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Reactions of a Gallium-Bridged Diiron Complex with Alkyl Lithium, HCl, and Phosphines

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Gallium-bridged diiron complex Cp*(dppe)FeGaFe(CO)$_4$ (**2**, Cp* = η-C$_5$Me$_5$, dppe = Ph$_2$CH$_2$CH$_2$PPh$_2$) did not react with [PPN]Cl, DMAP (4-*N*,*N*-dimethylaminopyridine), and bpy (2,2′-bipyridine); however, reaction of **2** with HCl caused Ga−Fe(CO)$_4$ bond fission to give Cp*(dppe)FeGaCl$_2$ (**4**). The Ga−Fe(CO)$_4$ bond cleavage also occurred by the reaction of **2** with RLi (R = Me, ^{n}Bu) to afford Cp*(dppe)FeGaR$_2$ (R = Me (**5a**), ^{n}Bu (**5b**)). Irradiation of **2** in the presence of phosphine PR$_3$ (R = OPh, Me, and OMe) gave Cp*(dppe)FeGaFe(CO)$_3$L (L = P(OPh)$_3$ (**6a**), PMe$_3$ (**6b**), and P(OMe)$_3$ (**6c**)) and Cp*(dppe)-FeGaFe(CO)$_2$L$_2$ (L = PMe$_3$ (**7b**) and P(OMe)$_3$ (**7c**)) depending on the reaction conditions. Cleavage of the Cp*(dppe)Fe−Ga bond occurred by irradiation of **2** in the absence of PR$_3$ to give hydridoiron complex Cp*(dppe)FeH (**8**) via abstraction of hydrogen from solvent. Structural investigation of **6a** and **6b** revealed that substitution of CO with an electron-releasing ligand PR$_3$ caused shortening of the Ga−Fe(CO)$_3$L bond and elongation of the Cp*(dppe)Fe−Ga bond.

Introduction

Much attention has recently been concentrated on the compounds with multiple bonding between transition metals and group 13 elements E.[1] Isolation of terminal diyl complexes such as boranediyl (OC)$_n$MBR (M = Fe (n = 4), R = Cp* (Cp* = η^5-C$_5$Me$_5$);[2a] M = Cr and W (n = 5), R = N(SiMe$_3$)$_2$[2d]), alanediyl (OC)$_4$FeAlCp*,[3a] gallanediyl (OC)$_4$FeGaAr* (**1**, Ar* = 2,6-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$),[4a] and indanediyl complex Ni{InC(SiMe$_3$)$_3$}$_4$[5a] inspired the discussion regarding the bonding between the transition metal and the ER ligand.[2–5] Especially, Robinson's complex **1** triggered extensive discussion on the contribution of π-back-bonding from iron to gallium atom. Though the nature of M−E bonding is still under investigation, recent theoretical studies demonstrated that the transition metal−E bonding is dominated by electrostatic interaction between a transition metal and group 13 elements E, but covalent contributions composed of σ-donation and π-back-donation are still important.[3b,6,7] The degree of σ-donation and π-back-donation depends on the π-basicity of both the transition metal fragment and the R substituent on E. Thus, essentially 5e donor ligand Cp* sufficiently filled the empty p-orbital of E to suppress the π-back-donation from the metal to E, while a weak π-donor

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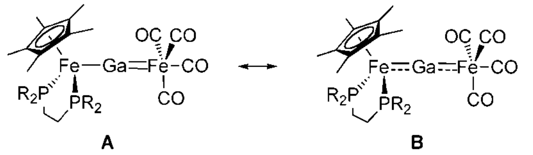
Scheme 1



R = Ph (**2**), Me (**3**)

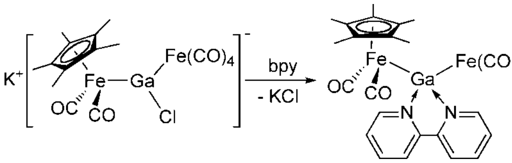
substituent such as Ph cannot compensate for the π-acidity of E to cause significant π-back-donation from the metal fragment.

Dinuclear complexes bridged by a naked E atom ($L_nM^1(\mu_2$-E)M^2L_m; M^1, M^2 = Cr, Fe, Ru, Pt; E = B, Ga, In, Tl) are also particularly interesting since this type of complexes contains an sp-hybridized, two-coordinate E atom and unsaturated M−E bonds.[8] We recently reported the first dimetal complex bridged by a gallium atom, Cp*(dppe)FeGaFe$(CO)_4$ (**2**; dppe = $Ph_2PCH_2CH_2PPh_2$).[8d] The bonding in **2** is formally depicted as Cp*(dppe)Fe−Ga=Fe$(CO)_4$, i.e., a single bond between Cp*(dppe)Fe and Ga and a double bond between Ga and Fe$(CO)_4$ based on the 18-electron rule (Scheme 1A). However, both Fe−Ga bonds are significantly shorter than the usual Fe−Ga single bonds (2.36−2.46 Å).[1a] Furthermore, the former (2.2479(10) Å) is even shorter than the latter (2.2931(10) Å). Substitution of the dppe ligand with a more electron-releasing ligand, dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$), causes shortening of the Cp*(dmpe)Fe−Ga bond (2.2409(5) Å) and elongation of Ga−Fe$(CO)_4$ bond (2.3205(5) Å) in complex Cp*(dmpe)-FeGaFe$(CO)_4$ (**3**) compared to the corresponding bonds in **2**.[8j] This implies that the π-back-donations from both Fe fragments to the Ga center compete with each other and the intensity of π-back-donation depends on the π-basicity of the Fe fragments. On the basis of these insights, contribution of canonical form B (Scheme 1) is proposed as the major one for complexes **2** and **3**.

