Articles

Synthesis of Cationic Germyleneiron Complexes and X-ray Structure of $[Cp^*(CO)_2Fe{=}GeMe_2{\cdot}DMAP]BPh_4{\cdot}CH_3CN$ ($Cp^* = C_5Me_5$, DMAP = 4-(Dimethylamino)pyridine)

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Chlorogermyliron complexes $Cp^*(CO)_2FeGeMe_2Cl$ (**1**) and $Cp^*(CO)(PPh_3)FeGeMe_2Cl$ (**2**) undergo chloride abstraction by $AgBPh_4$ in the presence of 4-(dimethylamino)pyridine (DMAP) to afford cationic germylene complexes $[Cp^*(CO)_2Fe{=}GeMe_2{\cdot}DMAP]BPh_4$ (**3**) and $[Cp^*(CO)(PPh_3)Fe{=}GeMe_2{\cdot}DMAP]BPh_4$ (**4**), respectively. Structural determination by X-ray crystallography of **1** and $\mathbf{3{\cdot}CH_3CN}$ revealed that both complexes have a gauche conformation with respect to the Fe−Ge bonds. The short Fe−Ge bond (2.329(3) Å) and very long Ge−N (DMAP) bond (1.989(8) Å) in $\mathbf{3{\cdot}CH_3CN}$ demonstrate the unsaturated bond character of the former and the dative bond character of the latter. The complexes **3** and **4** in dichloromethane revert to the parent complexes **1** and **2**, respectively, via an electron-transfer process from the counteranion, BPh_4^-, followed by chlorine abstraction from the solvent.

Introduction

The chemistry of transition metal complexes having multiple bonding between the metal and a heavier group 14 element has developed rapidly.[1−3] Their study is, however, still in an early stage compared with that of carbene and carbyne complexes. For instance, examples of cationic and mononuclear germylene complexes are very scarce and are limited to rhenium complexes.[4] Furthermore, no cationic germylene complex has been structurally analyzed by X-ray crystallography.

This paper describes the synthesis of the first cationic germyleneiron complexes. The strategy employed for their synthesis involves the abstraction of chloride from a chlorogermyliron complex using a chloride-abstracting agent in the presence of a donor molecule. Quite recently, we prepared the first donor-stabilized germylyne-bridged dinuclear complex $[Cp_2Fe_2(CO)_3(\mu\text{-}Ge^tBu{\cdot}DMAP)](CF_3SO_3)$ (DMAP = 4-(dimethylamino)pyridine) by a similar method.[5] An analogous reaction, i.e., abstraction of a triflate from a silyl group by a metal tetraarylborate, has been effectively used by Tilley et al. for the syntheses of donor-stabilized and donor-free cationic silylene complexes.[6]

In this work, $Cp^*Fe(CO)LGeClMe_2$ (L = CO, PPh_3), $AgBPh_4$, and DMAP were used as the chlorogermyliron complex, the chloride-abstracting agent, and the donor, respectively, to give a donor-stabilized germyleneiron complex (eq 1). It is noteworthy that chloride abstraction from chlorosilyl complexes using $AgBF_4$, $AgPF_6$, and $AgSbF_6$ resulted in fluorination of the silyl groups.[7,8]

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere or under a high vacuum. Reagent grade pentane, hexane, benzene, diethyl ether, toluene, and THF were distilled under a nitrogen atmosphere from sodium-benzophenone ketyl immediately before use. Acetonitrile was distilled from CaH_2, then from P_2O_5, and finally from CaH_2. Acetonitrile-d_3 and dichloromethane-d_2 were dried over CaH_2 and transferred

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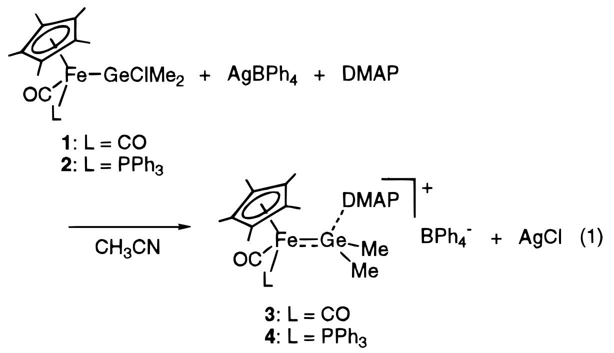

into NMR tubes under vacuum before use. $Cp^*_2Fe_2(CO)_4$,[9] Me_2GeCl_2,[10] and $AgBPh_4$[11] were prepared according to literature methods. PPh_3 and DMAP were recrystallized before use from ethanol and toluene, respectively. Photochemical reactions were carried out using a 450 W medium-pressure Hg lamp (Ushio UM-452) equipped with a Pyrex filter. IR spectra were recorded on a Jasco IR-810 spectrophotometer. ^1H NMR spectra were recorded on JEOL FX-90Q, Varian EM-390, and Varian XL-200 spectrometers at ambient temperature. ^{13}C NMR spectra were recorded on JEOL FX-90Q and Varian XL-200 spectrometers. Mass spectra were recorded on HITACHI M-2500 and JEOL JMS HX-110 spectrometers.

