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Synthesis and Structure of the First Base-Stabilized Germylyne-Bridged Dinuclear Complex $[Cp_2Fe_2(CO)_3(\mu\text{-Ge}{}^t\text{Bu}\cdot\text{DMAP})]OTf$ (DMAP = 4-(Dimethylamino)pyridine; OTf = CF_3SO_3)

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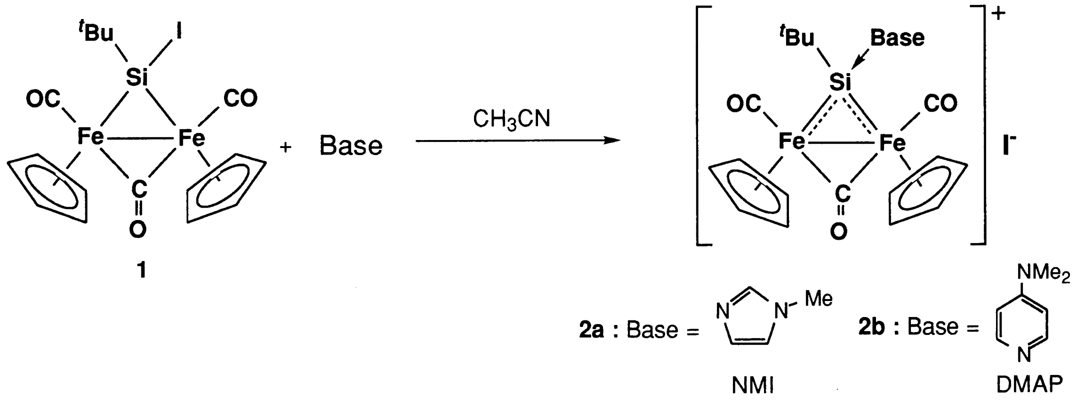
The germylene-bridged diiron complex $Cp_2Fe_2(CO)_3(\mu\text{-GeI}{}^t\text{Bu})$ reacts with DMAP in the presence of AgOTf to give the first base-stabilized germylyne-bridged complex *cis*-$[Cp_2Fe_2(CO)_3(\mu\text{-Ge}{}^t\text{Bu}\cdot\text{DMAP})]OTf$. The X-ray crystal structure reveals that the Fe-Ge bonds are very short (2.322(2) Å) while the Ge-N(DMAP) bond is unusually long (1.992(12) Å).

Transition metal complexes containing reactive organosilicon species have attracted much attention,$^{1,2)}$ and one of the challenging targets in particular is the synthesis of silylynemetal complexes. Recently, we synthesized the first base-stabilized silylyne-bridged dinuclear complex using the following reaction:



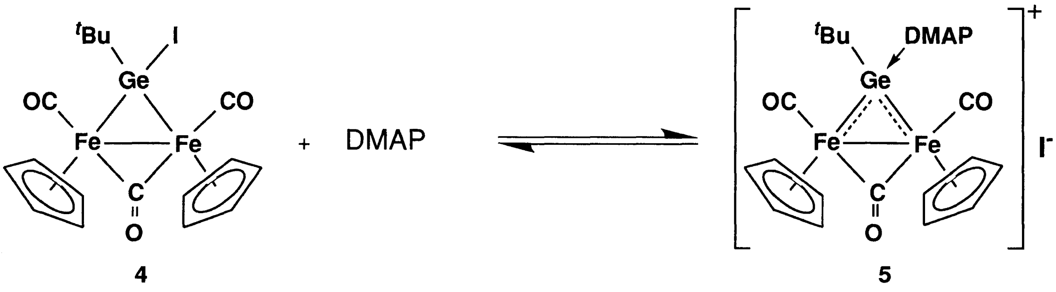
(1)

The addition of a strong Lewis base, *N*-methylimidazole (NMI) or 4-(dimethylamino)pyridine (DMAP), to a solution of the *t*-butyl(iodo)silylene-bridged diiron complex **1** caused the dissociation of the iodide ion from the silicon atom to give the cationic silylyne-bridged diiron complex **2a** or **2b**, respectively.$^{3,4)}$ Tilley et al. then reported the synthesis of a cationic mononuclear silylyne complex stabilized by phenanthroline as the base, $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Si(STol\text{-}p)(phen)](OTf)_2$.$^{5)}$ Furthermore, they reported the synthesis of base-free silylyne-bridged dinuclear complex, $(OC)_4Os{=}Si(STol\text{-}p)[Ru(\eta^5\text{-}C_5Me_5)(PMe_3)_2]$.$^{6)}$ This paper describes the synthesis and crystal structure of the germanium analogue of **2**, the first base-stabilized germylyne-bridged dinuclear complex.