Several types of E atom-bridged complexes M^1−E−M^2 as well as terminal group 13 diyl complexes M−ER have been synthesized so far; however, their reactivity remains largely unexplored. Cationic terminal borylene complexes are rare examples whose reactivity has been investigated extensively, which includes reactions with nucleophiles[2c,i] and unsaturated metal fragments,[9] borylene transfer reactions,[2e,g,10] and M=B metathesis reactions.[2h] For bimetallic complexes bridged by an E atom, reported reactions are limited to addition of a nucleophile to the unsaturated E.[8g,h] In this paper, we report the reaction of **2** with Lewis base, [PPN]Cl, RLi, and HCl, as well as photolysis of **2** in the presence and absence of PR_3. We also show the electronic effect of metal fragments on the Fe−Ga bonds in Cp*(P_2)FeGaFe$(CO)_3$L complexes (P_2 = dppe, dmpe; L = CO, $P(OPh)_3$, and PMe_3).

Results and Discussion

Reaction of 2 with Lewis Base, [PPN]Cl, and HCl. Complex **2** contains a coordinatively unsaturated electron-deficient gallium center. Thus it seems feasible to bind a donor molecule on the Ga center. Indeed, we have reported the formation of base adduct complex Cp*$(OC)_2$FeGa(2,2′-bpy)-Fe$(CO)_4$ by the reaction of anionic chlorogallylene-bridged diiron complex K[Cp*$(OC)_2$FeGa(Cl)Fe$(CO)_4$] with bpy (2,2′-bipyridine) (eq 1).[8d] Aldridge also reported that the reaction of cationic Ga-bridged diiron complex $[\{Cp^*(OC)_2Fe\}_2Ga]^+$ with [PPN]Cl ($[PPN]^+ = [Ph_3P{=}N{=}PPh_3]^+$) and 4-picoline gave $[Cp^*(OC)_2Fe]_2GaCl$ and $[\{Cp^*(OC)_2Fe\}_2Ga(4\text{-picoline})]^+$, respectively.[8g,h] Contrary to our expectation, no reaction occurred in the treatment of **2** with [PPN]Cl, DMAP (4-*N*,*N*-dimethylaminopyridine), and bpy. The low reactivity of **2** toward the donor reagents is attributable to the steric protection of the Ga center by Ph groups of the dppe ligand as well as the electron-donating nature of the dppe ligand. The latter enhances π-back-donation from the Cp*Fe fragment to the Ga center to decrease the electrophilicity of Ga.



(1)

In contrast to [PPN]Cl, DMAP, and bpy, complex **2** reacted with 2 equiv of HCl to give Cp*(dppe)FeGaCl_2 (**4**) in 66% yield (eq 2). During the reaction, a resonance at −9.71 ppm was transiently observed in the ^1H NMR spectrum, which is assignable to the hydride resonance of $H_2Fe(CO)_4$.[11] This result suggests that the reaction proceeds via the preceding protonation on the Fe$(CO)_4$ fragment, which decreases π-back-donation from the metal fragment and consequently enhances electrophilicity of the Ga center, addition of Cl^- on Ga, and subsequent cleavage of the Fe=Ga bond. Protonation of the iron center in neutral iron complexes has been reported previously with strong protic acids such as HCl,[12] CF_3SO_3H,[13] and HBF_4.[14]

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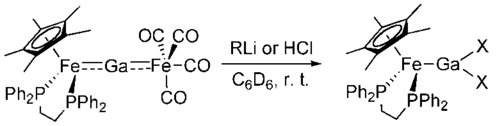


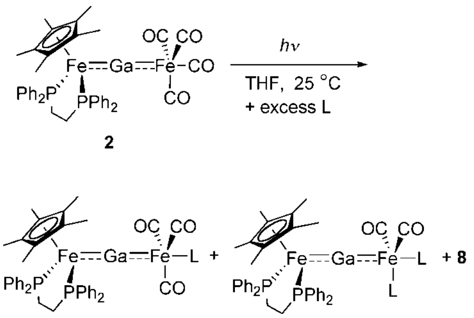
(2)

2

4; X = Cl, 66%
5a; X = Me, 8%
5b; X = ^{n}Bu, 39%

A strong Lewis base, alkyl lithium, also reacted with **2** to cause the cleavage of the Ga═Fe(CO)$_4$ bond. Thus, reaction of **2** with 2 equiv of MeLi and ^{n}BuLi in C_6D_6 at ambient temperature afforded dialkylgallyliron complex Cp*(dppe)-FeGaR$_2$ (R = Me (**5a**) and ^{n}Bu (**5b**)) in 8% and 39% yield, respectively (eq 2). The reactions also formed a white precipitate, which is tentatively assigned to Li$_2$Fe(CO)$_4$. Identification of **5a** and **5b** was achieved by comparing their spectroscopic data with those of the authentic samples prepared by the reaction of **4** with 2 equiv of MeLi and ^{n}BuLi, respectively.