Synthesis of $Cp^*(CO)_2FeGeMe_2Cl$ (1). To a solution of Me_2GeCl_2 (10.3 g, 59.2 mmol) in THF (60 mL) was added a THF (180 mL) solution of $Na[Cp^*Fe(CO)_2]$[12] (57.0 mmol) with stirring over a period of 50 min at 0 °C. The mixture was stirred overnight at room temperature and then evaporated to dryness. Molecular distillation (110 °C/0.15 Torr) of the residue followed by recrystallization from hexane afforded orange crystals of **1** (16.1 g, 41.7 mmol) in 73% yield. ^1H NMR: (90 MHz, CD_3CN) δ 0.89 (s, 6H, $GeMe_2$), 1.87 (s, 15H, Cp*); (90 MHz, CD_2Cl_2) δ 0.94 (s, 6H, $GeMe_2$), 1.91 (s, 15H, Cp*). ^{13}C NMR: (50 MHz, CD_3CN) δ 10.2 ($C_5\mathit{Me}_5$), 13.5 ($GeMe_2$), 97.1 (C_5Me_5), 216.6 (CO); (50 MHz, CD_2Cl_2) δ 10.1 ($C_5\mathit{Me}_5$), 13.5 ($GeMe_2$), 96.3 (C_5Me_5), 215.7 (CO). IR (KBr): ν(CO) 1940 (vs), 1990 (vs) cm^{-1}. MS (EI): *m/z* 386 (10, M^+), 358 (50, $M^+ - CO$), 351 (9, $M^+ - Cl$), 330 (100, $M^+ - 2CO$). Anal. Calcd for $C_{14}H_{21}ClFeGeO_2$: C, 43.65; H, 5.49; Cl, 9.20. Found: C, 43.63; H, 5.46; Cl, 8.97.

Synthesis of $Cp^*(CO)(PPh_3)FeGeMe_2Cl$ (2). A Pyrex tube (3 cm o.d. × 33 cm) was charged with a solution of **1** (3.39 g, 8.80 mmol) and PPh_3 (3.11 g, 11.9 mmol) in a 3:2 mixture of pentane and benzene (100 mL). The solution was photolyzed with stirring for 1 h, giving a brown solution. The resulting mixture was transferred into a three-necked flask equipped with a reflux condenser. To the mixture was added CH_3I (2.0 mL, 32 mmol), and this was heated to 50 °C in order to remove the excess PPh_3. After 45 min of heating, precipitated $[PMePh_3]I$ was removed by filtration and the filtrate was evaporated under reduced pressure. Recrystallization of the residue from toluene/pentane afforded **2** (3.91 g, 6.31 mmol, 72%) as orange microcrystals. ^1H NMR: (200 MHz, CD_3CN): δ 0.20 (s, 3H, GeMe), 0.40 (s, 3H, GeMe), 1.49 (s, 15H, Cp*), 7.33–7.40, 7.50–7.61 (m, 15H, PPh_3). ^{13}C NMR (50 MHz, CD_3CN): δ 9.8 ($C_5\mathit{Me}_5$), 14.6 (GeMe), 15.5 (GeMe), 93.7 (C_5Me_5), 128.4 (d, $J_{CP} = 9.3$ Hz), 129.6 (s), 133.9 (d, $J_{CP} = 10.4$ Hz), 136.6 (d, $J_{CP} = 38.3$ Hz, PPh_3 ring carbons), 221.0 (d, $J_{CP} = 22.7$ Hz, CO). ^{31}P NMR (36.2 MHz, CD_2Cl_2): δ 78.0. IR (KBr): ν(CO) 1900 (vs) cm^{-1}. MS (EI): *m/z* 620 (2, M^+), 592 (7, $M^+ - CO$), 585 (27, $M^+ - Cl$), 557 (5, $M^+ - CO - Cl$), 358 (17, $M^+ - PPh_3$), 330 (22, $M^+ - CO - PPh_3$). Anal. Calcd for $C_{31}H_{36}ClFeGeOP$: C, 60.10; H, 5.86. Found: C, 59.81; H, 5.55.

