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

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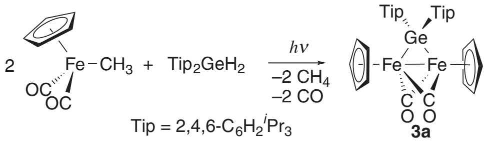
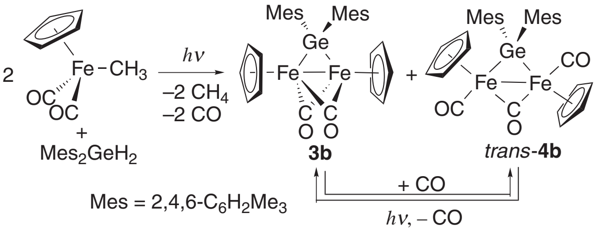
Photoreaction of $CpFe(CO)_2Me$ with sterically congested R_2GeH_2 [R = 2,4,6-$C_6H_2{}^iPr_3$ (Tip), 2,4,6-$C_6H_2Me_3$ (Mes)] afforded paramagnetic germylene-bridged diiron complexes having a triplet ground state, $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}GeR_2)$ (**3a**, R = Tip; **3b**, R = Mes), while the analogous reaction with R_2SnH_2 afforded diamagnetic complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SnR_2)$ (*trans*-**5a**, R = Tip; *trans*-**5b**, R = 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, $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}SiR_2)$ (**1a**, R = 2,4,6-$C_6H_2{}^iPr_3$ (Tip); **1b**, R = 2,4,6-$C_6H_2Me_3$ (Mes); **1c**, R = 2,6-$C_6H_3Et_2$)[2a] and $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)_2\{\mu\text{-}SiH(p\text{-}C_6H_4Me)\}$ (**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, $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}GeTip_2)$ (**3a**), was prepared in 47% yield by photolysis of a 2:1 mixture of $CpFe(CO)_2Me$ 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, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeMes_2)$ (*trans*-**4b**), was mainly formed as well as a small amount of triplet $Cp_2Fe_2(CO)_2(\mu\text{-}GeMes_2)$ (**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 $CpFe(CO)_2Me$ 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 $Cp_2Fe_2(CO)_4$ 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.



3a (1)



3b *trans*-**4b** (2)

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-$C_6H_2{}^iPr_3$ 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 ν(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) Å) of **3a** is significantly shorter than those of related complexes, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeH^tBu)$ (2.641(1) Å)[6a] and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)$ (2.628(1) Å):[6b] This distance is comparable to that of the complex with a formal Fe–Fe double bond, $Cp_2Fe_2(\mu\text{-}NO)_2$ (2.326(4) Å)[7] and is similar to triplet complexes **1a** (2.303(3) Å)[2a] and **2** (2.300(4) Å).[2b] The Fe–Ge bond distance (2.3965(4) Å) is within a range reported for those of other (μ-germylene)(μ-carbonyl) diiron complexes (2.32–2.47 Å).[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 2.81–2.83 μ_B from 15 to 300 K, which agrees well with the theoretical value (2.83 μ_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 $CpFe(CO)_2Me$ and diarylstannane R_2SnH_2 with the

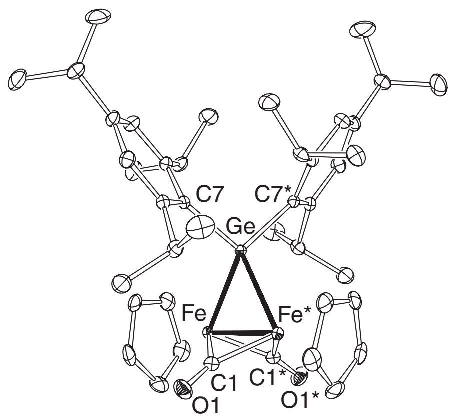
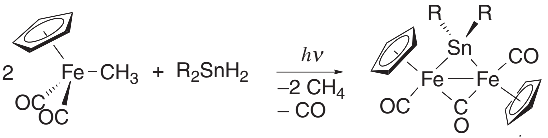


Figure 1. ORTEP drawing of **3a**, showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Fe–Fe* 2.3103(6), Fe–Ge 2.3965(4), Fe–C1 1.847(2), Fe*–C1 2.008(2); Fe–Ge–Fe* 57.633(15), Fe–Fe*–Ge 61.184(8), C7–Ge–C7* 102.86(11).

same substituents afforded only diamagnetic $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SnR_2)$ (*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.



