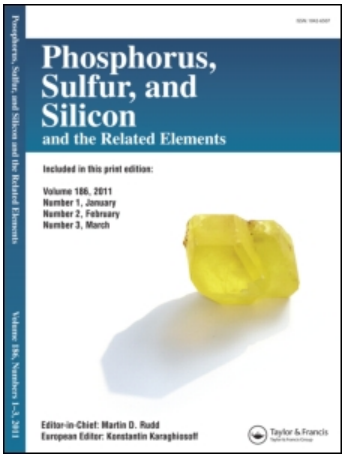

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Synthesis, Characterization, and Crystal Structure of Germyl(phosphine)iron Complexes, $Cp(CO)Fe(PPh_3)(GeR_3)$ (R = Et, nBu, Ph), Prepared from $Cp(CO)Fe(PPh_3)(Me)$ and $HGeR_3$

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SYNTHESIS, CHARACTERIZATION, AND CRYSTAL STRUCTURE OF GERMYL(PHOSPHINE)IRON COMPLEXES, $Cp(CO)Fe(PPh_3)(GeR_3)$ (R = Et, ^{n}Bu, Ph), PREPARED FROM $Cp(CO)Fe(PPh_3)(Me)$ AND $HGeR_3$

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Photoreaction of $Cp(CO)_2Fe(Me)$ (Cp stands for η^5-cyclopentadienyl) with PPh_3 afforded $Cp(CO)Fe(PPh_3)(Me)$. Reaction of the methyl iron complex with $HGeR_3$ (R = Et, ^{n}Bu, Ph) produced $Cp(CO)Fe(PPh_3)(GeR_3)$ (R = Et: 1, ^{n}Bu: 2, Ph: 3). All new complexes were fully characterized using ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR measurements and elemental analyses. Furthermore, the structure of 3 was determined using single crystal X-ray analysis.

Keywords Crystal structure; iron; hydrogermane; phosphine; photolysis

INTRODUCTION

Transition metal alkyl complexes have attracted considerable attention because they are catalytic precursors or key intermediates in many catalytic reactions.[1] Recently, we reported that a methyl iron complex, $Cp(CO)_2Fe(Me)$, is an effective catalytic precursor for the C–CN bond cleavage of organonitriles,[2] the N–CN bond cleavage of cyanamides,[3] and the dehydrogenative Si–O–Si bond formation of various tertiary silanes in DMF.[4] On the other hand, phosphine ligands have played indispensable roles in transition metal catalysis for organic syntheses.[5] We believe that synthesis and reactivity of iron complexes having both methyl and phosphine ligands are important. Si and Ge atoms are situated below the C atom in the periodic table. Although a large number of silyliron complexes having a phosphine ligand have been reported, examples of germyl analogues were rare. Very recently, we found a metathesis reaction between Mo–Me and R_3Ge–H bonds affording Mo–Ge and Me–H bonds.[6] These results led us to examine the possibility of Fe–Ge bond formation through demethanation of an Fe–Me complex with a Ge–H compound. We here

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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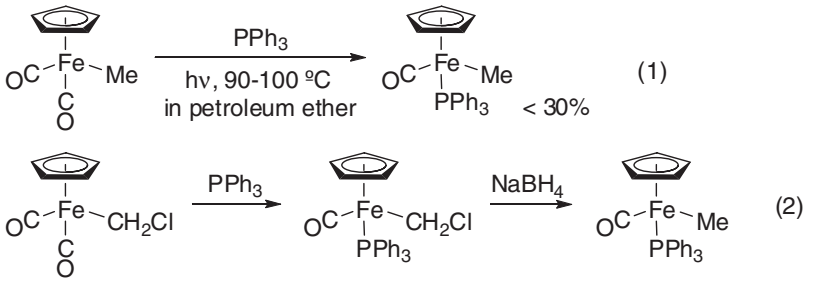
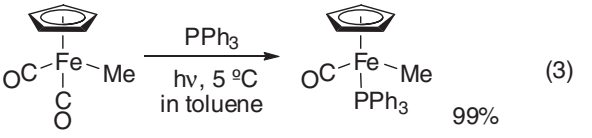
report the synthesis of a methyl iron complex having a triphenylphosphine ligand and reaction of $Cp(CO)Fe(PPh_3)(Me)$ with R_3GeH.

