-TolGeH₃. Three classes of complexes were isolated as products: (1) a red mixture of the *cis* and *trans* isomers of mono(germylene)-bridged diiron complex

$\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeHp-Tol})$ as the major product, (2) a violet mixture of the *syn*- and *anti-trans* isomers of bis(germylene)-bridged diiron complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$, and (3) an orange complex with two Fe-H-Ge 3-center 2-electron bonds $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH}_2)_2$ as shown in eq 1. These products are markedly different from the products of the analogous reaction with *p*-TolSiH₃. In the case of the photochemical reaction of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$ with *p*-TolSiH₃, only the *cis* and *trans* isomers of mono(silylene)-bridged diiron complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Gep-TolH})$ were isolated. Such difference in the behavior between Si and Ge in the similar reaction is attributable to the difference in the atomic size of Si and Ge, and also to the difference in the bond lengths of Fe-Si and Fe-Ge.

The ratio of *syn*- and *anti-trans* isomers of bis(germylene)-bridged diiron complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$ in the photostationary state is 61:39. The ¹H NMR signals of the aromatic protons of *syn*- and *anti-trans* isomers of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$ were found to be temperature-dependent. Such behavior apparently results from the hindered rotation of *p*-tolyl groups in the presence of the adjacent bulky Cp* groups.

Unlike an analogous complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Get-BuH}_2)_2$ that affords, by both thermolysis and photolysis, only one isomer of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Get-BuH}_2)_2$ (*syn-cis(H)*) with evolution of H₂ gas, the behavior of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH}_2)_2$ complex in thermolysis is different from that in photolysis. Thus, the photolysis of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH}_2)_2$ afforded a mixture of *syn*- and *anti-trans* isomers of bis(germylene)-bridged diiron complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$ (Scheme 1). In contrast, thermolysis of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH}_2)_2$ afforded the third isomer of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$ which adopted the *syn-cis(H)* configuration (Scheme 1). Interestingly, photochemical isomerization of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$ was observed, where *syn-cis(H)* isomer converted to a mixture of *syn*- and *anti-trans* isomers only after 1 min of photolysis as shown in Scheme 2.

In Chapter III, I studied the thermal and photochemical interconversion of *cis* and *trans* isomers of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Gep-TolH})$ by kinetic methods (eq 2). The equilibrium constants indicate that the *trans* isomer is thermodynamically more stable than the *cis* isomer. Scheme 2 shows the mechanism of isomerization for both thermal and photochemical processes. The large negative entropies of activation imply participation of the solvent (benzene) in the thermal isomerization of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Gep-TolH})$.

Comparing the isomerization of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Gep-TolH})$ with the analogous silylene complex, it was found that the ΔH^\ddagger values for the isomerizations of the germylene complex are lower than the analogous silylene complex. The proportion of the *cis* isomer in equilibrium at room temperature is larger in germylene complex (5%) than in the silicon analogue (2%), apparently due to the longer Fe-Ge bond compared to the Fe-Si bond that relieves the steric repulsion in the *cis* isomer.

In Chapter IV, I studied the photoreaction of $\text{Cp}'\text{Fe}(\text{CO})_2\text{SiMe}_3$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_5(\text{Cp})$ and $\eta^5\text{-C}_5\text{Me}_5(\text{Cp}^*)$] with the secondary germane (*p*-Tol)₂GeH₂. The photochemical reaction of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$ with the secondary germane (*p*-Tol)₂GeH₂ gave only monoiron complex $\text{Cp}^*\text{Fe}(\text{CO})_2\text{GeH}(\text{p-Tol})_2$ (eq 3). On the other hand, the photochemical reaction of $\text{Cp}'\text{Fe}(\text{CO})_2\text{SiMe}_3$ with the secondary germane (*p*-Tol)₂GeH₂ gave *cis* and *trans* isomers of both Cp₂

$\text{Fe}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-Ge}(p\text{-Tol})_2\}_2$ and $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Ge}(p\text{-Tol})_2\}_2$ (eq 4).

