Photochemical Synthesis and Properties of Diiron Complexes Bridged by Sterically Hindered Divalent Group-14 Species

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学位論文題目	Photochemical Synthesis and Properties of Diiron Complexes Bridged by Sterically Hindered Divalent Group-14 Species （かさ高い２価１４族元素化学種が架橋した鉄二核錯体の光化学的合成と性質）
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論文内容要旨

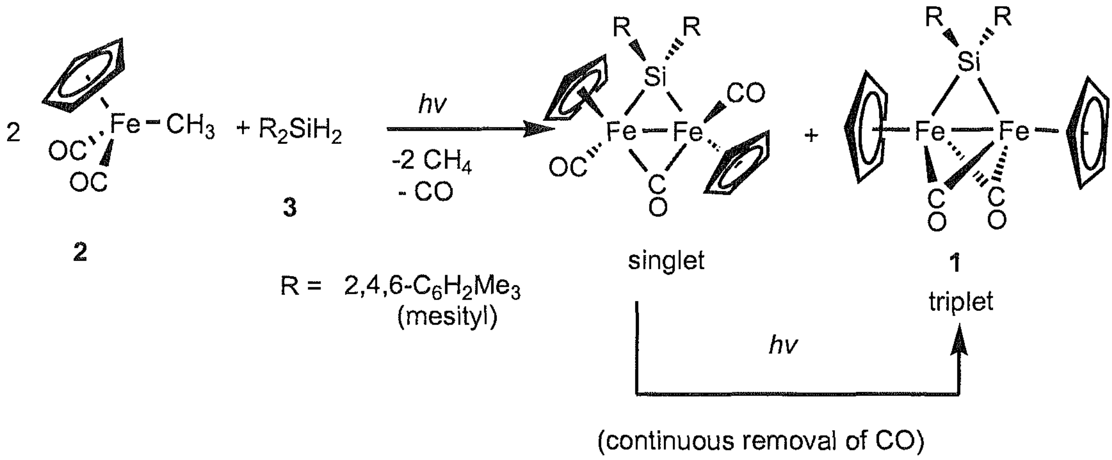
Among a variety of dinuclear organometallic complexes, complexes having a triplet ground state are very rare though they are considered to be an important class of reactive organometallic compounds. A considerable effort has been made to explore and understand their chemistry. To date, most of these investigations have focused on theoretical studies on the electronic structure; only a few have focused on their structure and reactivities. There are several reasons for this lack, one is the necessity of the existence of stringent steric protection for these highly reactive species. This paper addresses the influence of the substituents and the size of the bridging atoms on the ground state spin multiplicity of the resulting dinuclear complexes. Also described are the reactivity of the triplet complexes towards 2-electron donor ligands.

In **Chapter 2**, the yield of the previously reported triplet silylene-bridged complex, $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Si(2,4,6\text{-}C_6H_2Me_3)_2]$ (**1**), was doubled (45%) by carrying out the photolysis of $CpFe(CO)_2CH_3$ (**2**) with $H_2Si(2,4,6\text{-}C_6H_2Me_3)_2$ (**3**) in a CO-free system (eq. 1). Photolysis of a pentane solution of **2** with less sterically congested diarylsilane,

