

Synthesis and Characterization of Triplet Germylene-bridged Diiron Complexes and Singlet Stannylene-bridged Diiron Complexes

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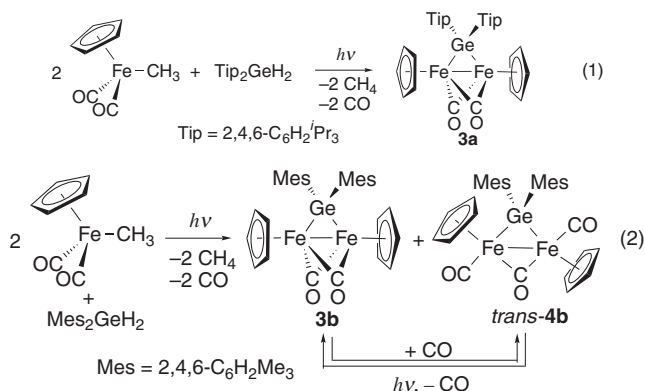
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Photoreaction of $\text{CpFe}(\text{CO})_2\text{Me}$ with sterically congested R_2GeH_2 [$\text{R} = 2,4,6\text{-C}_6\text{H}_2^i\text{Pr}_3$ (Tip), $2,4,6\text{-C}_6\text{H}_2\text{Me}_3$ (Mes)] afforded paramagnetic germylene-bridged diiron complexes having a triplet ground state, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\mu\text{-GeR}_2)$ (**3a**, $\text{R} = \text{Tip}$; **3b**, $\text{R} = \text{Mes}$), while the analogous reaction with R_2SnH_2 afforded diamagnetic complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SnR}_2)$ (*trans*-**5a**, $\text{R} = \text{Tip}$; *trans*-**5b**, $\text{R} = \text{Mes}$). The structure of **3a** was determined by X-ray crystallography.

Among a variety of dinuclear organometallic complexes, the ones having a triplet ground state are very rare though they are considered to be an important class of reactive organometallic compounds.¹ We recently reported the first triplet silylene-bridged dinuclear complexes, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\mu\text{-SiR}_2)$ (**1a**, $\text{R} = 2,4,6\text{-C}_6\text{H}_2^i\text{Pr}_3$ (Tip); **1b**, $\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$ (Mes); **1c**, $\text{R} = 2,6\text{-C}_6\text{H}_3\text{Et}_2$)^{2a} and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-CO})_2\{\mu\text{-SiH}(p\text{-C}_6\text{H}_4\text{Me})\}$ (**2**).^{2b} Since these complexes possess only nondegenerated MOs due to the symmetry, the triplet state of the silylene-bridged complexes would originate in the small energy splitting between the HOMO and the next HOMO that renders the orbitals both half-filled. To gain further insight into the properties of such complexes, we have studied the ones possessing much heavier group 14 species as a bridging ligand. We report here the synthesis and structure of the first germylene-bridged diiron complexes having a triplet ground state and their reactions with CO. The attempts to prepare the stannylene-bridged analog, which resulted in the isolation of only diamagnetic species, are also described.

Germylene-bridged diiron complex having a triplet ground state, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\mu\text{-GeTip}_2)$ (**3a**), was prepared in 47% yield by photolysis of a 2:1 mixture of $\text{CpFe}(\text{CO})_2\text{Me}$ and sterically congested diarylgermane Tip_2GeH_2 in pentane at 5°C for 6 h (Eq 1).³ When the substituents on the Ge atom were less bulky mesityl groups, a singlet diiron complex with three CO ligands, $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeMes}_2)$ (*trans*-**4b**), was mainly formed as well as a small amount of triplet $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-GeMes}_2)$ (**3b**) (Eq 2).⁴ Separation of these complexes from this mixture was unsuccessful. Pure complex *trans*-**4b** was isolated in 40% yield when the irradiation of a solution of $\text{CpFe}(\text{CO})_2\text{Me}$ and Mes_2GeH_2 was followed by CO bubbling, while **3b** was isolated in 13% yield when the irradiation was performed with removal of CO gas. A main by-product was $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ in all cases. In the experiments monitored by ^1H NMR spectroscopy, **3b** was observed to react readily with CO (1 atm) at room temperature to give *trans*-**4b** quantitatively, while irradiation of *trans*-**4b** yielded a substantial amount of **3b** with CO dissociation. Formation of *cis*-**4b** was not observed,

probably because of large steric repulsion between the Cp groups and the *ortho*-substituents on the aryl groups.