The interconversion of the *cis* and *trans* isomers of $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Ge}(p\text{-Tol})_2\}_2$ was found to occur photochemically, and the molar ratio between *cis* and *trans* isomers at the photostationary state was 85 : 15 (eq 5).

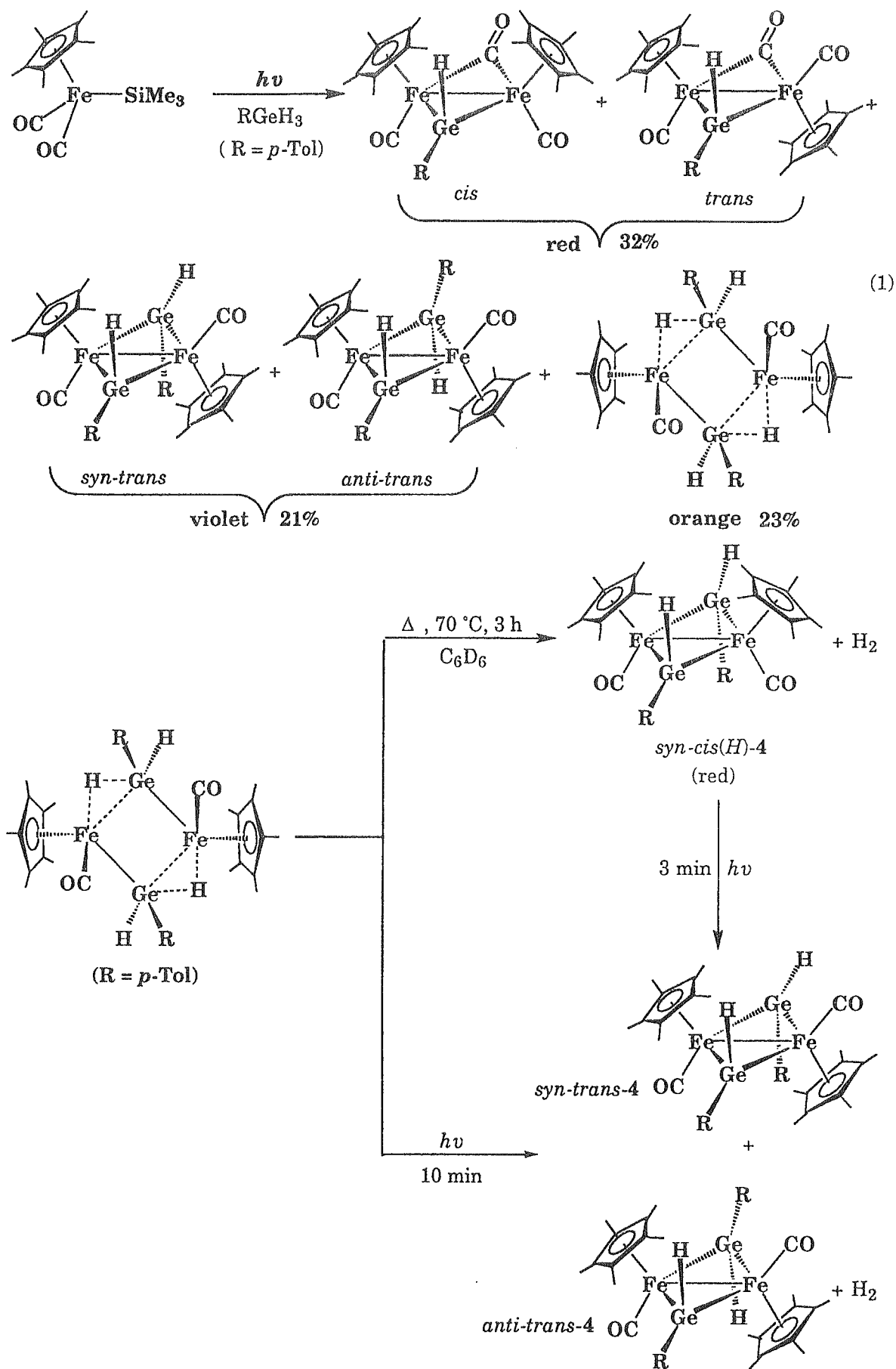
In Chapter V, I studied the photochemical reaction of $\text{Cp}'\text{Fe}(\text{CO})_2\text{SiMe}_3$ [$\text{Cp}' = \text{Cp}$ and Cp^*] with secondary or tertiary stannane $(p\text{-Tol})_n\text{SnH}_{4-n}$ ($n = 2, 3$). The photolysis of $\text{CpFe}(\text{CO})_2\text{SiMe}_3$ with $(p\text{-Tol})_2\text{SnH}_2$ gave a complex containing two Fe-H-Sn 3-center 2-electron bonds $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\text{H}\}_2$ (eq 6). This complex is considered as the first example of a complex containing Fe...H...Sn 3-center 2-electron bond and also the first example of a complex containing two 3-center 2-electron M...H...Sn bonds. This complex adopts the *trans* configuration and is stable upon heating up to 90 °C. On the other hand, $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\text{m-Sn}(p\text{-Tol})_2\text{H}\}_2$ loses H_2 during photolysis, and the ^1H NMR spectrum shows the formation of *cis* and *trans* isomers of bis(stannylene)-bridged diiron complex $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\}_2$ (eq 7). Unfortunately, this green complex is not stable enough to isolate. The bulkiness of the Cp ligand and *p*-tolyl groups is thought to be not enough to stabilize such a bis(stannylene)-bridged diiron complex.