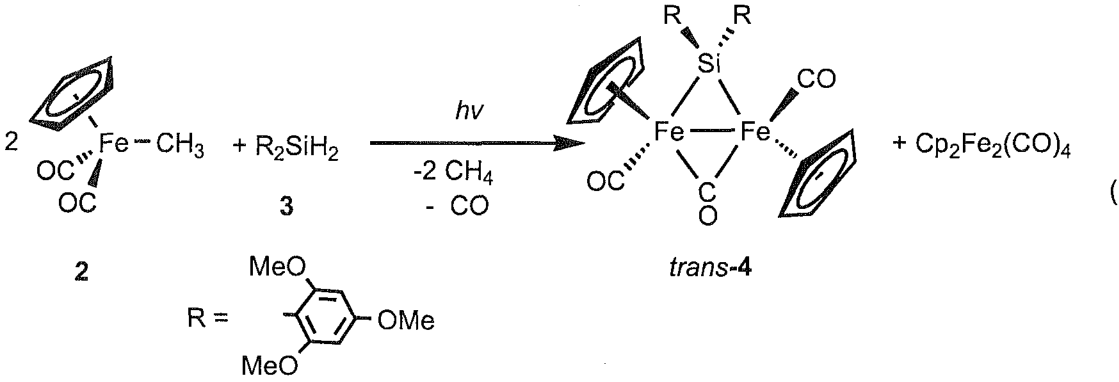
$H_2Si\{2,4,6\text{-}C_6H_2(OMe)_3\}_2$ (**3**), gave a singlet complex with three CO ligands, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}Si[2,4,6\text{-}C_6H_2(OMe)_3]_2\}$ (*trans*-**4**) (eq. 2). Decarbonylation of *trans*-**4** by irradiation under continous removal of CO did not give the expected doubly CO-bridged complex, presumably because the steric bulk of the 2,4,6-trimethoxyphenyl substituents is not enough to stabilize such complexes. Photolysis of $CpFe(CO)_2CH_3$ (**2**) with diarylgermane $H_2Ge(2,4,6\text{-}C_6H_2Me_3)_2$ (**5**) afforded a mixture of a diamagnetic complex, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}Ge(2,4,6\text{-}C_6H_2Me_3)_2]$ (*trans*-**6**), and a paramagnetic complex, $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Ge(2,4,6\text{-}C_6H_2Me_3]_2\}$ (**7**). Complex **7** was isolated in 13% yield when the irradiation was performed with removal of CO gas (eq. 3). In the case of more sterically congested diarylgermane $H_2Ge(2,4,6\text{-}C_6H_2{}^iPr_3)_2$ (**8**), only doubly CO-bridged complex $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Ge(2,4,6\text{-}C_6H_2{}^iPr_3)_2]$ (**9**) was formed and isolated in higher yield; 47% (eq. 4). These results support the notation that the bulkiness of the substituents on the bridging atom plays a crucial role in the preferred structure of the formed complexes. X-ray crystal structures of triplet complexes **1** and **9** showed a conspicuous shortening of the Fe—Fe bond distances (2.2990(8) Å for **1** and 2.3103(6) Å) for **9** which are comparable to the known Fe—Fe double bonds (2.2—2.4 Å). The molecules have a C_2 symmetry. The effective magnetic moments of paramagnetic silylene- and germylene-bridged complexes **1**, **9**, and $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Si(2,6\text{-}C_6H_3Et_2)_2]$ (**10**) are nearly constant within 2.8—2.9 μ_B (from 50—300 K) which agree well with the theoritical value (2.83 μ_B) expected for spin-only moment with $S = 1$, namely triplet state. The triplet ground state originates from the low splitting energy of the two HOMOs compared to the electron pairing energy to let them both half-filled.

In **Chapter 3**, the photochemical reactions of secondary stannane R_2SnH_2 [**11**, R = $2,4,6\text{-}C_6H_2(CH_3)_3$ (Mes); **12**, R = $2,4,6\text{-}C_6H_2{}^iPr_3$] with $Cp'Fe(CO)_2Me$ [**2**, Cp' = $\eta^5\text{-}C_5H_5$ (Cp); **13**, $\eta^5\text{-}C_5Me_5$ (Cp*)] were described. In contrast with the silicon and germanium cases, the photoreaction of **2** and diarylstannane with the same substituents afforded only singlet complexes, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SnR_2)$ (*trans*-**14**, R = Mes; *trans*-**15**, R = $2,4,6\text{-}C_6H_2{}^iPr_3$) in 40% and 35% yields, respectively (eq. 5). No sign of formation of the corresponding triplet complexes was observed even when the more sterically hindered complex **15** was irradiated alone with continuous removal of CO. These results underscore the notation that relatively subtle changes in the size of the bridging ligand have a strong effect on the preferred structure of the resulting complexes. That is, the larger the bridging unit, the longer the Fe-bridging ligand distances and so less efficient the steric protection of the highly reactive metal centers. The photolysis of the much bulkier Cp* complex **13** with diarylstannane **11** or **12** did not afford any stannylene-bridged complexes but an iron dimer $Cp^*{}_2Fe_2(CO)_4$ in case of the latter and a monoiron complex $Cp^*Fe(CO)_2SnHMes_2$ (**16**) in case of the former (eq. 6) were formed. These results reflect the effect of the steric bulk of the ligands on the iron complex on the preferential structure of the products. The highly thermodynamic and kinetic stabilization conferred by the bulky Cp* and mesityl ligands were reflected on the pronounced stability of **16**. That is, complex **16** was so stable under photolysis conditions alone or in the presence of the iron complex **13**.