Photolysis of 2. Irradiation of **2** in the presence of P(OPh)$_3$, PMe$_3$, and P(OMe)$_3$ resulted in the substitution of CO to give monosubstituted complex Cp*(dppe)FeGaFe(CO)$_3$L (L = P(OPh)$_3$ (**6a**), PMe$_3$ (**6b**), and P(OMe)$_3$ (**6c**)), disubstituted complex Cp*(dppe)FeGaFe(CO)$_2$L$_2$ (L = PMe$_3$ (**7b**) and P(OMe)$_3$ (**7c**)), and hydride complex Cp*(dppe)FeH (**8**) depending on reaction conditions (eq 3). For example, irradiation of a THF solution containing **2** and 3 equiv of PMe$_3$ for 12 h gave a 87:13:0 mixture of **6b**, **7b**, and **8**, respectively, while a 13:69:18 mixture was obtained after prolonged irradiation (250 h) with 10 equiv of PMe$_3$. Complexes **6a**−**c** and **7b**,**c** were isolated as red crystals in 40−62% yields and were characterized by spectroscopic methods and elemental analysis. Complexes **6a** and **6b** were also investigated by X-ray crystal structure analysis. Complexes **6** and **7** showed ν(CO) bands in the range 1872−1820 cm^{-1}, which are significantly shifted to lower frequencies compared to those of **2** (1998, 1923, 1890, and 1878 cm^{-1}), suggesting stronger π-basic character of the Fe(CO)$_{4-n}$-(PR$_3$)$_n$ fragment than that of Fe(CO)$_4$.[8d] Phosphorus-31 NMR of **6a** showed a triplet and a doublet signal ($^4J_{pp}$ = 7.8 Hz) at 192.2 and 92.6 ppm, which are assignable to P(OPh)$_3$ and the dppe ligand, respectively. Complexes **6b** and **6c** also showed the corresponding two multiplet signals with $^4J_{pp}$ = 3.4 and 7.5 Hz, respectively.



(3)

2

6a; L = P(OPh)$_3$
6b; L = PMe$_3$
6c; L = P(OMe)$_3$

7b; L = PMe$_3$
7c; L = P(OMe)$_3$

As described later, crystal structure analysis of **6a** and **6b** revealed that the substituted PR$_3$ ligand occupied the position trans to the gallium atom. Thus the phosphine ligands in **7** are considered to be at the positions trans and cis to the gallium atom, as depicted in eq 3. In contrast to our expectations, ^{31}P and ^{1}H NMR showed only one signal for the two PR$_3$ ligands. Furthermore, ^{31}P NMR signals for dppe and PR$_3$ ligands appeared as a singlet. Observation of only one signal for the two PR$_3$ ligands as well as disappearance of the $^4J_{PP}$ coupling indicates the rapid scrambling of the two phosphines on the NMR time scale.

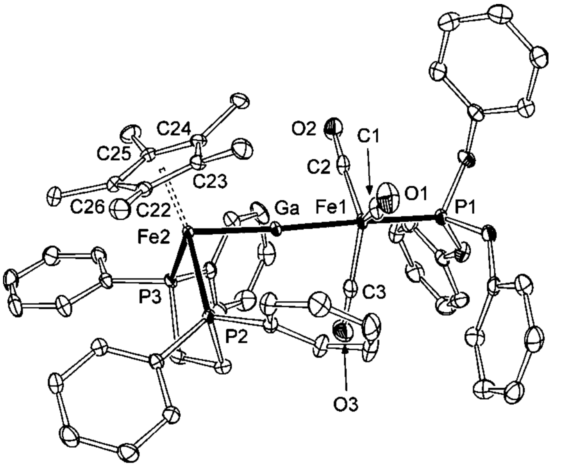
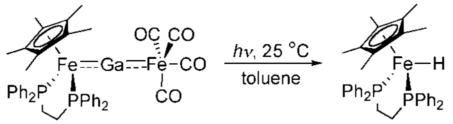


Figure 1. ORTEP drawing of **6a** (thermal ellipsoids at the 50% probability level).

Hydride complex **8** was formed upon prolonged irradiation (eq 3). The same product was also formed by irradiation of **2** in toluene (by NMR) (eq 4). The ^{1}H NMR spectrum of **8** showed a characteristic triplet resonance at −16.8 ppm assignable to the hydride ligand on iron ($^2J_{PH}$ = 68.0 Hz).[15] The formation mechanism of the hydride complex **8** is not clear at present, but the hydride ligand was evidently abstracted from the solvent molecules since deuteridoiron complex Cp*(dppe)FeD (**8-D**)[15b] was exclusively obtained upon photolysis of **2** in C_6D_6.