Complex **3a** is fairly stable in the solid state in air for weeks at room temperature. It remained intact even under pressurized CO. In contrast, **3b** is highly reactive to moisture and air probably because the steric protection of mesityl groups are less effective than that of $2,4,6\text{-C}_6\text{H}_2^i\text{Pr}_3$ groups. The NMR signals of **3a** and **3b** exhibit the characteristic paramagnetic shifts and line broadening.^{3,4} The IR spectrum of each complex shows two $\nu(\text{CO})$ bands in a bridging CO region (1822 and 1791 cm^{-1} for **3a**; 1806 and 1774 cm^{-1} for **3b**).^{3,4} The mass spectra and elemental analyses of them also support their formulas.^{3,4}

Complex **3a** was structurally characterized by X-ray crystallography (Figure 1).⁵ The overall structure of **3a** is almost identical to that of the silicon analog **1a**.^{2a} The two Cp rings coordinated to the iron atoms are almost parallel. The *ortho*-substituents on the aryl groups are positioned to protect the Fe_2Ge three-membered ring core. The Fe–Fe distance ($2.3103(6)\text{ \AA}$) of **3a** is significantly shorter than those of related complexes, $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeH}^i\text{Bu})$ ($2.641(1)\text{ \AA}$)^{6a} and $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeMe}_2)$ ($2.628(1)\text{ \AA}$).^{6b} This distance is comparable to that of the complex with a formal Fe–Fe double bond, $\text{Cp}_2\text{Fe}_2(\mu\text{-NO})_2$ ($2.326(4)\text{ \AA}$)⁷ and is similar to triplet complexes **1a** ($2.303(3)\text{ \AA}$)^{2a} and **2** ($2.300(4)\text{ \AA}$).^{2b} The Fe–Ge bond distance ($2.3965(4)\text{ \AA}$) is within a range reported for those of other (μ -germylene)(μ -carbonyl) diiron complexes ($2.32\text{--}2.47\text{ \AA}$).⁸

The magnetic susceptibility of **3a** was measured in the solid state on a SQUID magnetometer at 10000 G . The effective magnetic moment (μ_{eff}) after the diamagnetic correction is constant within $2.81\text{--}2.83\text{ }\mu_{\text{B}}$ from 15 to 300 K , which agrees well with the theoretical value ($2.83\text{ }\mu_{\text{B}}$) for a spin-only magnetic moment with $S = 1$, namely the triplet state.

In contrast with the silicon and germanium cases, the photoreaction of $\text{CpFe}(\text{CO})_2\text{Me}$ and diarylstannane R_2SnH_2 with the

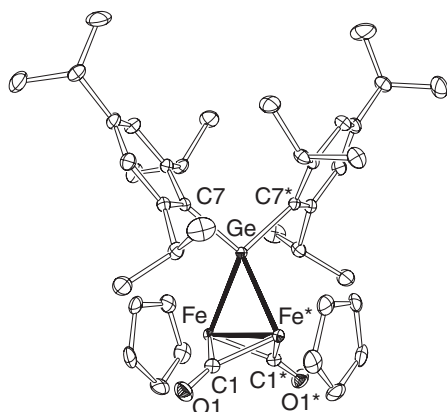
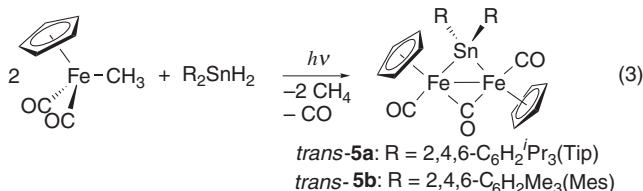