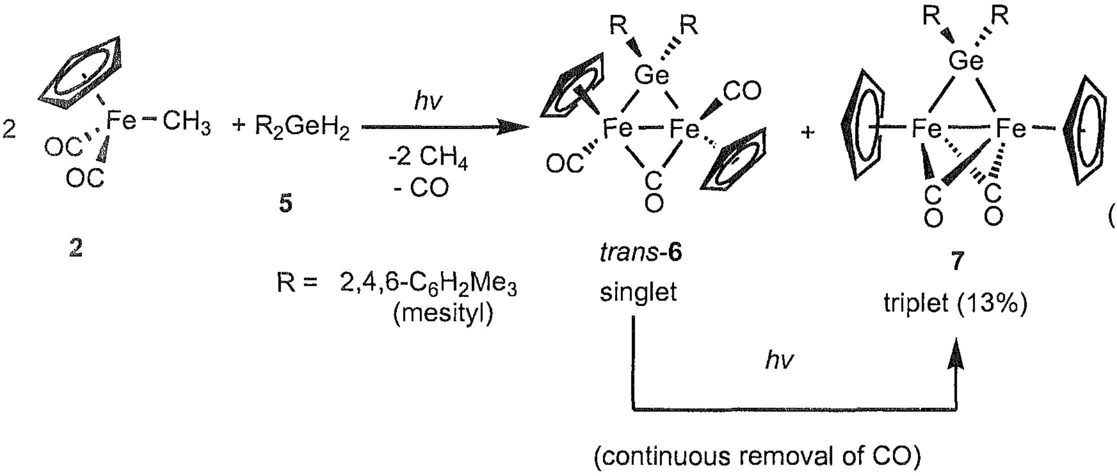
In **Chapter 4**, the reactivities of triplet silylene- and germylene-diiron complexes was investigated. It was found that the reactivity depends not only on the size of the bridging ligand but also on the steric bulk of the substituents on the bridging atom. In general, germylene-bridged complexes are less stable compared with their silylene analogues. The presence of the bulky triisopropyl phenyl substituents in $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Ge(2,4,6\text{-}C_6H_2{}^iPr_3)_2]$ (**9**) confer high stability and low reactivity. That is, complex **9** is highly stable and showed sluggish reactions towards most reagents (CO, H_2, disulphides). The only reactivity pattern of **9** that was clarified was the one with ^{t}BuNC giving $Cp_2Fe_2(CO)(^tBuNC)(\mu\text{-}CO)[\mu\text{-}Ge(2,4,6\text{-}C_6H_2{}^iPr_3)_2]$ (*trans*-**17**) in 73% isolated yield (eq. 7). Germylene-bridged complex $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Ge(2,4,6\text{-}C_6H_2Me_3)_2]$ (**7**) with relatively less bulkier mesityl substituents was found to be extremely reactive to moisture and air. It quantitatively added CO to give $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}Ge(2,4,6\text{-}C_6H_2Me_3)_2]$ (*trans*-**18**). The reaction of **7** with ^{t}BuNC afforded an isocyanide adduct $Cp_2Fe_2(CO)(^tBuNC)(\mu\text{-}CO)[\mu\text{-}Ge(2,4,6\text{-}C_6H_2Me_3)_2]$ (*trans*-**19**) in 57% isolated yield (eq. 8). The silylene-bridged complex $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Si(2,4,6\text{-}C_6H_2Me_3)_2]$ (**1**) was found to be a promising model for studying the reactivity of triplet complexes (i.e. high isolated yield and moderate stability). Reaction of **1** with ^{t}BuNC gave a mixture of *cis* and *trans* (5 : 4 ratio) isomers $Cp_2Fe_2(CO)(^tBuNC)(\mu\text{-}CO)[\mu\text{-}Si(2,4,6\text{-}C_6H_2Me_3)_2]$ (**20**) in 90% yield (eq. 9). Irradiation of terminal isocyanide complexes **17**, **19**, and **20** gave the ancestry triplet complexes **9**, **7**, and **1**, respectively. The reaction of **1** with 2,6-xylylisocyanide gave $Cp_2Fe_2[\mu\text{-}CN(2,6\text{-}C_6H_3Me_2)](CO)_2[\mu\text{-}Si(2,4,6\text{-}C_6H_2Me_3)_2]$ (*trans*-**21**) with the xylylisocyanide ligand occupying the bridging position (eq. 10). Photolysis of complex **21** afforded a mixture of **1** and $Cp_2Fe_2[\mu\text{-}CN(2,6\text{-}C_6H_3Me_2)]_2[\mu\text{-}Si(2,4,6\text{-}C_6H_2Me_3)_2]$(**22**) from which compex **22** was isolated in 38% yield (eq. 11). Complex **22** was found to be paramagnetic, and the NMR spectra exhibit the characteristic paramagnetic shifts and line broadening. The structure of **22** was confirmed by X-ray crystal structure analysis. Interestingly, one of the isocyanide ligands is slightly bent while the other one is largely bent. Complex **22** is the first paramagnetic dinuclear complex doubly bridged by isocyanide ligands.