Synthesis of $[Cp^*(CO)_2Fe{=}GeMe_2{\cdot}DMAP]BPh_4$ (3). Crystals of **1** (306 mg, 0.80 mmol), $AgBPh_4$ (528 mg, 1.24 mmol), and DMAP (99 mg, 0.81 mmol) were placed in a Pyrex tube (2 cm o.d. × 10 cm) connected to a vacuum line and then dissolved in acetonitrile (4 mL), which was transferred by a conventional trap-to-trap method. The sample tube was flame-sealed under high vacuum and shaken vigorously at ambient temperature. Precipitated silver chloride was removed by centrifugation. The solution was transferred into another vessel, concentrated, and then cooled in a refrigerator. Orange crystals of **3·CH$_3$CN** were collected by filtration. ^1H NMR (200 MHz, CD_3CN): δ 0.96 (s, 6H, $GeMe_2$), 1.82 (s, 15H, Cp*), 3.06 (s, 6H, NMe_2), 6.74, 7.96 (ABq, $J = 7.6$ Hz, 2H × 2, DMAP ring protons), 6.81–6.88, 6.96–7.03, 7.24–7.33 (m, 20H, BPh_4). ^{13}C NMR (50 MHz, CD_3CN): δ 8.5 ($GeMe_2$), 10.3 ($C_5\mathit{Me}_5$), 40.1 (NMe_2), 97.7 (C_5Me_5), 108.7 (DMAP ring), 122.7 (Ph), 126.6 (Ph), 136.7 (Ph), 144.8 (DMAP ring), 157.2 (DMAP ring), 164.8 (q, $J_{CB} = 49.4$ Hz, *ipso*-Ph), 216.2 (CO). IR (KBr): ν(CO) 1980 (vs), 1925 (vs) cm^{-1}. MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 473 (58, M^+), 445 (3, $M^+ - CO$), 417 (6, $M^+ - 2CO$), 351 (100, $M^+ - DMAP$), 323 (10, $M^+ - DMAP - CO$), 295 (28, $M^+ - DMAP - 2CO$). Anal. Calcd for $C_{47}H_{54}BFeGeN_3O_2$: C, 67.83; H, 6.54; N, 5.05. Found: C, 67.49; H, 6.59; N, 4.97.

Reaction of 1 with $AgBPh_4$ in the Presence of DMAP in CD_2Cl_2. Crystals of **1** (14.4 mg, 3.72×10^{-2} mmol), $AgBPh_4$ (29.3 mg, 6.87×10^{-2} mmol), and DMAP (6.0 mg, 4.9×10^{-2} mmol) were placed in an NMR tube connected to a vacuum line and then dissolved in CD_2Cl_2 (0.3 mL), which was introduced by trap-to-trap distillation. The sample tube was flame-sealed under high vacuum. The progress of the reaction was followed by ^1H and ^{13}C NMR spectroscopies at room temperature (4 days) and then at 38 °C (20 days).

Reaction of 2 with $AgBPh_4$ in the Presence of DMAP in CD_2Cl_2. Similarly, **2** (16.6 mg, 2.68×10^{-2} mmol), $AgBPh_4$ (17.7 mg, 4.13×10^{-2} mmol), DMAP (3.6 mg, 2.9×10^{-2} mmol), and CD_2Cl_2 (0.3 mL) were combined in an NMR tube which was flame sealed. The reaction was monitored by ^1H and ^{13}C NMR spectroscopies at room temperature (2 days) and then at 40 °C (2 days).

Reaction of DMAP with $AgBPh_4$ in CH_2Cl_2. A CH_2Cl_2 solution (30 mL) containing DMAP (610 mg, 5.0 mmol) and $AgBPh_4$ (2.66 g, 6.23 mmol) was stirred for 7 days at room temperature. The resulting mixture was centrifuged, and the supernatant liquid was evaporated to give a white solid. The latter was identified as a mixture of $BPh_3{\cdot}DMAP$ and biphenyl by comparing the NMR and IR spectra with those of authentic samples (vide infra).