RESULTS AND DISCUSSION

Two synthetic routes of methyl(phosphine)iron complex, $Cp(CO)Fe(PPh_3)(Me)$, have been reported: the reaction of $Cp(CO)_2Fe(Me)$ with PPh_3 in petroleum ether at 90–100°C under photo-irradiation for 20 h [Equation (1)] [7a] and the reduction of $Cp(CO)Fe(PPh_3)(CH_2Cl)$, prepared from $Cp(CO)_2Fe(CH_2Cl)$ with PPh_3, by $NaBH_4$ [Equation (2)].[7b] The method shown in Eq. (2) has several steps. In contrast, the method shown in Eq. (1) consists of one step, but it has some disadvantages, namely its low yield (less than 30%) caused by some byproduct formation. One of the byproducts is an acyl complex, because it is well known that a migratory insertion of a CO ligand in a methyl iron complex having carbonyl ligands takes place at 40°C or more.[8] If CO/PPh_3 substitution proceeds at lower temperature than 40°C in the reaction of $Cp(CO)_2Fe(Me)$ with PPh_3, formation of byproducts such as $Cp(CO)Fe(PPh_3)\{C(O)Me\}$ is expected to be suppressed.



We examined a photoreaction of $Cp(CO)_2Fe(Me)$ with PPh_3 at a 1:1 molar ratio in toluene in place of petroleum ether because these reactants are soluble in toluene even at low temperature. The photoreaction at 5°C for 12 h afforded a methyl(phosphine)iron complex, $Cp(CO)Fe(PPh_3)(Me)$, as an orange powder in excellent yield [Equation (3)].

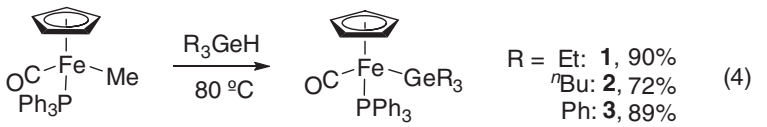


To obtain an iron complex having both germyl and phosphine ligands, a few synthetic routes have been reported. A typical one is a reaction of a phosphine ligand with a (germyl)iron complex, prepared from halogermane $XGeR_3$ and an alkali metal anionic species $M[(C_5R'_5)(CO)_2Fe]$ (M = Na, K etc.; R′ = Me, H etc.).[9] In this article, we report a new route, demethanative Fe–Ge bond formation. Reaction of $Cp(CO)Fe(PPh_3)(Me)$ with a three-fold molar excess of tertiary germane $HGeR_3$ (R = Et, ^{n}Bu) at 80°C for 2 h in toluene solution afforded a corresponding germyl(phosphine)iron complex $Cp(CO)Fe(PPh_3)(GeR_3)$ (R = Et: **1**, ^{n}Bu: **2**) in high yield. A germyl complex $Cp(CO)Fe(PPh_3)(GePh_3)$ **3** was also synthesized in the reaction of $Cp(CO)Fe(PPh_3)(Me)$ with $HGePh_3$ in *ca.* 1:1 molar ratio at 80°C for 6 h [Equation (4)]. The $^{31}P\{^1H\}$ NMR spectra of **1**–**3** show singlets at δ 79.43, 79.43, and 73.64, respectively. In the IR spectra,

Table I Crystal data and experimental parameters used for intensity data collection of **3**: Procedures and final results of the structure determination

Empirical formula	$C_{42}H_{35}OPGeFe$ **3**
Formula weight	715.11
T (K)	100(1)
Crystal system	Triclinic
Space group	P^{-1}
a (Å)	12.6774(6)
b (Å)	14.1854(7)
c (Å)	18.8052(13)
α (°)	88.158(8)
β (°)	88.144(8)
γ (°)	76.771(7)
Volume (Å^3)	3289.3(3)
Z	4
ρ_{calcd} (mg m^{-3})	1.444
μ (cm^{-1})	1.437
F(000)	1472
Crystal size (mm^3)	0.15 × 0.15 × 0.08
Reflections collected	25407
Independent reflections (R(int))	14184 (0.0355)
$R1$ ($I > 2\sigma(I)$)	0.0685
w$R2$	0.1144
Goodness of fit	1.224

1–3 exhibit one absorption assignable to CO stretching at 1900 cm^{-1} for **1**, 1902 cm^{-1} for **2**, and 1900 cm^{-1} for **3**. The value for **1** (1900 cm^{-1}) is slightly lower than that for the corresponding silyl complex, Cp(CO)Fe(PPh$_3$)(SiEt$_3$) (1907 cm^{-1}),[10] indication that a germyl group has a more electron-donating character than a silyl group.