2
+ R_2SiH_2
3
hv
-2 CH_4
- CO
R = 2,4,6-$C_6H_2Me_3$ (mesityl)
singlet
+
1
triplet
hv
(continuous removal of CO)

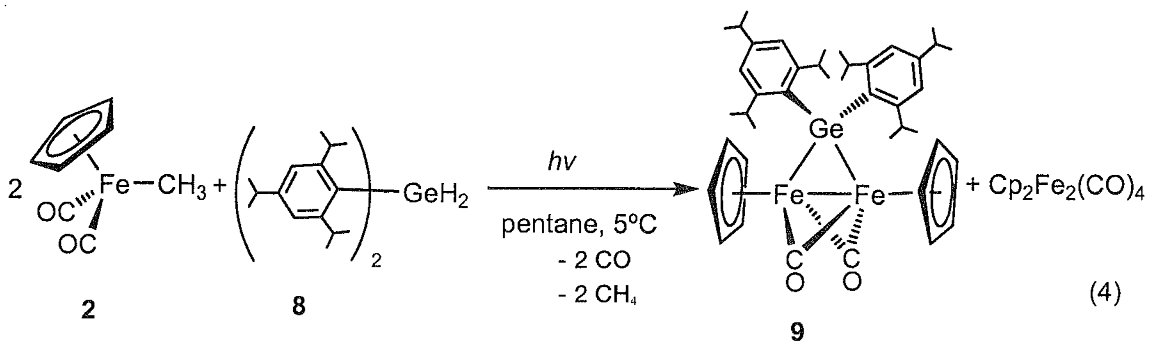
(1)