Figure 1. ORTEP drawing of **3a**, showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Fe–Fe* 2.3103(6), Fe–Ge 2.3965(4), Fe–C1 1.847(2), Fe*–C1 2.008(2); Fe–Ge–Fe* 57.633(15), Fe–Fe*–Ge 61.184(8), C7–Ge–C7* 102.86(11).

same substituents afforded only diamagnetic $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SnR}_2)$ (*trans*-**5a**, R = Tip; *trans*-**5b**, R = Mes) in 35 and 40% yields (Eq 3), respectively.⁹ No sign of formation of the corresponding triplet complexes was observed even when *trans*-**5a** or *trans*-**5b** was irradiated under continuous removal of CO.



It appears that subtle changes in the size of the bridging atom and its substituents have a strong effect on the stability of the triplet complexes. Triplet silylene- and germylene-bridged complexes with congested 2,4,6- $\text{C}_6\text{H}_2\text{iPr}_3$ groups are kinetically much stabler than those with less bulky mesityl ligands. Triplet tin complexes corresponding to **1** and **3** seem extremely vulnerable to the attack of CO to produce the singlet complexes **5** just as **3b** reacts with CO to give *trans*-**4b**. For the synthesis of a triplet tin complex, even larger substituents on Sn must be required since the Fe–Sn bond is much longer than Fe–Si and Fe–Ge bonds (e.g. covalent radii (Å): Si (1.17) < Ge (1.22) < Sn (1.40)).¹⁰ To prove this, we are now trying to introduce bulkier ligands on the tin atom.