(4)

Table II Selected bond lengths (Å) and bond angles (°) for **3**

Fe1–C1	2.109(4)	Fe2–C43	2.102(4)
Fe1–C2	2.099(4)	Fe2–C44	2.094(4)
Fe1–C3	2.106(4)	Fe2–C45	2.113(4)
Fe1–C4	2.115(4)	Fe2–C46	2.109(4)
Fe1–C5	2.114(4)	Fe2–C47	2.112(4)
Fe1–C6	1.733(5)	Fe2–C48	1.737(4)
Fe1–Ge1a(P1b)	2.3848(11)	Fe2–Ge2a(P2b)	2.3778(9)
Fe1–P1a(Ge1b)	2.205(3)	Fe2–P2a(Ge2b)	2.210(3)
C6–O1	1.162(5)	C48–O2	1.162(5)
C6–Fe1–Ge1a(P1b)	87.82(14)	C48–Fe2–Ge2a(P2b)	84.05(14)
C6–Fe1–P1a(Ge1b)	92.26(17)	C48–Fe2–P2a(Ge2b)	96.13(15)
P1a(Ge1b)–Fe1–Ge1a(P1b)	100.31(9)	P2a(Ge2b)–Fe2–Ge2a(P2b)	103.08(8)

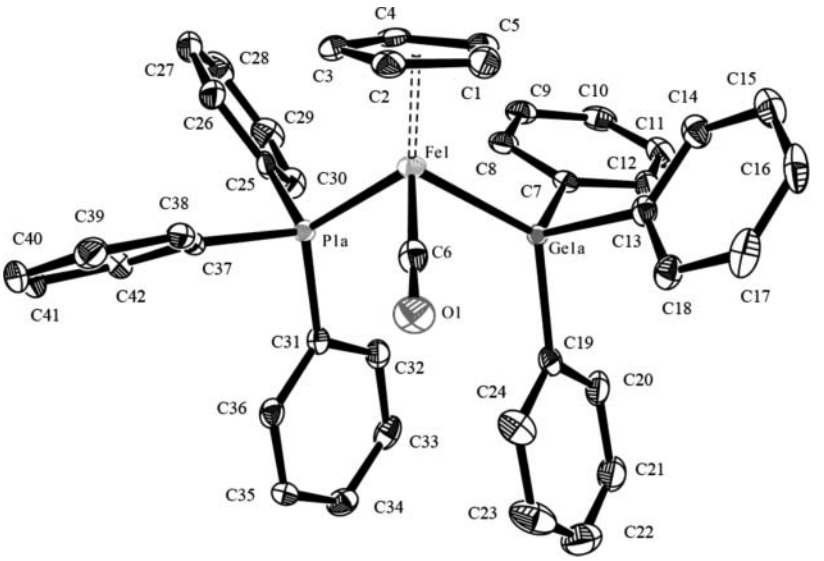


Figure 1 ORTEP drawing of Fe1 molecule of **3** at the 50% ellipsoidal level. Hydrogen atoms are omitted for simplicity.

Single crystals of **3** were obtained by solvent diffusion at room temperature over a few days from a dichloromethane layer containing **3** and an overlayer of hexane. The molecular structure of **3** was determined by single crystal X-ray analysis. Crystal data and the selected bond lengths and angles are listed in Tables I and II. Two independent molecules were crystallized in the unsymmetric unit. The ORTEP drawings of **3** are depicted in Figure 1 for the Fe1 molecule and Figure 2 for the Fe2 molecule. The Fe has a three-legged, piano-stool geometry bearing C_5H_5 in η^5-fashion, a terminal CO ligand, a PPh_3 ligand, and a

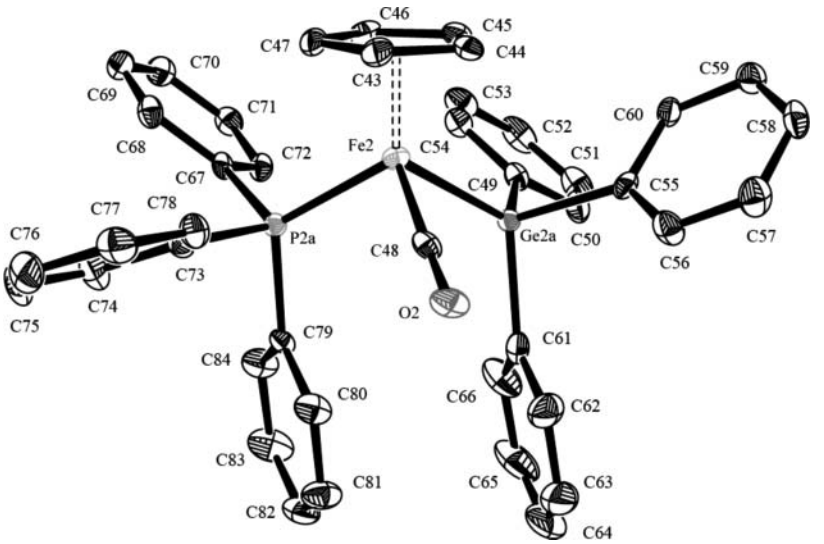
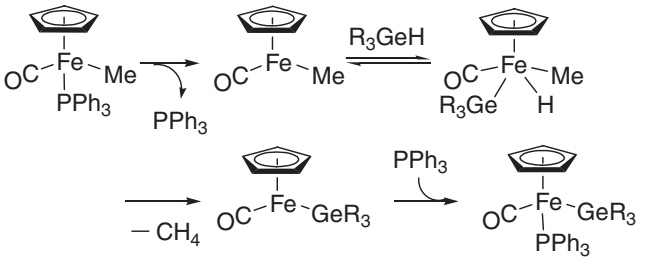