(4)

2 **8**

Structures of 6a and 6b. ORTEP drawings of **6a** and **6b** are shown in Figures 1 and 2, and selected bond distances and angles are listed in Tables 2 and 3, respectively. The structures of **6a** and **6b** are characteristics of the linear Fe1−Ga−Fe2 framework (176.430(12)° and 177.389(19)°, respectively), indicating sp-hybridization of the gallium atom. The incorporated PR$_3$ ligand is at the position trans to the gallium atom. Both of the Fe−Ga bonds in **6a** and **6b** are significantly shorter than the usual Fe−Ga single bond (2.36−2.46 Å), which indicates multiple-bond character of the Fe−Ga bonding.[1b] The Fe1−Ga bond of **6a** (2.2844(8) Å) and **6b** (2.2686(5) Å) is shorter than the (OC)$_4$Fe−Ga bond in **2** (2.2931(10) Å), while the Fe2−Ga bond in **6a** (2.2690(8) Å) and **6b** (2.2769(5) Å) is longer than the corresponding bond in **2** (2.2479(10) Å).

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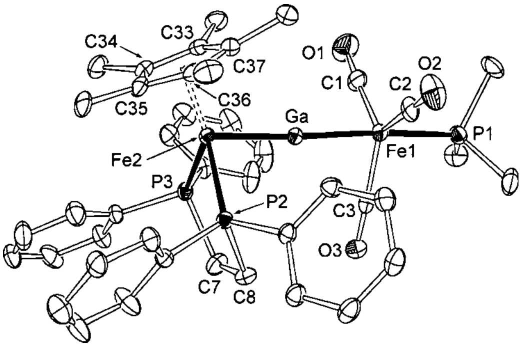

Figure 2. ORTEP drawing of **6b** (thermal ellipsoids at the 50% probability level).

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Cp*(dppe)FeGaFe(CO)$_3${P(OPh)$_3$} (6a)

Fe1−Ga	2.2845(3)	Fe2−Ga	2.2691(3)
Fe1−P1	2.1104(5)	Fe2−P2	2.1908(5)
Fe2−P3	2.1940(5)	Fe1−C1	1.778(2)
Fe1−C2	1.764(2)	Fe1−C3	1.773(2)
Fe2−C22	2.152(2)	Fe2−C23	2.122(2)
Fe2−C24	2.126(2)	Fe2−C25	2.129(2)
Fe2−C26	2.154(2)	O1−C1	1.157(2)
O2−C2	1.160(2)	O3−C3	1.158(2)
Fe1−Ga−Fe2	176.430(12)	P1−Fe1−Ga	176.993(17)
P1−Fe1−C1	92.89(6)	P1−Fe1−C2	95.03(6)
P1−Fe1−C3	96.57(6)	C1−Fe1−C2	118.09(9)
C2−Fe1−C3	117.16(9)	C3−Fe1−C1	122.65(9)
Fe1−C1−O1	177.4(2)	Fe1−C2−O2	176.9(2)
Fe1−C3−O3	179.0(2)	P2−Fe2−Ga	85.05(1)
P3−Fe2−Ga	91.06(2)	P2−Fe2−P3	86.10(2)

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Cp*(dppe)FeGaFe(CO)$_3$(PMe$_3$) (6b)

Fe1−Ga	2.2686(5)	Fe2−Ga	2.2769(5)
Fe1−P1	2.1805(8)	Fe2−P2	2.1735(8)
Fe2−P3	2.1695(7)	Fe1−C1	1.768(3)
Fe1−C2	1.764(3)	Fe1−C3	1.760(3)
Fe2−C33	2.113(3)	Fe2−C34	2.141(3)
Fe2−C35	2.148(3)	Fe2−C36	2.129(3)
Fe2−C37	2.123(3)	O1−C1	1.159(4)
O2−C2	1.165(4)	O3−C3	1.167(4)
Fe1−Ga−Fe2	177.389(19)	P1−Fe1−Ga	176.26(3)
P1−Fe1−C1	92.48(10)	P1−Fe1−C2	90.70(9)
P1−Fe1−C3	92.48(9)	C1−Fe1−C2	117.93(16)
C2−Fe1−C3	124.35(15)	C3−Fe1−C1	117.40(10)
Fe1−C1−O1	176.7(3)	Fe1−C2−O2	177.7(3)
Fe1−C3−O3	177.9(3)	P2−Fe2−Ga	87.99(2)
P3−Fe2−Ga	89.36(2)	P2−Fe2−P3	85.65(3)

Interestingly, the Fe2−Ga bond in **6a** is shorter than the Fe1−Ga bond in the same molecule, while the former in **6b** is longer than the latter. Thus, the strong electron-releasing ligand PMe$_3$ significantly shortens the Fe1−Ga bond and elongates the Fe2−Ga bond.