We previously reported the photochemical synthesis of the germylene-bridged diiron complex

$Cp_2Fe_2(CO)_3(\mu\text{-GeH}^t\text{Bu})$ (**3**) from $CpFe(CO)_2SiMe_3$ and $^t\text{BuGeH}_3$.[7] Iodination of **3** to give $Cp_2Fe_2(CO)_3(\mu\text{-GeI}^t\text{Bu})$ (**4**) proceeds under very mild conditions since the Ge-H bond in **3** is highly activated: Stirring a solution of **3** (205 mg, 0.45 mmol) in CH_3I (8 ml) at room temperature for 15 h and the usual workup afforded **4** in 67% isolated yield.[8]

When DMAP was added to an acetonitrile solution containing **4**, the formation of the DMAP-stabilized germylyne-bridged diiron complex (**5**) was observed by ^{1}H NMR spectroscopy. However, the reaction attained an equilibrium (**4**:**5** ≈ 1:2 when ca. 10 equiv. of DMAP was added):



(2)

This behavior of the germylene-bridged complex **4** is in sharp contrast to that of the silylene-bridged complex **1** in which the equilibrium lies far to the product side (Eq. 1). The difference is most likely to be due to the softness of germanium which makes the strength of the Ge-I bond in **4** and the Ge-N bond in **5** comparable. To ensure the completion of the reaction, silver trifluoromethanesulfonate (AgOTf) was used to remove iodide from the system. Thus, DMAP (28 mg, 2.3×10^{-4} mol), **4** (100 mg, 1.7×10^{-4} mol), and AgOTf (50 mg, 1.9×10^{-4} mol) were dissolved in acetonitrile (15 ml) and the solution was stirred vigorously. After precipitated AgI was removed by centrifugation, the solution was cooled at -30 °C for 2 days. Resulting red crystals of $[Cp_2Fe_2(CO)_3(\mu\text{-Ge}^t\text{Bu}\cdot\text{DMAP})]\text{OTf}$ (**6**) were collected, giving an isolated yield of 13.8 mg (1.9×10^{-5} mol, 11%).[9]

The X-ray structure analysis of germylyne-bridged complex **6** was carried out.[10] The structural features of **6** closely resemble those of its silicon analogues, **2a** and **2b**. The cation has a mirror plane bisecting the Fe-Fe bond through the germanium atom (Fig. 1). Each Fe atom bears a Cp ring and a terminal CO ligand. The two Fe atoms are doubly connected by a CO bridge and a germylyne bridge. The two Cp rings are mutually *cis*, and the bulky *t*-Bu group is located on the same side to the Cp rings with respect to the Fe_2GeC bicyclic ring. This renders **6** much more sterically crowded than the germylene-bridged complex **3** in which the *t*-Bu group and Cp rings are mutually *trans*.

Coordination of the lone pair on the nitrogen atom of DMAP to the Ge atom in the germylyne bridge causes pyramidalization of the Ge atom. The angle between the Fe_2Ge plane and Ge-C(8) is 145.4°, which is larger than the corresponding angles of silicon analogues **2a** (143.2°)[3] and **2b** (140.3°).[4] In contrast, the angle between the Fe_2Ge plane and Ge-N(1) is 118.99°, which is smaller than the corresponding angles of **2a** (120.7°)[3] and **2b** (122.2°).[4] These differences cannot be attributed to steric reasons: As the atomic radius of Ge is larger than that of Si (which is clearly reflected in the following bond lengths: **6** Ge-Fe 2.322(2), Ge-C(^{t}Bu) 2.015(18), Ge-N(1) 1.992(12) Å; **2b**[4] Si-Fe 2.266(3), Si-C(^{t}Bu)