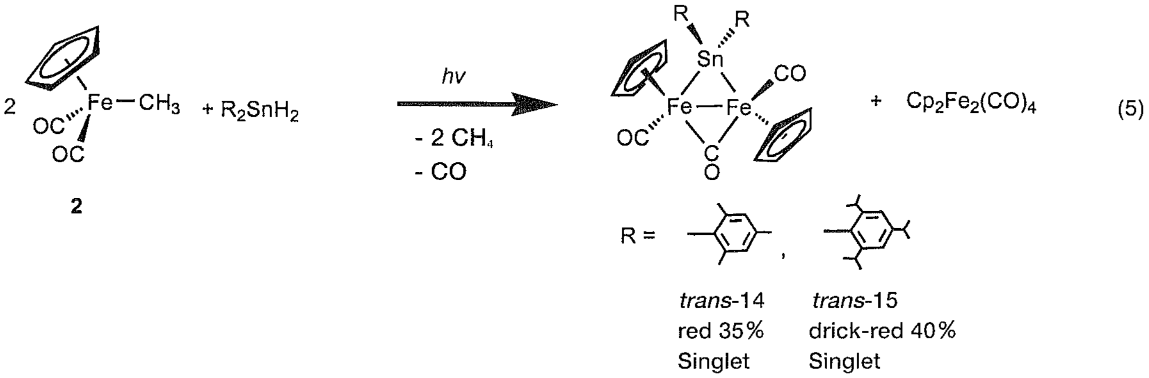

2
+ R_2SiH_2
3
hv
-2 CH_4
- CO
R =
MeO
OMe
MeO
trans-4
+ $Cp_2Fe_2(CO)_4$

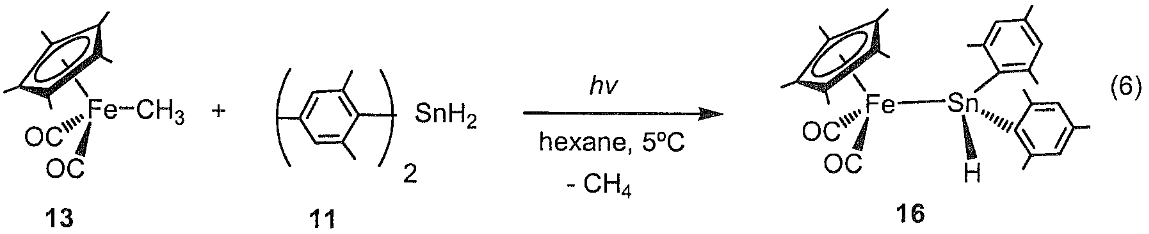
(2)

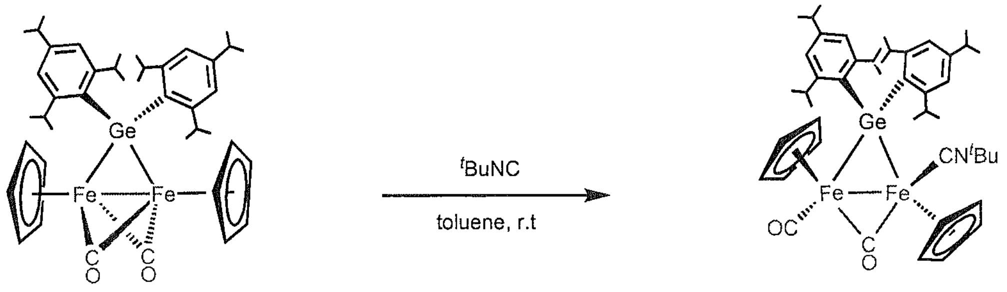

2
+ R_2GeH_2
5
hv
-2 CH_4
- CO
R = 2,4,6-$C_6H_2Me_3$ (mesityl)
trans-6
singlet
+
7
triplet (13%)
hv
(continuous removal of CO)

(3)


2
Fe—CH3
OC
OC
2
GeH2
2
8
hv
pentane, 5°C
- 2 CO
- 2 CH4
Ge
Fe
Fe
C
O
C
O
9
+ Cp2Fe2(CO)4
(4)


2
Fe—CH3
OC
OC
+ R2SnH2
2
hv
- 2 CH4
- CO
R
R
Sn
CO
Fe—Fe
OC
C
O
+ Cp2Fe2(CO)4
(5)
R =
trans-14
red 35%
Singlet
trans-15
drick-red 40%
Singlet