Table 3 summarizes the Fe−Ga bond lengths and ν(CO) frequencies of Ga-bridged diiron complexes **6a**−**c** and **7b**,**c** as well as those of previously reported complexes **2** and **3**. Substitution of one carbonyl ligand of **2** by the more electron-releasing ligand P(OPh)$_3$ elongates the Cp*(dppe)Fe−Ga bond and shortens the Ga−Fe(CO)$_3$L bond (complex **6a**). This is attributable to the fact that the increased electron density on the Fe(CO)$_3$L fragment enhances the π-back-donation from the Fe(CO)$_3$L fragment to the Ga center and, consequently, suppresses that from the Cp*(dppe)Fe fragment. The red shift of the ν(CO) frequencies also suggests the increase of π-basicity in the Fe(CO)$_{4-n}$L$_n$ fragment. This explanation is also supported by the fact that substitution of P(OPh)$_3$ in **6a** by the more electron-releasing ligand PMe$_3$ in **6b** further shortens the Ga−Fe(CO)$_3$L bond and elongates the Cp*(dppe)Fe−Ga bond. Substitution of dppe in **2** by the more electron-releasing ligand dmpe in **3**, in contrast, shortens the Cp*(P2)Fe−Ga bond and elongates the Ga−Fe(CO)$_4$ bond, which is also rationalized by the changes of the π-basicity of the metal fragment. These results indicate that the contributions of π-back-donation from two iron fragments toward Ga compete with each other; in other words, the electronic effect of a metal fragment affects another metal fragment via the gallium−metal unsaturated bonding.

Experimental Section

General Procedures. All manipulations were performed using either standard Schlenk tube techniques under nitrogen, vacuum line techniques, or a drybox under nitrogen. The syntheses of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) and Cp*(dppe)FeGaCl$_2$ (**4**) were reported previously.[8d] Toluene, THF, and hexane were dried by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere before use. Dichloromethane was dried by refluxing over CaH$_2$ and distilled under nitrogen before use. Benzene-d_6 was distilled from a potassium mirror under vacuum and stored on 4 Å molecular sieves. Dichloromethane-d_2 was used as received. [PPN]Cl was recrystallized from dichloromethane/hexane. 4,4-Dimethylaminopyridine (DMAP) and 2,2′-bipyridine (2,2′-bpy) were purified according to standard methods.[16] The concentrations of MeLi in Et$_2$O (1.20 M), ^{n}BuLi in hexane (1.01 M), and HCl in Et$_2$O (0.92 M) were determined by standard titration techniques. P(OPh)$_3$ and PMe$_3$ were used as received. P(OMe)$_3$ was dried over 4 Å molecular sieves.

NMR spectra were recorded on a JEOL JNM-AL300 or a JEOL JNM-AL500 Fourier transform spectrometer at room temperature. IR spectra were recorded on a JASCO FT/IR-600 Plus spectrometer at room temperature. Elemental analyses were performed by the Microanalytical Center, Gunma University. Photolysis was carried out using an Ushio UV-452 450W medium-pressure Hg lamp placed in a water-cooled quartz jacket immersed in a water bath (4 °C) and a Pyrex reaction vessel.

Reaction of 2 with Alkyl Lithium. An ether solution of MeLi (2.6 μL, 3.2×10^{-3} mmol) was added to a C$_6$D$_6$ solution (0.5 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (1.3 mg, 1.6×10^{-3} mmol) in a NMR sample tube with a Teflon vacuum valve. The color of the reaction mixture immediately changed from orange to red-purple with formation of white precipitates. The precipitates were removed from the reaction mixture by decantation. Volatiles were evaporated from the solution under reduced pressure. The residue was dissolved in C$_6$D$_6$ (0.5 mL) and subjected to NMR measurements. Reaction of **2** with ^{n}BuLi is also performed in a similar manner using **2** (1.6 mg, 1.9×10^{-3} mmol) and a hexane solution of ^{n}BuLi (1.9 μL, 1.9×10^{-3} mmol).

Preparation of Cp*(dppe)FeGaR$_2$ (R = Me (5a), ^{n}Bu (5b)). Complex **5a** was prepared according to the following procedure: To a toluene solution (20 mL) of Cp*(dppe)FeGaCl$_2$ (**4**) (90 mg, 1.2×10^{-4} mol) in a 50 mL round-bottomed flask was added a Et$_2$O solution of MeLi (200 μL, 2.4×10^{-4} mol) with vigorous stirring. The resultant mixture was stirred for 1 h at 25 °C and then filtered through a glass filter. After removal of volatiles from the filtrate in vacuo, the residue was extracted with toluene (10 mL). The extract was allowed to stand at −30 °C to give red-orange crystals of Cp*(dppe)FeGaMe$_2$ (**5a**) in 63% yield (52 mg, 7.5×10^{-5} mol). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 7.51−7.06 (m, 20H, PPh), 2.56 (m, 2H, PCH_2CH_2P), 2.28 (m, 2H, PCH_2CH_2P), 1.58 (s, 15H, C$_5$Me$_5$), −0.04 (s, 6H, GaMe$_2$). ^{13}C{^{1}H} NMR (125.7

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Table 3. Fe−Ga Bond Lengths and ν(CO) Frequencies of Cp*(P2)Fe−Ga−Fe$(CO)_{4-n}L_n$

complex	P2	L	n	Cp*(P2)Fe−Ga^a	Ga−Fe$(CO)_{4-n}L_n$^{a}	ν(CO)^b
3	dmpe	CO	1	2.2410(3)	2.3204(3)	1991, 1917, 1882, 1869
2	dppe	CO	1	2.2479(10)	2.2931(10)	1998, 1923, 1890, 1878
6a	dppe	$P(OPh)_3$	1	2.2690(8)	2.2844(8)	1872, 1851
6b	dppe	PMe_3	1	2.2769(5)	2.2686(5)	1831
6c	dppe	$P(OMe)_3$	1			1853, 1837
7b	dppe	PMe_3	2			1837, 1782
7c	dppe	$P(OMe)_3$	2			1872, 1820

^{a} Å. ^{b} cm^{-1}.