1.947(11), Si-N(1) 1.866(9) Å), the steric crowding between the *t*-Bu group and Cp ligand is rather reduced in complex **6** compared with that in **2a** and **2b**. The difference mentioned above indicates therefore that the atomic orbital of the germanium atom used to form the Fe-Ge bonds in **6** has greater *s* character than the corresponding atomic orbitals of the silicon atoms in **2a** and **2b**. The Ge-Fe bond length of **6** (2.322(2) Å) is shorter than those in the germylene-bridged diiron complexes, **3** (2.345(1) and 2.344(1) Å)[7] and [$Cp_2Fe_2(CO)_3(\mu\text{-}GeMe_2)$] (2.345(1) and 2.347(1) Å),[11] though the steric congestion around the germanium atom for the former is apparently greater than that for the latter two. This clearly indicates that the Ge-Fe bonds in **6** have unsaturated bonding character. The Ge-N distance in **6** (1.992(12) Å) is much longer than the usual Ge-N covalent bond lengths (ca. 1.84 Å).[12]

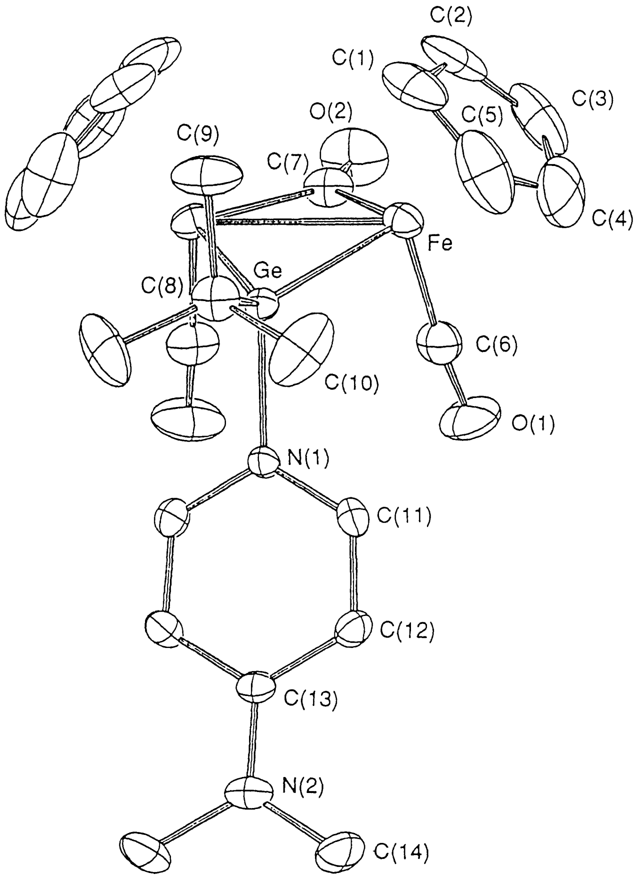


Fig. 1. ORTEP drawing of the cationic moiety of **6**. Selected bond distances (Å) and angles (deg): Fe-Fe' 2.665 (3), Ge-Fe 2.322 (2), Ge-N(1) 1.992 (12), Ge-C(8) 2.015 (18), Fe-C(6) 1.738 (14), Fe-C(7) 1.924 (12); Fe-Ge-Fe' 70.05 (7).

The FAB mass spectrum of **6** in sulfolane matrix shows the peak of the cation [$Cp_2Fe_2(CO)_3(\mu\text{-}Ge\,{}^t\!Bu{\cdot}DMAP)$]$^+$ at *m*/*z* = 579 (31, M^+) and also a strong peak assignable to the base-free germylyne complex [$Cp_2Fe_2(CO)_3(\mu\text{-}Ge\,{}^t\!Bu)$]$^+$ at *m*/*z* = 457 (72, M^+-DMAP). This trend is analogous to those observed for the silicon analogues **2a** and **2b**.

The CO stretching frequencies of germylyne complex **6** (νCO_{term} 1980 and 1945 cm^{-1}; νCO_{brid} 1778 cm^{-1}, KBr pellet) are higher than those of neutral germylene complexes **3** (νCO_{term} 1945 and 1920 cm^{-1}; νCO_{brid} 1715 cm^{-1}, KBr pellet), **4**,[8] and $Cp_2Fe_2(CO)_3(\mu\text{-}GeMe_2)$[11] ($\nu CO_{term}$ 1953-1915 cm^{-1}; νCO_{brid} 1733-1715 cm^{-1}, KBr pellet). This suggests a decrease in back-donation from the Fe atoms to the carbonyl ligands due to strong back-donation from the Fe atoms to the electron-deficient Ge atom in **6**. The SO stretching band of the triflate (trifluoromethanesulfonate) in **6** appears at 1257 cm^{-1}, indicating that the triflate acts as a counter anion: The SO stretching frequencies range between 1395-1365 cm^{-1} for the compounds containing covalently bound triflates and between 1280-1270 cm^{-1} for ionic triflates.[13,14]

Reduction of **6** by $NaBH_4$ in acetonitrile proceeds smoothly at room temperature to give **3** in a good yield (90%), whereas **4** does not react with $NaBH_4$ under the same experimental conditions. This result demonstrates the high electron deficiency of the Ge atom in **6**.