The photochemical reaction of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$ with the secondary stannane $(p\text{-Tol})_2\text{SnH}_2$ gave the *trans* isomer of bis(stannylene)-bridged diiron complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\}_2$, and hydrido bis(stannyl)iron complex $\text{Cp}^*\text{Fe}(\text{CO})\text{H}\{\text{Sn}(p\text{-Tol})_2\text{H}\}_2$ (eq 8). In contrast to $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\}_2$, the combination of bulky Cp^* ligands and *p*-tolyl groups stabilizes the *trans* isomer of bis(stannylene)-bridged diiron complex $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\}_2$.

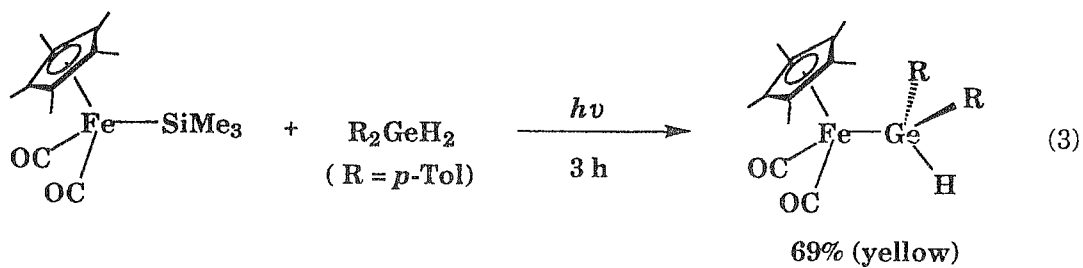
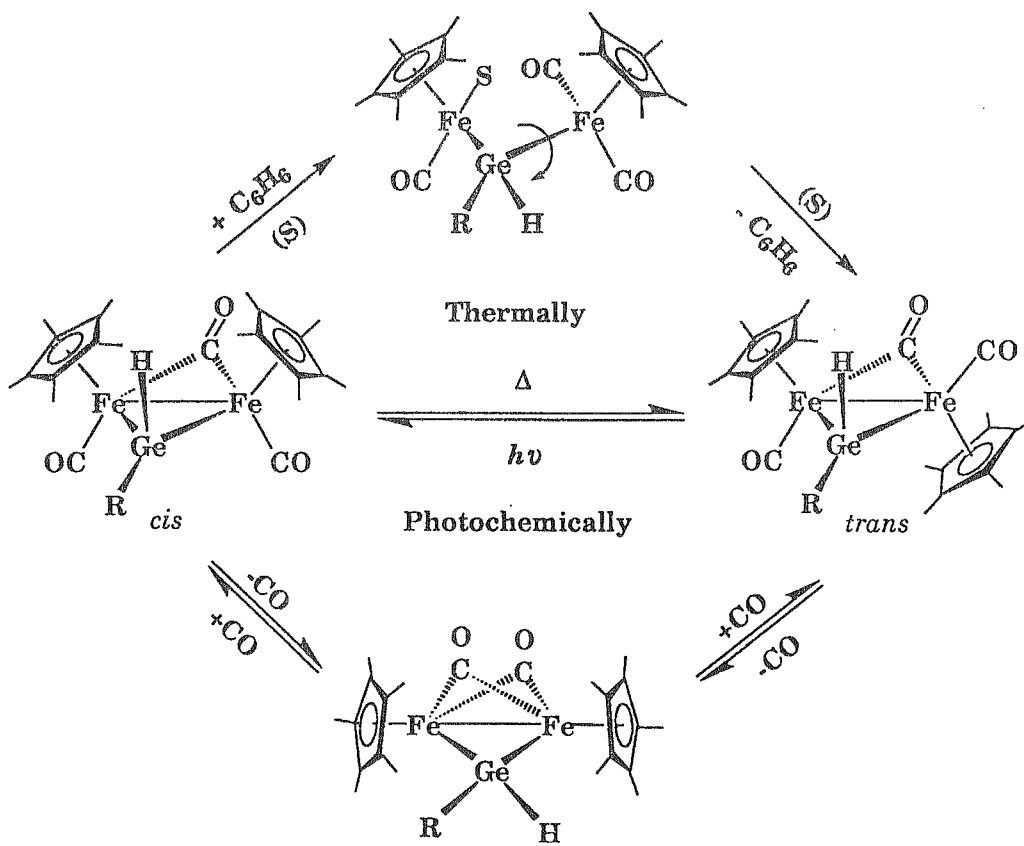
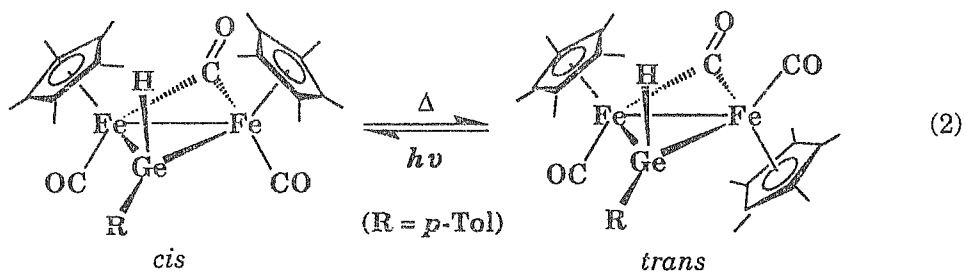
Photolysis of a benzene- d_6 solution of $\text{Cp}^*\text{Fe}(\text{CO})\text{H}\{\text{Sn}(p\text{-Tol})_2\text{H}\}_2$ leads to the formation of the *trans*- $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\}_2$ (eq 9).