Table 4. Crystal Data and Structure Refinement for Complexes 6a and 6b·2THF

	6a	**6b**·2THF
empirical formula	$C_{57}H_{54}Fe_2GaO_6P_3$	$C_{50}H_{64}Fe_2GaO_5P_3$
fw	1109.33	1019.34
temp (K)	150(2)	150(2)
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	*P*1	*C*2/*c*
unit cell dimens		
a (Å)	11.3945(8)	25.3048(11)
b (Å)	14.6164(10)	21.5508(10)
c (Å)	17.6617(11)	18.0423(9)
α (deg)	108.5590(10)	
β (deg)	99.294(2)	92.599(2)
γ (deg)	110.135(2)	
volume (Å^3)	2493.7(3)	9829.0(8)
Z	2	8
D_{calc} (Mg/m^3)	1.477	1.378
absorp coeff (mm^{-1})	1.259	1.269
F(000)	1144	4256
cryst size (mm^3)	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
θ range for data collection (deg)	1.28−32.05	1.65−32.03
index ranges	$-14 \le h \le 14$ $-21 \le k \le 21$ $-23 \le l \le 23$	$-33 \le h \le 34$ $-31 \le k \le 29$ $-26 \le l \le 20$
no. of reflns collected	24 989	35 211
no. of indep reflns [*R*(int)]	12 727 [0.0177]	14 107 [0.0205]
absorp corr	semiempirical from equivalents	semiempirical from equivalents
maximum and minimum transmn	1.000 and 0.811	1.0000 and 0.6049
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	12 727/0/627	14 107/0/577
goodness-of-fit on F^2	1.136	1.213
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0370$, w$R_2 = 0.0908$	$R_1 = 0.0618$, w$R_2 = 0.1729$
R indices (all data)	$R_1 = 0.0382$, w$R_2 = 0.0918$	$R_1 = 0.0710$, w$R_2 = 0.2141$
largest diff in peak and hole (e Å^{-3})	0.490 and −0.822	1.677 and −3.199

MHz, C_6D_6): δ/ppm 133.2−127.3 (m, PPh), 86.1 (s, C_5Me$_5$), 33.4 (dd, $^1J_{PC}$ = 32 Hz, $^2J_{PC}$ = 14 Hz, PCH_2), 11.9 (t, $^3J_{PC}$ = 3.6 Hz, GaMe), 11.6 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ/ppm 106.9 (s, dppe). Anal. Calc for $C_{38}H_{45}FeGaP_2$: C, 66.22; H, 6.58. Found: C, 65.12; H, 6.54. Although attempted extensively, agreeable elemental analysis data were not obtained probably due to its instability toward moisture and air.

Cp*(dppe)FeGa^{n}Bu$_2$ (**5b**) was prepared in a similar manner using Cp*(dppe)FeGaCl$_2$ (**4**) (100 mg, 1.4 × 10^{-4} mol) and a hexane solution of ^{n}BuLi (170 μL, 2.7 × 10^{-4} mol) as red-orange crystals in 77% yield (82 mg, 1.1 × 10^{-4} mol). ^{1}H NMR (300 MHz, C_6D_6): δ/ppm 7.07−7.57 (m, 20H, PPh), 2.67 (m, 2H, PC*H*$_2$C*H*$_2$P), 2.46 (m, 2H, PC*H*$_2$C*H*$_2$P), 1.59 (s, 15H, C_5Me_5), 1.33 (m, 4H, ^{n}Bu), 1.13 (m, 4H, ^{n}Bu), 0.95 (t, 6H, ^{n}Bu), 0.60 (m, 4H, ^{n}Bu). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ/ppm 127.2−145.8 (m, PPh), 86.4 (s, C_5Me$_5$), 34.0 (dd, $^1J_{PC}$ = 29.4 Hz, $^2J_{PC}$ = 14.7 Hz, PCH_2), 29.6 (s, ^{n}Bu), 29.1 (s, ^{n}Bu), 27.5 (s, ^{n}Bu), 14.2 (s, ^{n}Bu), 11.7 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ/ppm 108.7 (s, dppe). Anal. Calc for $C_{44}H_{57}FeGaP_2$: C, 68.33; H, 7.43. Found: C, 67.41; H, 7.32.

Reaction of 2 with HCl. To a C_6D_6 solution (0.5 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (3.5 mg, 4.2 × 10^{-3} mmol) in a NMR sample tube with a Teflon vacuum valve was added a Et_2O solution of HCl (9.0 μL, 8.4 × 10^{-3} mmol). The color of the reaction mixture immediately changed from orange to red-purple with formation of precipitates. The reaction was monitored by ^{31}P{^{1}H} and ^{1}H NMR. Yield of Cp*(dppe)FeGaCl$_2$ (**4**)[8d] was determined from the ^{1}H NMR spectrum (66%).