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8) Data for **4**: **4** exists in solution at room temperature as a mixture of *cis* and *trans* isomers (the relative abundance of *cis* and *trans* isomers in C_6D_6 solution = 97:3). ^{1}H NMR (90 MHz, C_6D_6) δ/ppm *cis*-**4**; 1.61 (s, 9H, ^{t}Bu), 4.25 (s, 10H, Cp). *trans*-**4**; 1.52 (s, 9H, ^{t}Bu), 4.30 (s, 5H, Cp), 4.41 (s, 5H, Cp). ^{13}C NMR (22.5 MHz, C_6D_6) δ/ppm *cis*-**4**; 29.9 ($\mathrm{C}Me_3$), 58.1 ($C\mathrm{Me}_3$), 87.2 ($C_5\mathrm{H}_5$), 212.1 ($C\mathrm{O}_{\mathrm{term}}$), 272.1 ($C\mathrm{O}_{\mathrm{brid}}$). IR (KBr) *cis*-**4**; 1954(vs) and 1928 (m) ($\nu\mathrm{CO}_{\mathrm{term}}$), 1770 ($\nu\mathrm{CO}_{\mathrm{brid}}$). MS (EI, 70 eV) *m/z* 584 (28, M^+), 556 (100, M^+-CO). Anal. Found: C, 35.04; H, 3.47%. Calcd for $C_{17}H_{19}IFe_2GeO_3$: C, 35.05; H, 3.29%.

9) Data for **6**: ^{1}H NMR (90 MHz, CD_3CN) δ/ppm 1.54 (s, 9H, ^{t}Bu), 3.09 (s, 6H, $\mathrm{N}Me_2$), 5.09 (s, 10H, Cp), 6.71, 8.22 (ABq, J = 7.6 Hz, 4H, $\mathrm{NC_5}H_4\mathrm{NMe_2}$). ^{13}C NMR (50 MHz, CD_3CN) δ/ppm 30.0 ($\mathrm{C}Me_3$), 40.1 ($\mathrm{N}Me_2$), 50.3 ($C\mathrm{Me}_3$), 85.5. ($C_5\mathrm{H}_5$), 107.1 (*meta,* $\mathrm{N}C_5\mathrm{H_4NMe_2}$), 148.1 (*ortho,* $\mathrm{N}C_5\mathrm{H_4NMe_2}$), 156.9 (*para,* $\mathrm{N}C_5\mathrm{H_4NMe_2}$), 212.4 ($C\mathrm{O}_{\mathrm{term}}$), 277.4 ($C\mathrm{O}_{\mathrm{brid}}$). IR (KBr) 1980(vs) and 1945 (m) ($\nu\mathrm{CO}_{\mathrm{term}}$), 1780 ($\nu\mathrm{CO}_{\mathrm{brid}}$). MS (FAB, sulfolane) *m/z* 579 (31, M^+), 457 (72, M^+-DMAP), 234 (25, CpFe$\cdot$DMAP$^+$), 123 (100, DMAP$\cdot$H$^+$).

10) Crystallographic data for **4**; $C_{25}H_{29}F_3Fe_2GeN_2O_6S$, M = 714.84, *orthorhombic,* space group $Pm2_1n$ (variant No.31), a = 10.864(9) Å, b = 14.047(1) Å, c = 9.735(8) Å, V = 1485(2) Å^3, Z = 2, D_c = 1.60 g cm^{-3}, μ(Mo-K α) = 21.9 cm^{-1}. The structure was solved by heavy atom methods and refined by block diagonal least-squares methods using UNICS-III. Hydrogen atoms on the five and six membered-rings were calculated and fixed. All other atoms were refined anisotropically. 2581 unique reflections were collected by $2\theta-\omega$ scan in the range 3° < 2θ < 60°, with 1901 ($|F_o| > 3\sigma(F_o)$) used in calculations. The final reliability factors converged R = 0.072 and R_w = 0.109.

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