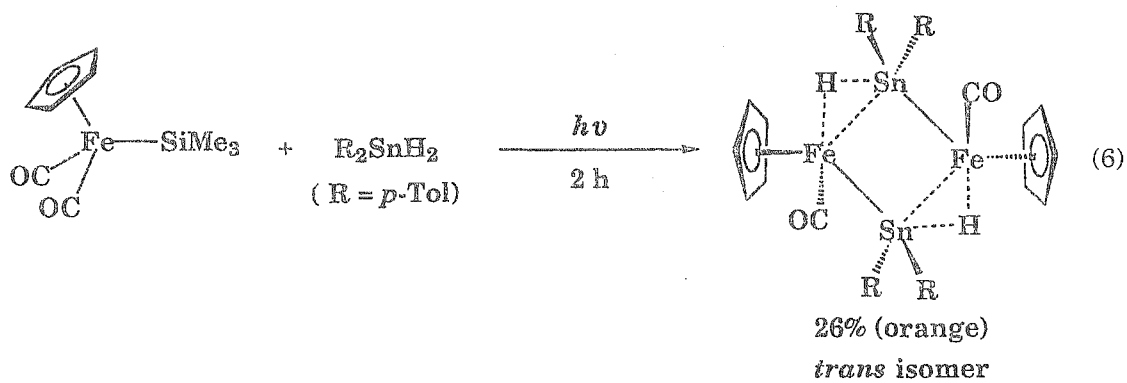
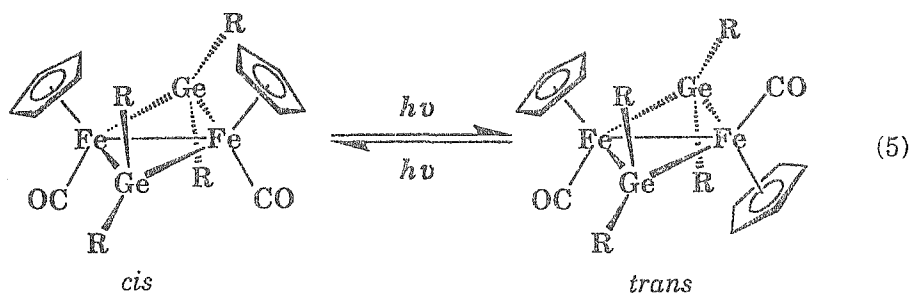
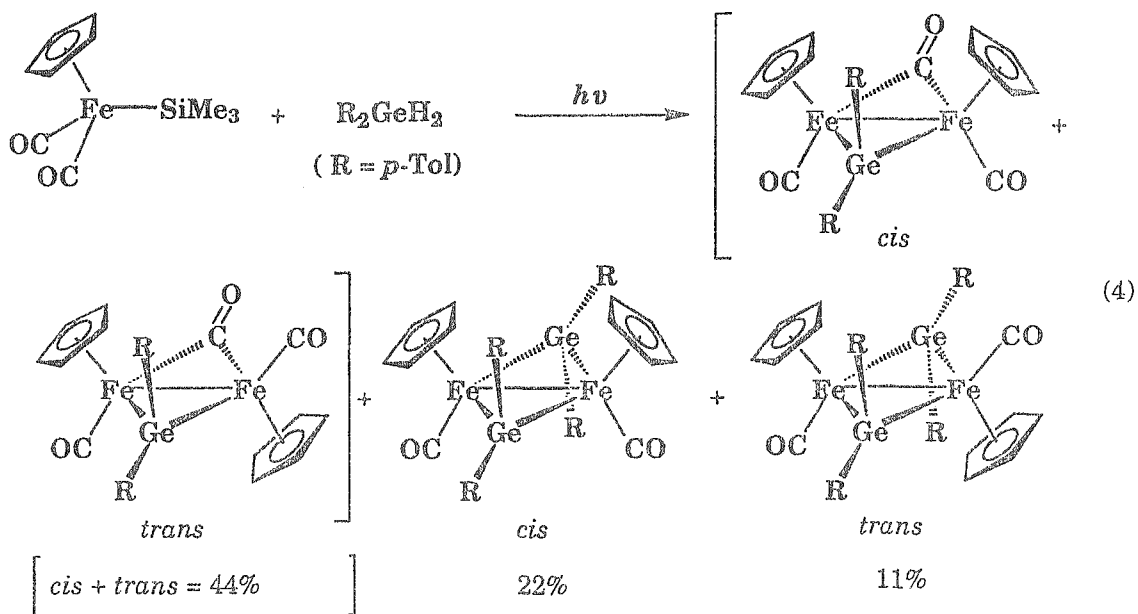
Photolysis of $\text{CpFe}(\text{CO})_2\text{SiMe}_3$ in the presence of tertiary stannane $(p\text{-Tol})_3\text{SnH}$ afforded bis(stannyl)hydridoiron complex $\text{CpFe}(\text{CO})\text{H}\{\text{Sn}(p\text{-Tol})_3\}_2$ (eq 10).