Preparation of $BPh_3{\cdot}DMAP$. BPh_3 (200 mg, 0.93 mmol) and DMAP (110 mg, 0.86 mmol) were allowed to react in benzene (15 mL) overnight with stirring. A white precipitate was isolated by filtration. ^1H NMR (90 MHz, CD_2Cl_2): δ 3.09 (s, 6H, NMe_2), 6.53, 7.98 (ABq, $J = 7.8$ Hz, 2H × 2, DMAP ring protons), 7.02–7.30 (m, 15H, Ph). ^{13}C NMR (22.5 MHz, CD_2Cl_2): δ 39.6 (NMe_2), 106.3 (DMAP ring), 125.0 (Ph), 127.2 (Ph), 135.0 (Ph), 146.9 (DMAP ring), 154.1 (br, *ipso*-Ph), 155.6 (DMAP ring). ^{11}B NMR (28.8 MHz, CD_2Cl_2): δ 2.8 (br). MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 363 (10, M^+), 287 (100, $M^+ - Ph$), 211 (15, $M^+ - 2Ph$), 165 (20, BPh_2^+), 154 (77, Ph_2^+), 123 (36, $DMAP{\cdot}H^+$).

X-ray Crystal Structure Determination. The intensity data for **1** and **3·CH$_3$CN** were collected on Rigaku AFC-6A and AFC-5R four-circle diffractometers, respectively, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Data collection for **3·CH$_3$CN** was carried out at −123 °C to avoid desolvation. The reflection data were corrected with Lorentz and polarization factors but not for absorption and extinction. The space groups were determined from the systematic absences. Crystallographic and experimental data for both crystals are listed in Table 1. The structures of both complexes were solved by direct methods. All non-hydrogen atoms were located and were refined by block-diagonal least-

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Table 1. Crystallographic Data for 1 and 3·CH_3CN

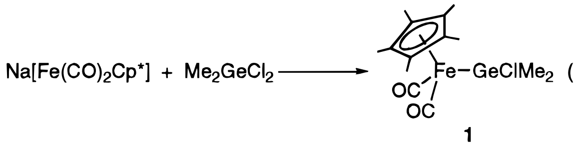
	1	3·CH_3CN
sample	$Cp^*(CO)_2FeGeMe_2Cl$	$[Cp^*(CO)_2Fe{=}GeMe_2{\cdot}DMAP]BPh_4{\cdot}CH_3CN$
formula	$C_{14}H_{21}ClFeGeO_2$	$C_{47}H_{54}BFeGeN_3O_2$
fw	385.23	832.24
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/a$
systematic absence	(h 0 l): $l = 2n + 1$	(h 0 l): $h = 2n + 1$
(0 k 0): $k = 2n + 1$	(0 k 0): $k = 2n + 1$	
a/Å	29.784(5)	18.506(4)
b/Å	12.728(1)	15.171(7)
c/Å	9.394(2)	15.631(8)
β/deg	108.37(2)	103.73(3)
V/Å	3379.8(8)	4263(3)
Z	8	4
d_{calcd}/g cm^{-3}	1.52	1.30
μ(Mo Kα)/cm^{-1}	29.14	11.39
cryst size/mm	0.3 × 0.5 × 0.5	0.2 × 0.3 × 0.5
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	Mo Kα ($\lambda = 0.710\ 73$ Å)
monochromator	graphite	graphite
temp/°C	20	−123
no. of refln measd	±h, k, l	±h, k, l
2θ range/deg	3−60	5−48
scan mode	ω	$\omega-2\theta$
ω-scan width/deg	$1.0 + 0.35 \tan\theta$	$1.1 + 0.30 \tan\theta$
bkgd (count time)/s	7.0	5.0
ω-scan rate/deg min^{-1}	4.0	8.0
no. of unique data	10 767	10 039
no. of data used with $\vert F_o\vert > 3\sigma(F_o)$	6060	4330
no. of params	344	497
R	0.067	0.095
R_w[a]	0.115	0.113
$GooF$	0.79	2.03
largest shift/final cycle	0.40	0.21
max resid electron density/e Å^{-3}	0.72	1.06

[a] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + aF_o^2]^{-1}$, where $a = 0.001$.

squares methods applying anisotropic temperature factors. The coordinates of the hydrogen atoms for **3·CH_3CN** were calculated and fixed. Those of **1** were not determined. Atomic scattering factors for the non-hydrogen atoms and hydrogen atoms were taken from refs 13 and 14, respectively. Calculations were performed on a Nippon Electric Co. ACOS-2000 computer at the Tohoku University Computer Center using the program UNICS III[15] and RANTAN 81.[16]

Results and Discussion

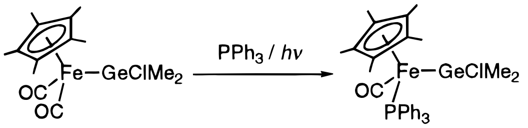
Preparation of Chlorogermyliron Complexes 1 and 2, and X-ray Crystal Structure of 1. Orange crystals of chlorogermyliron complex **1** were prepared by the conventional salt-elimination method (eq 2). The molecular structure was confirmed by X-ray structural analysis (vide infra).