Figure 2 ORTEP drawing of Fe2 molecule of **3** at the 50% ellipsoidal level. Hydrogen atoms are omitted for simplicity.

$GePh_3$ ligand. Although silyl analogues of **3** have been reported, the X-ray structure of **3** is the first example of a germyl iron complex having a phosphine ligand. The Fe–C bond distances for **3** [1.733(5), 1.737(4) Å for carbonyl and 2.094(4)–2.115(4) Å for Cp ligand] are similar to those for the silyl analogue.[11]

The formation mechanism of $Cp(CO)Fe(PPh_3)(GeR_3)$ is exhibited in Scheme 1. A PPh_3 ligand in $Cp(CO)Fe(PPh_3)(Me)$ is released to give Cp(CO)Fe(Me). The oxidative addition of an H–Ge bond to the 16e Fe complex yields $Cp(CO)Fe(H)(GeR_3)(Me)$. Reductive elimination of CH_4 gives $Cp(CO)Fe(GeR_3)$, and the re-coordination of the PPh_3 ligand affords the desired germyl(phosphine)iron complex.



Scheme 1

CONCLUSIONS

We established a convenient synthetic route to obtain a methyl(phosphine)iron complex, $Cp(CO)Fe(PPh_3)(Me)$. We also presented the reaction of $Cp(CO)Fe(PPh_3)(Me)$ with tertiary germane $HGeR_3$ (R = Et, ^{n}Bu, Ph), which affords a corresponding germyl(phosphine)iron complex $Cp(CO)Fe(PPh_3)(GeR_3)$.

EXPERIMENTAL

All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. A methyl iron complex, $Cp(CO)_2Fe(Me)$, was prepared according to the methods in the literature.[12] The other chemicals were purchased. All solvents were distilled from appropriate drying agents under dry nitrogen prior to use. NMR spectra (^1H, ^{13}C, ^{31}P) were measured on JEOL JNM-AL400 spectrometer at 25°C. ^1H and $^{13}C\{^1H\}$ NMR data were referred to the residual peaks of the solvent. Peak positions of $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. IR spectra were recorded on a Perkin Elmer FTIR-Spectrum one. Photo-irradiation was performed with a 400 W medium-pressure mercury arc lamp at 5°C.

Preparation of $Cp(CO)Fe(PPh_3)(Me)$

A toluene solution (10 mL) containing $Cp(CO)_2Fe(Me)$ (192 mg, 1.00 mmol) and PPh_3 (262 mg, 1.00 mmol) was stirred at 5°C under photo-irradiation. After 12 h, removing volatile materials under reduced pressure led to the formation of an orange solid of $Cp(CO)Fe(PPh_3)(Me)$ (421 mg, 0.99 mmol, 99%). The spectral data agreed with those of the literature.[7b]

Preparation of Cp(CO)Fe(PPh$_3$)(GeEt$_3$) (1)