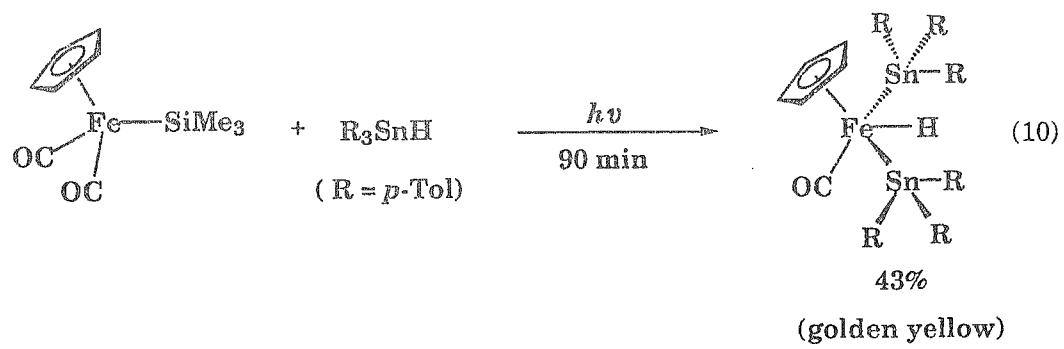
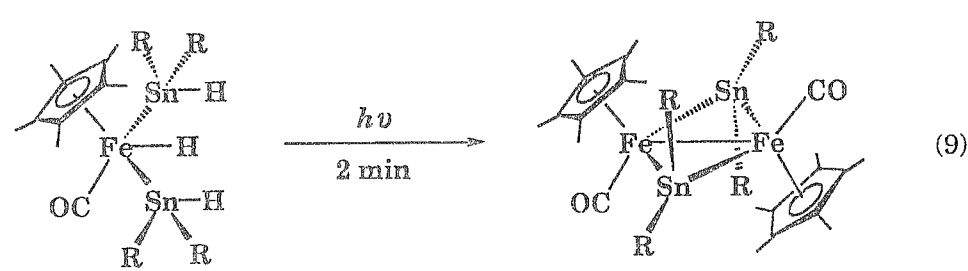
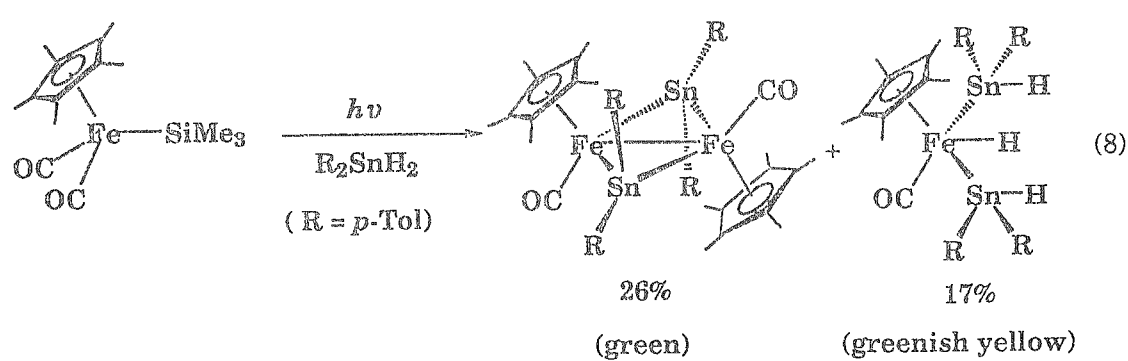
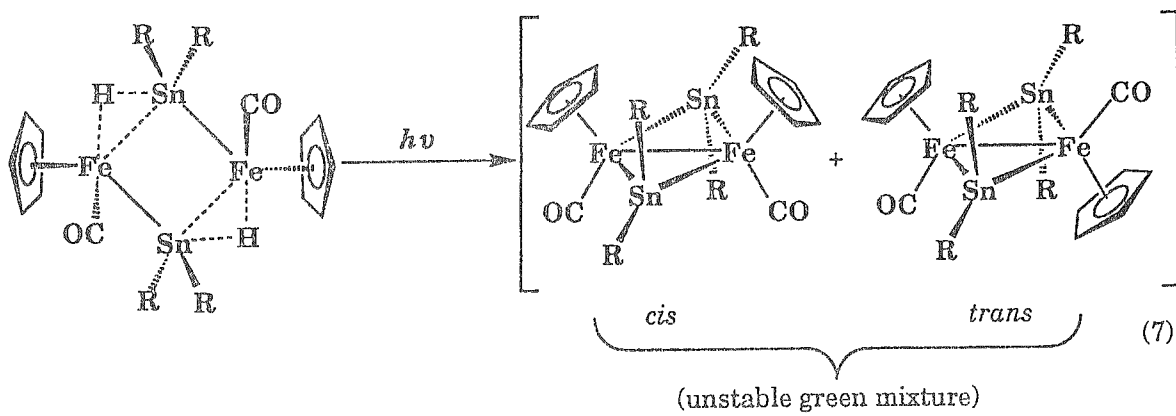
On the basis of the coupling constant values of $^1J_{\text{Sn-H}}$ and $^2J_{\text{SnMH}}$, I suggested that $\text{Cp}_2\text{Fe}_2(\text{CO})_2\{\mu\text{-Sn}(p\text{-Tol})_2\text{H}\}_2$ contains two 3-center 2-electron bonds.