(2)

1

A germyl complex having a chiral iron center **2** was also synthesized by photochemical ligand substitution of **1** with PPh_3 (eq 3). The two methyl groups on the germyl ligand in **2** give two singlet signals in both the ^1H and ^{13}C spectra, because these methyl groups are mutually diastereotopic.



(3)

1 **2**

The crystal of germyl complex **1** consists of two crystallographically independent molecules, the structures of which are almost identical. Figure 1 shows the ORTEP diagram of the cationic moiety of **1** (molecule A). Selected interatomic distances and angles are listed in Table 2. Complex **1** adopts a distorted piano-stool structure with three legs. The Fe−Ge bond distances in **1** (2.340(1) Å for molecule A and 2.338(2) Å for molecule B) are shorter than those of any known germyliron complex (2.416(1)−2.484(1) Å)[17−19] and germylene-bridged diiron complexes (2.344(1)−2.432(1) Å).[20−25] This is attributable to the existence of an elec-

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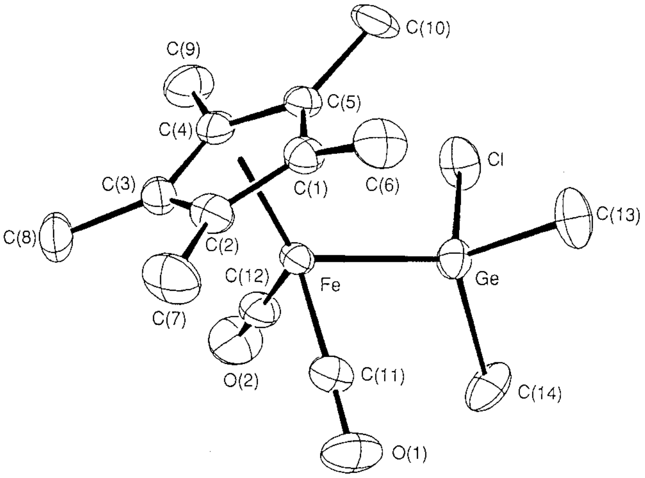


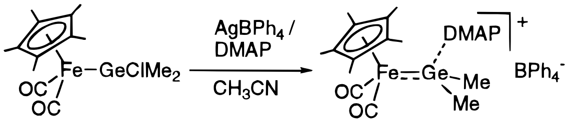
Figure 1. Crystal structure of Cp*(CO)$_2$FeGeMe$_2$Cl (**1**; molecule A). Thermal ellipsoids were drawn at the 30% probability level.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Cp*(CO)$_2$FeGeMe$_2$Cl (1)

	molecule A	molecule B
Fe−Ge	2.340(1)	2.338(2)
Ge−Cl	2.263(3)	2.256(3)
Ge−C(13)	1.979(11)	1.965(9)
Ge−C(14)	2.028(12)	2.038(10)
Fe−C(11)	1.744(8)	1.751(9)
Fe−C(12)	1.751(11)	1.736(8)
O(1)−C(11)	1.163(10)	1.142(11)
O(2)−C(12)	1.146(15)	1.150(11)
Fe−C(Cp)$_{av}$	2.109(9)	2.104(9)
Fe−Ge−Cl	111.38(7)	111.24(8)
Fe−Ge−C(13)	120.1(3)	119.6(3)
Fe−Ge−C(14)	113.4(3)	113.2(3)
Cl−Ge−C(13)	103.4(3)	103.4(3)
Cl−Ge−C(14)	99.1(4)	99.5(3)
C(13)−Ge−C(14)	107.0(5)	107.7(4)
Ge−Fe−C(11)	85.5(3)	85.7(3)
Ge−Fe−C(12)	86.0(4)	86.0(3)
C(11)−Fe−C(12)	95.4(4)	95.3(4)
Fe−C(11)−O(1)	177.5(7)	176.8(8)
Fe−C(12)−O(2)	178.9(10)	178.8(7)

tronegative chlorine atom on the germyl ligand in **1**. A similar trend also is found in transition metal silyl complexes.[2]

Synthesis and X-ray Crystal Structure of 3. Reaction of **1** with AgBPh$_4$ in the presence of DMAP in acetonitrile-d_3 solution was monitored by NMR spectroscopy and was confirmed to give **3** almost quantitatively (eq 4). However, **3** was so moisture- and air-sensitive that a reliable value of the isolated yield could not be determined. The ^{1}H NMR chemical shift of the N-methyl groups of the coordinated DMAP (3.06 ppm) is higher (downfield shifted) by 0.18 ppm than that of free DMAP, indicating that the electron density of the N-methyl groups is lowered by coordination of DMAP to the electron-deficient germylene ligand. The FAB mass spectrum of **3** shows the peak for the cationic part of **3** at m/z = 473 as well as the base peak at m/z = 351, which is assignable to a base-free cationic germylene complex [Cp*(CO)$_2$Fe=GeMe$_2$]$^+$.