A toluene solution (10 mL) containing Cp(CO)Fe(PPh$_3$)(Me) (133 mg, 0.31 mmol) and Et$_3$GeH (154 μL, 0.95 mmol) was stirred at 80°C. After 2 h, removing volatile materials under reduced pressure led to the formation of an orange solid, which was washed with hexane, collected by filtration, and dried in vacuo to give an orange powder of **1** (161 mg, 0.28 mmol, 90%). NMR spectroscopic analysis: ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 0.81 (m, 3H, one of CH_2), 1.07 (m, 3H, one of CH_2), 1.28 (t, $J_{HH} = 7.8$ Hz, 9H, CH_3), 4.15 (s, 5H, Cp), 7.00 (m, 9H, Ph), 7.60 (m, 6H, Ph); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, δ, ppm): 11.60 (s, CH_2), 12.53 (s, CH_3), 82.44 (s, Cp), 129.40 (s, Ph), 133.69 (d, $J_{PC} = 10.0$ Hz, Ph), 139.22 (d, $J_{PC} = 1.7$ Hz, Ph), 139.62 (d, $J_{PC} = 1.7$ Hz, Ph), 221.25 (d, $J_{PC} = 30.7$ Hz, CO); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ, ppm): 79.43 (s). Anal. Calc. for $C_{30}H_{35}OPGeFe$: C, 63.10; H, 6.18%. Found: C, 62.96; H, 6.20%. IR (cm^{-1}, KBr): ν(CO) 1900.

Preparation of Cp(CO)Fe(PPh$_3$)(Ge^{n}Bu$_3$) (2)

In a procedure analogous to that outlined above, Cp(CO)Fe(PPh$_3$)(Me) (54 mg, 0.13 mmol) and ^{n}Bu$_3$GeH (95 μL, 0.37 mmol) gave an orange powder of **2** (60 mg, 0.09 mmol, 72%). NMR spectroscopic analysis: ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 0.81 (dt, $J_{HH} =$ 4.9, 12.7 Hz, 3H, one of CH_2), 1.03 (t, 9H, $J_{HH} = 7.3$ Hz, CH_3), 1.09 (dt, $J_{HH} = 4.9$, 12.7 Hz, 3H, one of CH_2), 1.46 (m, 6H, CH_2), 1.64 (m, 6H, CH_2), 4.19 (s, 5H, Cp), 7.04 (m, 9H, Ph), 7.62 (m, 6H, Ph); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, δ, ppm): 14.47 (s, Bu), 21.10 (s, Bu), 27.86 (s, Bu), 29.92 (s, Bu), 82.49 (s, Cp), 129.41 (s, Ph), 133.71 (d, $J_{PC} = 10.0$ Hz, Ph), 139.27 (s, Ph), 139.67 (s, Ph), 221.20 (d, $J_{PC} = 29.9$ Hz, CO); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ, ppm): 79.43 (s). Anal. Calc. for $C_{36}H_{47}OPGeFe$: C, 65.99; H, 7.23%. Found: C, 66.05; H, 7.14%. IR (cm^{-1}, KBr): ν(CO) 1902.

Preparation of Cp(CO)Fe(PPh$_3$)(GePh$_3$) (3)

In a procedure analogous to that outlined above, Cp(CO)Fe(PPh$_3$)(Me) (148 mg, 0.35 mmol) and Ph$_3$GeH (95 mg, 0.31 mmol) at 80°C for 6 h gave an orange powder of **3** (204 mg, 0.28 mmol, 89%). Orange crystals of complex **3** suitable for an X-ray diffraction study were obtained by CH_2Cl_2/hexane solution at room temperature for a few days. NMR spectroscopic analysis: ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 4.18 (s, 5H, Cp), 6.85 (m, 6H, Ph), 6.89 (m, 3H, Ph), 7.11 (m, 9H, Ph), 7.28 (m, 6H, Ph), 7.66 (m, 6H, Ph); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, δ, ppm): 84.00 (s, Cp), 127.00 (s, Ph), 127.70 (s, Ph), 129.46 (d, $J_{PC} =$ 1.7 Hz, Ph), 133.54 (d, $J_{PC} = 10.0$ Hz, Ph), 136.02 (s, Ph), 137.51 (s, Ph), 137.92 (s, Ph), 148.88 (s, Ph), 221.82 (d, $J_{PC} = 29.9$ Hz, CO); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ, ppm): 73.64 (s). Anal. Calc. for $C_{42}H_{35}OPGeFe$: C, 70.53; H, 4.93%. Found: C, 70.12; H, 4.85%. IR (cm^{-1}, KBr): ν(CO) 1900.

Investigation Technique: X-Ray Diffraction

X-ray intensity data were collected at –173(1)°C on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were performed with the CrystalClear software package of Molecular Structure Corporation. The structures were solved by direct methods SIR97[13] and expanded using Fourier techniques. The structures were refined by full matrix least-squares technique using the program SHELXL-97.[14] Non-hydrogen atoms, except the Ge and P atoms, were refined

anisotropically. The positions of Ge and P atoms were refined as a disordered model with these atoms, each having about 0.85:0.15 occupancy. The hydrogen atoms were included in fixed positions. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 710102. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Tel.; +44 1223 336408; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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