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- A solution of bis(2,4,6-triisopropylphenyl)germane (1.21 g, 2.51 mmol) and $\text{CpFe}(\text{CO})_2\text{CH}_3$ (1.00 g, 5.21 mmol) in pentane (200 mL) was irradiated with a 450 W medium pressure Hg immersion lamp through a Pyrex sleeve at 5 °C for 6 h. Evaporation of volatiles and subsequent separation of the residue by flash chromatography (silica gel, eluent; hexane:toluene = 2:1) gave violet $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2[\mu\text{-Ge}(2,4,6\text{-C}_6\text{H}_2\text{iPr}_3)_2]$ **3a** (0.95 g, 1.23 mmol, 47%), and $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (227 mg, 0.641 mmol, 25%). **3a**: ^1H NMR (C_6D_6 , 300 MHz) δ 8.38, 4.28, 2.11, 1.94, 1.30, –1.04, –1.67, –2.18. IR (KBr) 1822, 1791 $\nu(\text{CO}_{\text{brid}})$ cm^{-1} . MS (FAB) m/z 779 (6, $\text{M}^+ + 1$), 750 (14, $\text{M}^+ - \text{CO}$), 657 (56, $\text{M}^+ - 2\text{CO} - \text{Cp}$), 601 (100, $\text{M}^+ - 2\text{CO} - \text{Cp} - \text{Fe}$), 480 (19, $\text{M}^+ - 2\text{CO} - 2\text{Cp} - 2\text{Fe}$). Anal. Calcd for $\text{C}_{42}\text{H}_{56}\text{Fe}_2\text{GeO}_2$: C, 64.91; H, 7.26. Found: C, 65.21; H, 7.49.
- 3b**: ^1H NMR (C_6D_6 , 300 MHz) δ 9.01, 5.89, 5.07, 2.91, –1.51, –3.02; IR (KBr) 1806, 1774 $\nu(\text{CO}_{\text{brid}})$ cm^{-1} . MS (EI) m/z 610 (1, M^+), 582 (9, $\text{M}^+ - \text{CO}$), 554 (8, $\text{M}^+ - 2\text{CO}$). HRMS: Calcd for $\text{C}_{30}\text{H}_{32}\text{Fe}_2\text{GeO}_2$: 610.0312. Found: 610.0289. *trans*-**4b**: ^1H NMR (C_6D_6 , 300 MHz) δ 6.83 (s, 2H, ArH), 6.72 (s, 2H, ArH), 4.27 (s, 10H, C_5H_5), 2.86 (s, 6H, *o*-Me), 2.59 (s, 6H, *o*-Me), 2.14 (s, 6H, *p*-Me). IR (KBr) 1992, 1941 $\nu(\text{CO}_{\text{term}})$, 1772 $\nu(\text{CO}_{\text{brid}})$ cm^{-1} . MS (FAB) m/z 582 (41, $\text{M}^+ - 2\text{CO}$), 554 (22, $\text{M}^+ - 3\text{CO}$), 489 (63, $\text{M}^+ - 3\text{CO} - \text{Cp}$), 433 (100, $\text{M}^+ - 3\text{CO} - \text{Cp} - \text{Fe}$). Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{Fe}_2\text{GeO}_3$: C, 58.46; H, 5.06. Found: C, 58.61; H, 5.32.
- Crystal data for **3a**: $\text{C}_{42}\text{H}_{56}\text{Fe}_2\text{GeO}_2$; fw = 777.16; orthorhombic; *Pbcn*; $a = 18.2936(3)$, $b = 20.9585(7)$, $c = 9.8594(2)$ Å; $V = 3780.16(16)$ Å³; $Z = 4$; $D_{\text{calcd}} = 1.366$ g/cm³; $T = 150(2)$ K, 29300 reflections, 4170 independent ($R_{\text{int}} = 0.0326$); $R_1 = 0.0313(I > 2\sigma(I))$, $wR_2 = 0.0858$. Crystal data reported in this paper have been deposited with Cambridge Crystallographic Data Centre (CCDC 218198).
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- Based on a search of the Cambridge Structural Database, CSD version 5.24 (November 2002).
- trans*-**5a**: ^1H NMR (C_6D_6 , 300 MHz) δ 7.19 (s, 2H, ArH), 7.05 (s, 2H, ArH), 4.50 (s, 10H, C_5H_5), 3.91, 3.48, 2.77 (sept, 6H, *o/p*-CHMe₂), 1.43, 1.33, 1.24, 1.23, 1.21 0.47 (d, 36H, CHMe₂). ^{119}Sn NMR (C_6D_6 , 112 MHz) δ 828.9. IR (CH_2Cl_2) 2003, 1928 $\nu(\text{CO}_{\text{term}})$, 1743 $\nu(\text{CO}_{\text{brid}})$ cm^{-1} . MS (EI) m/z 852 (8, M^+), 703 (18, $\text{M}^+ - 3\text{CO} - \text{Cp}$), 647 (100, $\text{M}^+ - 3\text{CO} - \text{Fe} - \text{Cp}$). Anal. Calcd for $\text{C}_{43}\text{H}_{56}\text{Fe}_2\text{O}_3\text{Sn}$: C, 60.67; H, 6.63. Found: C, 60.54; H, 6.50. *trans*-**5b**: ^1H NMR (C_6D_6 , 300 MHz) δ 7.01 (s, 2H, ArH), 6.76 (s, 2H, ArH), 4.31 (s, 10H, C_5H_5), 2.80 (s, 6H, *o*-Me), 2.60 (s, 6H, *o*-Me), 2.14 (s, 6H, *p*-Me). ^{119}Sn NMR (C_6D_6 , 112 MHz) δ 835.5. IR (KBr) 2007, 1928 $\nu(\text{CO}_{\text{term}})$, 1751 $\nu(\text{CO}_{\text{brid}})$ cm^{-1} . MS (EI) m/z 684 (13, M^+), 628 (3, $\text{M}^+ - 2\text{CO}$), 600 (1, $\text{M}^+ - 3\text{CO}$), 535 (16, $\text{M}^+ - 3\text{CO} - \text{Cp}$), 479 (100, $\text{M}^+ - 3\text{CO} - \text{Fe} - \text{Cp}$). Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{Fe}_2\text{O}_3\text{Sn}$: C, 54.52; H, 4.72. Found: C, 54.31; H, 5.19.
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