Scheme 1







論文審査の結果の要旨

この論文は、著者が第1級または第2級ゲルマンおよびスタナンとシリル鉄錯体との光反応によって、様々なゲルミレン及びスタニレン架橋二核錯体、およびFe-H-E 3中心2電子結合 (E=Ge, Sn) を持つ二核錯体を合成し、さらにこれら錯体の分光学的性質および反応性を調べたことについて記述したものである。本研究の主な成果を以下に列記する。

第1級ゲルマン $p\text{-TolGeH}_3$ の存在下で $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) に照射すると、モノ(ゲルミレン)架橋錯体 $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Gep-TolH})$ (1) (*cis*体と*trans*体の混合物)、ビス(ゲルミレン)架橋錯体 $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH})_2$ (2) (*syn-trans*体と*anti-trans*体の混合物) およびFe-H-Ge 3中心-2電子結合を二つ持つ錯体 $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Gep-TolH}_2)_2$ (3) (*syn-cis*体) が得られた。1は熱と光の両方で幾何異性化を行い、熱平衡状態では*trans*体が、また光定常状態では*cis*体がそれぞれ優勢となることを見出した。一方、2は熱的には異性化しないが、照射によって異性化して、定常状態で *syn-trans*:*anti-trans*=61:39となることがわかった。また、3は照射しても加熱しても H_2 を放出してビス(ゲルミレン)錯体2を与えるが、光反応では2の*syn-trans*体と*anti-trans*体の混合物を与えるのに対して、熱反応(70°C)では*syn-cis(H)*体のみを与えることを見出した。同様の研究を第2級ゲルマン($p\text{-Tol}$) $_2\text{GeH}_2$ および $\text{CpFe}(\text{CO})_2\text{SiMe}_3$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) を用いて行い、シクロペンタジェニル配位子とゲルマンの置換基のかさ高さの関係によって生成物が様々に変化することを明らかにした。さらに、第2級スタナン($p\text{-Tol}$) $_2\text{SnH}_2$ と $\text{CpFe}(\text{CO})_2\text{SiMe}_3$ との光反応についても研究し、前例のないFe-H-Sn 3中心-2電子結合を二つ持つ錯体 $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Snp-Tol}_2\text{H})_2$ (4) を得た。4の大きな J_{SnH} 値 (56Hz) は、3中心-2電子結合の存在を強く支持している。また、4は3と異なり*trans*体であり、熱的には H_2 を放出しないが、光によって H_2 を放出してビス(スタニレン)架橋錯体 $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-Snp-Tol}_2)_2$ (5) (*cis-trans*混合物, 不安定) を与えることがわかった。

本論文は著者が自立して研究活動を行うに必要な高度の研究能力と学識を有していることを示している。よって、Amr Abd El-Aziz El-Maradny提出の論文は、博士(理学)の学位論文として合格と認める。