(4)

1 **3**

The ORTEP drawing for the cationic moiety of **3·CH$_3$CN** is shown in Figure 2. Selected interatomic distances and angles are listed in Table 3. A unit cell contains four molecules of **3** and four acetonitrile molecules with no interatomic distances shorter than the effective van der Waals radii among them. This complex also adopts a distorted piano-stool geometry with three legs. This is the first cationic germylene complex for which X-ray analysis was carried out. In **3·CH$_3$CN**, there is severe steric congestion between the Cp* ligand and the DMAP-coordinated germylene ligand: C(6)···C(15), C(10)···N(1), and C(10)···C(14) nonbonding distances are 3.59(2), 3.56(2), and 3.77(2) Å, respectively, which are shorter than the minimal approach of these groups.[26] Nevertheless, the Fe−Ge bond length in **3·CH$_3$CN** (2.329(3) Å) is still shorter than that in **1**. This clearly indicates that the Fe−Ge bond has unsaturated character. The complex with the Fe−Ge bond length which is shorter than that in **3·CH$_3$CN** is eq-(OC)$_4$Fe=Ge(OC$_6$H$_2$^{t}Bu$_2$-2,6-Me-4)$_2$ (2.240 Å),[27] which is a donor-free germylene complex. The

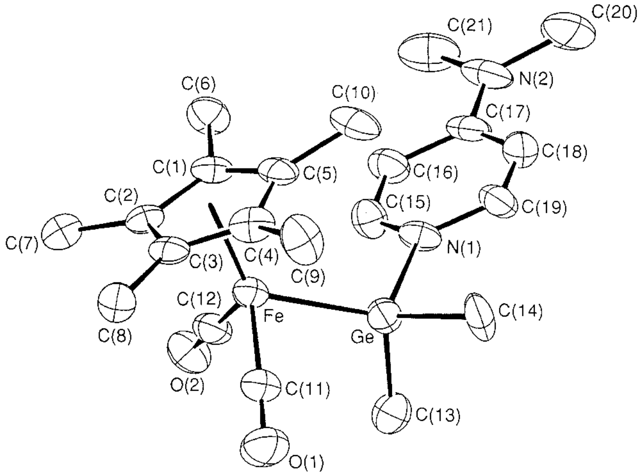


Figure 2. Crystal structure of the cationic moiety of [Cp*(CO)$_2$Fe=GeMe$_2$·DMAP]BPh$_4$·CH$_3$CN (**3**·CH$_3$CN). Thermal ellipsoids were drawn at the 30% probability level.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [Cp*(CO)$_2$Fe=GeMe$_2$·DMAP]$^+$(BPh$_4^-$)·CH$_3$CN (3·CH$_3$CN)

Fe−Ge	2.329(3)	Ge−N(1)	1.989(8)
Ge−C(13)	1.944(13)	Ge−C(14)	1.947(14)
Fe−C(11)	1.732(11)	Fe−C(12)	1.774(11)
O(1)−C(11)	1.166(13)	O(2)−C(12)	1.115(13)
Fe−C(Cp)$_{av}$	2.114(13)		
Fe−Ge−N(1)	113.5(2)	Fe−Ge−C(13)	112.2(4)
Fe−Ge−C(14)	121.4(4)	N(1)−Ge−C(13)	97.9(5)
N(1)−Ge−C(14)	101.9(5)	C(13)−Ge−C(14)	106.9(6)
Ge−Fe−C(11)	85.4(4)	Ge−Fe−C(12)	88.3(4)
C(11)−Fe−C(12)	96.9(5)	Fe−C(11)−O(1)	176.8(10)
Fe−C(12)−O(2)	179.2(10)		