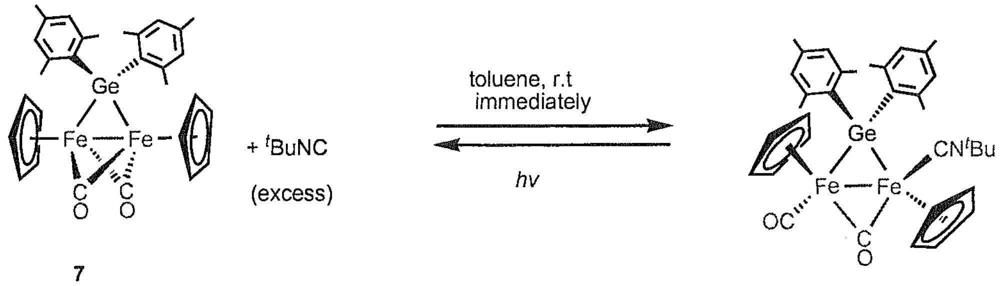

Fe—CH3
OC
OC
13
+
SnH2
2
11
hv
hexane, 5°C
- CH4
Fe
Sn
OC
OC
H
16
(6)



9

trans-**17**
(73%)

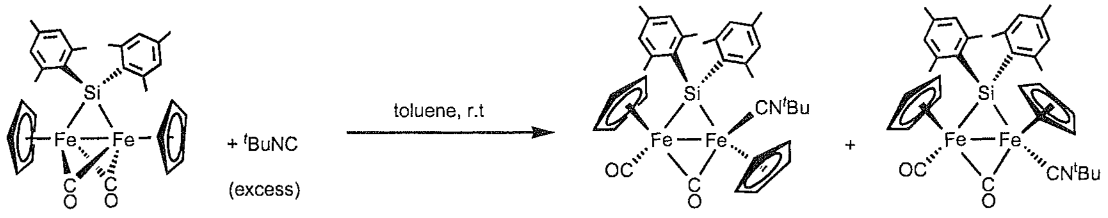
(7)



7

trans-**19** (57%)

(8)