Cp*(dppe)FeGaFe(CO)$_3${P(OPh)$_3$} (6a). A degassed THF solution (30 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (83 mg, 0.10 mmol) and P(OPh)$_3$ (26.2 μL, 0.100 mmol) was placed in a Pyrex sample tube with a Teflon vacuum valve and irradiated with a medium-pressure Hg lamp. During the photolysis, the solution color changed from orange to red-orange. After 15 h irradiation, volatiles were removed from the reaction mixture. The residue was washed with toluene (5 mL) to give orange crystals of Cp*(dppe)FeGa-Fe(CO)$_3${P(OPh)$_3$} (**6a**) in 50% yield (56 mg, 0.050 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ/ppm 7.63−7.15 (m, 35H, Ph), 2.22 (m, 4H, PCH_2), 1.46 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ/ppm 216.4 (d, $^2J_{PC}$ = 26 Hz, CO), 152.4−122.5 (m, Ph), 86.4 (s, C_5Me$_5$), 32.7 (m, PCH_2), 10.5 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ/ppm 192.2 (t, $^4J_{PP}$ = 7.8 Hz, P(OPh)$_3$), 92.6 (d, $^4J_{PP}$ = 7.8 Hz, dppe). IR (KBr): ν/cm^{-1} 1872 (vs, C=O), 1851 (vs, C=O). Anal. Calc for $C_{57}H_{54}Fe_2GaO_6P_3$: C, 61.71; H, 4.91. Found: C, 61.22; H, 4.85.

Cp*(dppe)FeGaFe(CO)$_3$(PMe$_3$) (6b). A THF solution (20 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (103 mg, 0.124 mmol) and PMe$_3$ (38.5 μL, 0.372 mmol) was irradiated in a manner similar to that for **6a** for 12 h. After removal of the volatiles from the reaction mixture, the residue was extracted with toluene (10 mL). Cooling the extract to −35 °C gave orange crystals of Cp*(dppe)FeGaFe(CO)$_3$(PMe$_3$) (**6b**) in 65% yield (71 mg, 0.081 mmol). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 8.04−6.99 (m, 20H, Ph), 2.62 (m, 2H, PCH_2CH_2P), 2.20 (m, 2H, PCH_2CH_2P), 1.58 (s, 15H, C$_5$Me$_5$), 1.28 (d, $^2J_{PH}$ = 9 Hz, 9H, PMe$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$): δ/ppm 220.7 (d, $^2J_{PC}$ = 22 Hz, CO), 140.5−127.5 (m, PPh), 86.3 (s, *C*$_5$Me$_5$), 33.2 (dd, $^1J_{PC}$ = 29 Hz, $^2J_{PC}$ = 8.9 Hz, PCH$_2$), 22.0 (d, $^1J_{PC}$ = 29 Hz, PMe$_3$), 10.8 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ/ppm 94.7 (d, $^4J_{PP}$ = 3.4 Hz, dppe), 36.4 (t, $^4J_{PP}$ = 3.4 Hz, PMe$_3$). IR (KBr): ν/cm^{-1} 1831 (vs, C═O). Anal. Calc for C$_{42}$H$_{48}$Fe$_2$GaO$_3$P$_3$: C, 57.64; H, 5.53. Found: C, 57.38; H, 5.57.

Cp*(dppe)FeGaFe(CO)$_3${P(OMe)$_3$} (6c). Complex **6c** was obtained as orange crystals according to a procedure similar to that for **6a** using Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (100 mg, 0.121 mmol) and P(OMe)$_3$ (43.0 μL, 0.365 mmol) in 62% yield (69 mg, 0.075 mmol). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 7.98−6.99 (m, 20H, Ph), 3.64 (d, $^3J_{PH}$ = 12 Hz, 9H, P(OMe)$_3$), 2.57 (m, 2H, PCH_2CH_2P), 2.11 (m, 2H, PCH_2CH_2P), 1.57 (s, 15H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$): δ/ppm 218.1 (d, $^2J_{PC}$ = 26 Hz, CO), 139.8−127.5 (m, PPh), 86.1 (s, *C*$_5$Me$_5$), 51.7 (s, P(OMe)$_3$), 32.9 (m, PCH$_2$), 10.7 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (202.5 MHz, C$_6$D$_6$): δ/ppm 204.3 (t, $^4J_{PP}$ = 7.5 Hz, P(OMe)$_3$), 93.9 (d, $^4J_{PP}$ = 7.5 Hz, dppe). IR (KBr): ν/cm^{-1} 1853 (vs, C═O), 1837 (vs, C═O). Anal. Calc for C$_{42}$H$_{48}$Fe$_2$GaO$_6$P$_3$: C, 54.64; H, 5.24. Found: C, 54.19; H, 5.41.