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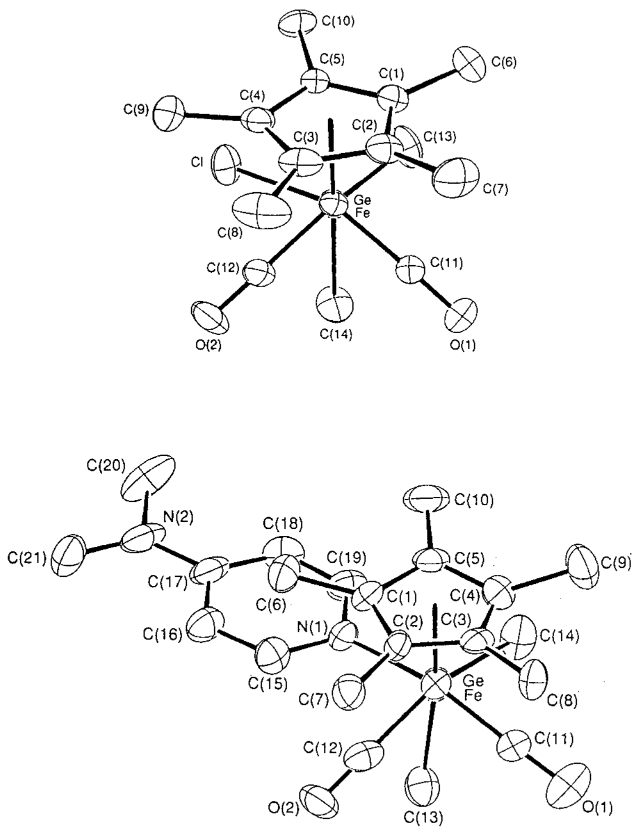
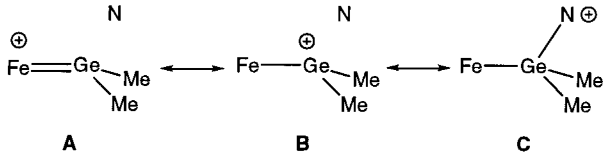


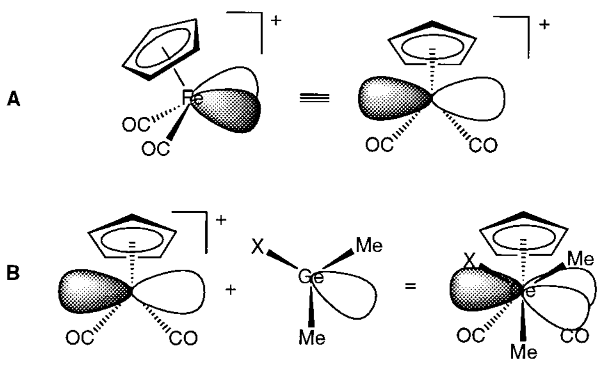
Figure 3. ORTEP diagrams of 1 (molecule A) and the cationic moiety of **3**·CH_3CN projecting along the Fe–Ge axes.

Scheme 1

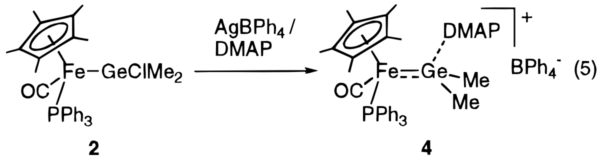


bond angles around the germanium atom also are informative. Complexes **1** and **3·CH_3CN** have a distorted tetrahedral geometry around their germanium atoms, so they closely resemble each other on this point. These observations suggest the predominance of canonical structure **C** (Scheme 1) in which the positive charge is on the coordinated DMAP. Complex **1** and **3·CH_3CN** adopt a gauche conformation with respect to the Fe–Ge axis (Figure 3). This may be strange at first glance considering the steric effect, especially in **3·CH_3CN**. This paradox can be explained by the electronic effect. The $[Cp^*Fe(CO)_2]^+$ moiety possesses the high-lying d orbital HOMO, which lies in the "horizontal" plane (Scheme 2, A) and is a potent π donor.[28] The gauche conformation in **1** and **3·CH_3CN** maximize the overlap of the d orbital with the Ge–Cl σ^* (for **1**) and the Ge–N σ^* (for **3·CH_3CN**) orbitals, which are energetically lower than the Ge–Me σ^* orbital and, therefore, can interact with the d orbital more effectively (Scheme 2, B).[29] In fact, the Ge–Cl (2.263(3) and 2.256(3) Å) and Ge–N(1) (1.989(8) Å) bonds found in **1** and **3·CH_3CN** are elongated by the donation of electron density from the iron fragment to the antibonding orbitals. Ge–Cl and Ge–N single bond distances are typically 2.10 and 1.84 Å, respectively. At the same time, the d_π–σ^* interaction increases the bond order between the germanium and iron, which is consistent with the shortness of the Fe–Ge bond in **1** and **3·CH_3CN**. Furthermore, it can be deduced that the d_π–σ^* interaction is substantially greater in **3·CH_3CN** than in **1** from comparison of their Fe–Ge bond lengths.