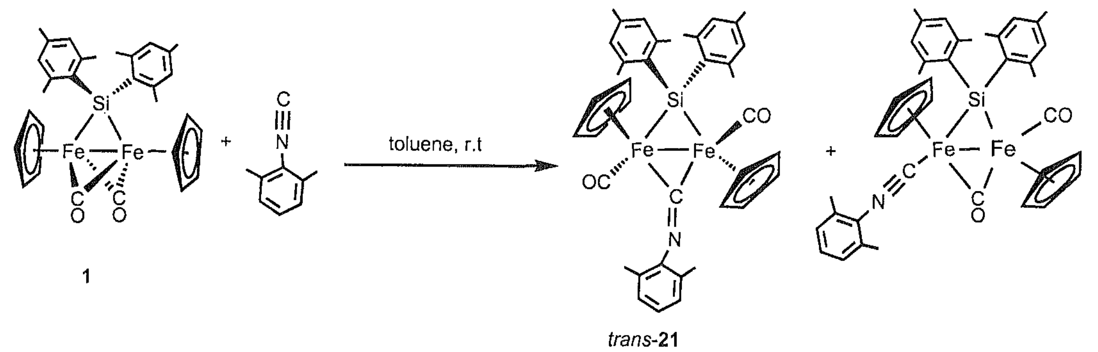


1

trans-**20**

cis-**20**

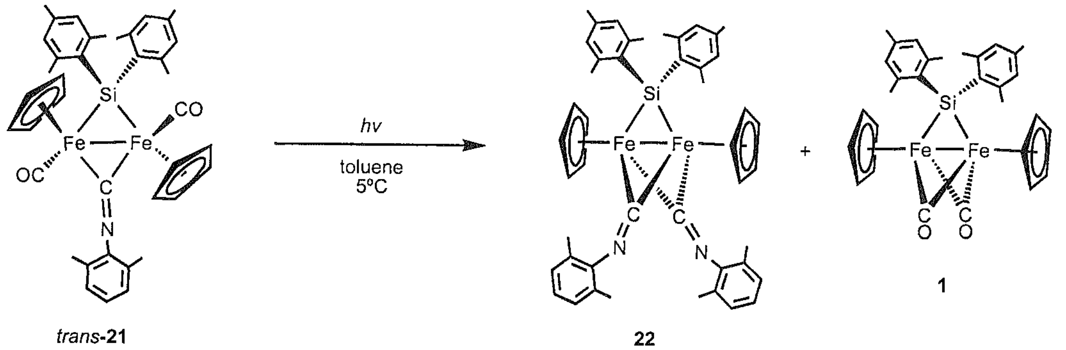
(9)



1

trans-**21**

(10)



trans-**21**

22

1

(11)

論文審査の結果の要旨

常磁性の有機金属二核錯体は，有機金属二核錯体の光異性化反応の中間体や，ラジカル反応における反応活性種のモデルとして重要な化学種であるが，単離例は少ない。最近，基底三重項状態を持つ２価のケイ素化学種（シリレン）が架橋した鉄二核錯体が単離されたが，その性質はあまり明らかにされていない。この論文は，一連の２価の高周期１４族元素化学種が架橋した三重項鉄二核錯体の合成，性質，および三重項錯体生成に影響する因子について，著者が行なった研究を記述したものである。本研究の成果を以下に要約する。

(1) 基底三重項状態をもつシリレン架橋二核錯体$Cp_2Fe_2(\mu\text{-CO})_2(\mu\text{-SiR}_2)$ (**1a**; R = 2,4,6-$C_6H_2{}^iPr_3$，**1b**: R = 2,4,6-$C_6H_2Me_3$)の高収率合成法を確立し，**1b**の結晶構造を明らかにした。

(2) $CpFe(CO)_2CH_3$ とかさ高いジアリールジヒドロゲルマンとの光反応から，ゲルミレン架橋二核錯体$Cp_2Fe_2(\mu\text{-CO})_2(\mu\text{-GeR}_2)$ (**2a**; R = 2,4,6-$C_6H_2{}^iPr_3$，**2b**: R = 2,4,6-$C_6H_2Me_3$) および$Cp_2Fe_2(CO)_2(\mu\text{-CO})[\mu\text{-Ge}(2,4,6\text{-}C_6H_2Me_3)_2]$ (**3**)を合成することに成功した。磁化率測定から，**2**は基底三重項状態をもつ初めてのゲルミレン架橋錯体であることを明らかにした。結晶構造解析により，鉄－鉄結合は二重結合に相当するほど短いことを明らかにした。

(3) 基底三重項状態をもつスタニレン架橋二核錯体の合成を種々試みたが，**3**と類似の一重項錯体のみが得られた。三重項二核錯体は，架橋配位子上の置換基がかさ高いほど，また架橋元素（Si, Ge, Sn）の原子サイズが小さくなるほど生成しやすいことが分かった。

(4) 最もかさ高い置換基を持つ**1a**や**2a**は極めて安定で，ほとんどの試薬と反応しなかった。しかし，**1b**や**2b**は熱的にCOやイソシアニドと容易に反応し，**3**に類似の一重項錯体を与えた。特に，**1b**と$(2.6\text{-}Me_2C_6H_3)NC$との反応生成物は，さらに光反応により，イソシアニドが２つ架橋配位した新しいタイプの三重項シリレン架橋錯体を与えることを見出した。

これらの研究は，研究例の少ない基底三重項状態をとる有機金属二核錯体の合成と構造および反応性を，系統的に明らかにしたものとして，極めて高く評価できる。

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。したがって，Bahaa A. S. E. Mohamed提出の博士論文は，博士（理学）の学位論文として合格と認める。