Cp*(dppe)FeGaFe(CO)$_2$(PMe$_3$)$_2$ (7b). A THF solution (15 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (150 mg, 0.181 mmol) and PMe$_3$ (190 μL, 1.84 mmol) was irradiated for 350 h in a manner similar to that for **6a**. Volatiles were removed from the reaction mixture. The residue was extracted with Et$_2$O (10 mL). Cooling the extract to −35 °C gave red-orange crystals of Cp*(dppe)FeGaFe(CO)$_2$(PMe$_3$)$_2$ (**7b**) in 40% yield (67 mg, 0.073 mmol). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 8.09−6.97 (m, 20H, Ph), 2.74 (m, 2H, PCH_2CH_2P), 2.30 (m, 2H, PCH_2CH_2P), 1.67 (s, 15H, C$_5$Me$_5$), 1.25 (d, $^2J_{PH}$ = 6.9 Hz, 18H, PMe$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$): δ/ppm 226.4 (t, $^2J_{PC}$ = 15 Hz, CO), 141.4−127.2 (m, PPh), 86.0 (s, *C*$_5$Me$_5$), 33.0 (m, PCH$_2$), 25.6 (dd, $^1J_{PC}$ = 15 Hz, $^3J_{PC}$ = 7.3 Hz, PMe$_3$), 10.9 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ/ppm 94.9 (s, dppe), 20.9 (s, PMe$_3$). IR (KBr): ν/cm^{-1} 1837 (vs, C═O), 1782 (vs, C═O). Anal. Calc for C$_{44}$H$_{57}$Fe$_2$GaO$_2$P$_4$: C:, 57.24; H, 6.22. Found: C, 53.28; H, 6.08. Although attempted extensively, agreeable elemental analysis data were not obtained probably due to its instability toward moisture and air.

Cp*(dppe)FeGaFe(CO)$_2${P(OMe)$_3$}$_2$ (7c). A THF solution (20 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (100 mg, 0.121 mmol) and P(OMe)$_3$ (143 μL, 1.21 mmol) was irradiated for 140 h in a manner similar to that of **6a**. Volatiles were removed from the reaction mixture. The residue was extracted with Et$_2$O (10 mL). The extract was concentrated to ca. 5 mL and cooled to −35 °C. Red-orange crystals of Cp*(dppe)FeGaFe(CO)$_2${P(OMe)$_3$}$_2$ (**7c**) were obtained in 48% yield (59 mg, 0.058 mmol). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 8.01−7.02 (m, 20H, Ph), 3.48 (t, $^2J_{PH}$ = 5.4 Hz, 18H, P(OMe)$_3$) 2.67 (m, 2H, PCH_2CH_2P), 2.22 (m, 2H, PCH_2CH_2P), 1.66 (s, 15H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$): δ/ppm 221.4 (t, $^2J_{PC}$ = 11 Hz, CO), 141.5−127.4 (m, PPh), 86.7 (s, *C*$_5$Me$_5$), 50.6 (s, P(OMe)$_3$), 33.2 (m, PCH$_2$), 10.9 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ/ppm 197.3 (s, P(OMe)$_3$), 95.9 (s, dppe). IR (KBr): ν/cm^{-1} 1872 (s, C═O), 1820 (vs, C═O). Anal. Calc for C$_{44}$H$_{57}$Fe$_2$GaO$_8$P$_4$: C, 51.85; H, 5.64. Found: C, 51.90; H, 5.64.

Photolysis of 2. A degassed toluene solution (15 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (50 mg, 0.060 mmol) in a Pyrex sample tube with a Teflon vacuum valve was irradiated with a medium-pressure Hg lamp. The color changed from orange to red with formation of black precipitates during the photolysis. After 150 h irradiation, the reaction mixture was filtered through a glass filter. After removal of volatiles from the filtrate, the residue was extracted with hexane (30 mL). Cooling the extract at −30 °C gave a small amount of red crystals of Cp*(dppe)FeH (**8**).[15] ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 7.82−7.12 (m, 20H, PPh), 1.74 (m, 2H, PCH_2CH_2P), 1.69 (m, 2H, PCH_2CH_2P), 1.62 (s, 15H, C$_5$Me$_5$), −16.8 (t, $^2J_{PH}$ = 68. 0 Hz, 1H, FeH).

Cp*(dppe)FeD (8-D). [15b] A degassed C$_6$D$_6$ solution (0.5 mL) of Cp*(dppe)FeGaFe(CO)$_4$ (**2**) (1.3 mg, 1.6 × 10^{-3} mmol) was irradiated in a NMR sample tube with a Teflon vacuum valve. The reaction was monitored by ^{1}H NMR. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ/ppm 7.82−7.12 (m, 20H, PPh), 1.74 (m, 2H, PCH_2CH_2P), 1.69 (m, 2H, PCH_2CH_2P), 1.69 (s, 15H, C$_5$Me$_5$).

X-ray Crystal Structure Determination of Cp*(dppe)FeGaFe(CO)$_3${P(OPh)$_3$}(6a)andCp*(dppe)FeGaFe(CO)$_3$(PMe$_3$)·2THF (6b·2THF). A single crystal of **6a** or **6b** suitable for X-ray crystal structure determination was obtained by recrystallization from CH$_2$Cl$_2$ or THF, respectively. The intensity data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated Mo Kα radiation at 150 K. Readout was performed in the 0.100 mm pixel mode. Empirical absorption corrections were applied. Crystallographic data are summarized in Table 4. The structure was solved by direct and Fourier transform methods using the SHELX-97 systems.[17] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. All hydrogen atoms except for that of THF molecules in **6b**·2THF were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The hydrogen atoms of the THF molecule were not included in the refinement. The final residue R_1 and the weighted wR_2 were 0.0370 and 0.0908 for **6a** and 0.0618 and 0.1729 for **6b**·2THF, respectively.

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Supporting Information Available: X-ray crystallographic data are available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.