Scheme 2



Synthesis and Reversion Reaction of $[Cp^*(CO)(PPh_3)Fe{=}GeMe_2{\cdot}DMAP]BPh_4$ (4). An NMR study indicated that a chiral complex **2** also undergoes chloride abstraction by $AgBPh_4$ in the presence of *a slight excess of* DMAP to generate a germylene complex $[Cp^*(CO)(PPh_3)Fe{=}GeMe_2{\cdot}DMAP]BPh_4$ (**4**) quantitatively (eq 5).



The ^1H NMR spectrum of the resulting mixture which contains **4** and free DMAP shows *only one* signal for the *N*-methyl groups of DMAP. On the other hand, the diastereotopic methyl groups give two singlet signals at −0.20 and 0.99 ppm at room temperature. This means that exchange between the coordinated and free DMAP occurs, but that inversion about the germanium atom does not occur or is at least slower than the NMR time scale. Gladysz and co-workers have reported that the germyl ligand in the triflate-substituted germylrhenium complex $Cp(NO)(PPh_3)ReGePh_2(OTf)$ undergoes inversion via the base-free germylene complex generated by dissociation of the triflate group so that rapid exchange between the diastereotopic phenyl groups occurs. It has also been reported that exchange between the phenyl groups was not observed in a pyridine-coordinated germylene complex $[Cp(NO)(PPh_3)Re{=}GePh_2{\cdot}C_5H_5N]^+$.[4]

Interestingly, it was found that **4** reverts to the parent chlorogermyl complex **2** in dichloromethane-d_2 on standing at room temperature. Biphenyl and $BPh_3{\cdot}DMAP$ were also produced during the reaction and were characterized by NMR spectroscopy (^1H, ^{13}C, ^{11}B). Similarly, complex **3** also reverts to the parent complex **1** in CD_2Cl_2, accompanied by formation of biphenyl and $BPh_3{\cdot}DMAP$. It is well-known that BPh_4^- anion has a tendency to decompose via a single electron transfer

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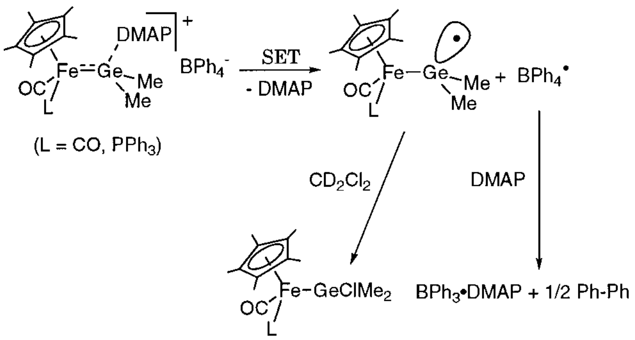
Scheme 3



(SET) process.[30−33] Dichloromethane has a lower dielectric constant than acetonitrile, and therefore, it poorly stabilizes ionic species. In fact, $[Ph_3C][BPh_4]$ decomposes more rapidly in dichloromethane than in acetonitrile.[34] Reversion reactions of **3** and **4** may be expressed as shown in Scheme 3, which includes a SET process from BPh_4^- to the cationic complex followed by chlorine atom abstraction from the solvent by the neutral and radical-like germylene complexes. Formation of biphenyl and BPh_3·DMAP can be explained by the reaction of a neutral $BPh_4^{\bullet}$ radical[31,33a] with DMAP. Formation of similar products (biphenyl and BPh_3·py) was also observed in the decomposition of $[Co(py)_3(thf)_3](BPh_4)_2$ to give $Co(py)_2(\eta\text{-}PhBPh_3)$.[30] These reactions are in contrast to the oxidation of BPh_4^- in the absence of a Lewis base such as pyridine and DMAP: It provides biphenyl via *intramolecular* Ph−Ph coupling and does not give a BPh_3 derivative.[31−33] Finally, it is noteworthy that reaction of DMAP with $AgBPh_4$ in CH_2Cl_2 also affords biphenyl and BPh_3·DMAP. This reaction probably is induced by electron transfer from BPh_4^- to $(CH_2Cl\text{·}DMAP)^+$, which is generated by chloride abstraction from the solvent.

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Supporting Information Available: Tables of final coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms, hydrogen positional parameters, anisotropic temperature factors, bond distances, and bond angles for **1** and **3·CH₃CN** (19 pages). Ordering information is given on any current masthead page.

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