(3)

trans-**5a**: R = 2,4,6-$C_6H_2{}^iPr_3$(Tip)
trans-**5b**: R = 2,4,6-$C_6H_2Me_3$(Mes)

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-$C_6H_2{}^iPr_3$ 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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References and Notes

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3 A solution of bis(2,4,6-triisopropylphenyl)germane (1.21 g, 2.51 mmol) and $CpFe(CO)_2CH_3$ (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 $Cp_2Fe_2(\mu\text{-}CO)_2[\mu\text{-}Ge(2,4,6\text{-}C_6H_2{}^iPr_3)_2]$ **3a** (0.95 g, 1.23 mmol, 47%), and $Cp_2Fe_2(CO)_4$ (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 $\nu(CO_{brid})$ cm^{-1}. MS (FAB) m/z 779 (6, $M^+ + 1$), 750 (14, $M^+ - CO$), 657 (56, $M^+ - 2CO - Cp$), 601 (100, $M^+ - 2CO - Cp - Fe$), 480 (19, $M^+ - 2CO - 2Cp - 2Fe$). Anal. Calcd for $C_{42}H_{56}Fe_2GeO_2$: C, 64.91; H, 7.26. Found: C, 65.21; H, 7.49.

4 **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 $\nu(CO_{brid})$ cm^{-1}. MS (EI) m/z 610 (1, M^+), 582 (9, $M^+ - CO$), 554 (8, $M^+ - 2CO$). HRMS: Calcd for $C_{30}H_{32}Fe_2GeO_2$: 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 $\nu(CO_{term})$, 1772 $\nu(CO_{brid})$ cm^{-1}. MS (FAB) m/z 582 (41, $M^+ - 2CO$), 554 (22, $M^+ - 3CO$), 489 (63, $M^+ - 3CO - Cp$), 433 (100, $M^+ - 3CO - Cp - Fe$). Anal. Calcd for $C_{31}H_{32}Fe_2GeO_3$: C, 58.46; H, 5.06. Found: C, 58.61; H, 5.32.

5 Crystal data for **3a**: $C_{42}H_{56}Fe_2GeO_2$; fw = 777.16; orthorhombic; *Pbcn*; $a = 18.2936(3)$, $b = 20.9585(7)$, $c = 9.8594(2)$ Å; $V = 3780.16(16)$ Å^3; $Z = 4$; $D_{calcd} = 1.366$ g/cm^3; $T = 150(2)$ K, 29300 reflections, 4170 independent ($R_{int} = 0.0326$); $R_1 = 0.0313 (I > 2\sigma(I))$, $wR_2 = 0.0858$. Crystal data reported in this paper have been deposited with Cambridge Crystallographic Data Centre (CCDC 218198).

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8 Based on a search of the Cambridge Structural Database, CSD version 5.24 (November 2002).

9 *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*-$CHMe_2$), 1.43, 1.33, 1.24, 1.23, 1.21 0.47 (d, 36H, $CHMe_2$). ^{119}Sn NMR (C_6D_6, 112 MHz) δ 828.9. IR (CH_2Cl_2) 2003, 1928 $\nu(CO_{term})$, 1743 $\nu(CO_{brid})$ cm^{-1}. MS (EI) m/z 852 (8, M^+), 703 (18, $M^+ - 3CO - Cp$), 647 (100, $M^+ - 3CO - Fe - Cp$). Anal. Calcd for $C_{43}H_{56}Fe_2O_3Sn$: 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 $\nu(CO_{term})$, 1751 $\nu(CO_{brid})$ cm^{-1}. MS (EI) m/z 684 (13, M^+), 628 (3, $M^+ - 2CO$), 600 (1, $M^+ - 3CO$), 535 (16, $M^+ - 3CO - Cp$), 479 (100, $M^+ - 3CO - Fe - Cp$). Anal. Calcd for $C_{31}H_{32}Fe_2O_3Sn$: C, 54.52; H, 4.72. Found: C, 54.31; H, 5.19.

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