

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

Takako Muraoka, Hideaki Motohashi, Masakazu Hirotsu,[†] and Keiji Ueno*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Gunma University, Kiryu 376-8515, Japan

Received April 7, 2008

Gallium-bridged diiron complex $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**2**, $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$, $\text{dppe} = \text{Ph}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) did not react with $[\text{PPN}]\text{Cl}$, 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 $\text{Cp}^*(\text{dppe})\text{FeGaCl}_2$ (**4**). The Ga–Fe(CO)₄ bond cleavage also occurred by the reaction of **2** with RLi (R = Me, ^{*n*}Bu) to afford $\text{Cp}^*(\text{dppe})\text{FeGaR}_2$ (R = Me (**5a**), ^{*n*}Bu (**5b**)). Irradiation of **2** in the presence of phosphine PR_3 (R = OPh, Me, and OMe) gave $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3\text{L}$ (L = P(OPh)₃ (**6a**), PMe_3 (**6b**), and P(OMe)₃ (**6c**)) and $\text{Cp}^*(\text{dppe})\text{-FeGaFe}(\text{CO})_2\text{L}_2$ (L = PMe_3 (**7b**) and P(OMe)₃ (**7c**)) depending on the reaction conditions. Cleavage of the $\text{Cp}^*(\text{dppe})\text{Fe-Ga}$ bond occurred by irradiation of **2** in the absence of PR_3 to give hydridoiron complex $\text{Cp}^*(\text{dppe})\text{FeH}$ (**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)₃L bond and elongation of the $\text{Cp}^*(\text{dppe})\text{Fe-Ga}$ 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 $(\text{OC})_n\text{MBR}$ (M = Fe (*n* = 4), R = Cp^* ($\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$),^{2a} M = Cr and W (*n* = 5), R = N(SiMe_3)₂^{2d}), alanediyli $(\text{OC})_4\text{FeAlCp}^*$,^{3a} gallanediyl $(\text{OC})_4\text{FeGaAr}^*$ (**1**, $\text{Ar}^* = 2,6\text{-}(2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$),^{4a} and indanediyl complex

$\text{Ni}\{\text{InC}(\text{SiMe}_3)_3\}_4$ ^{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

* To whom correspondence should be addressed. Tel & Fax: +81-277-30-1260. E-mail: ueno@chem-bio.gunma-u.ac.jp.

[†] Present address: Department of Material Science, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan.

(1) (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786. (b) Fischer, R. A.; Weiss, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2830. (c) Linti, G.; Schnöckel, H. *Coord. Chem. Rev.* **2000**, *206–207*, 285. (d) Braunschweig, H.; Colling, M. *Eur. J. Inorg. Chem.* **2003**, *393*. (e) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535. (f) Braunschweig, H. *Adv. Organomet. Chem.* **2004**, *51*, 163. (g) Gemel, C.; Steinke, T.; Cokoja, M.; Kempter, A.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2004**, 4161. (h) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254. (i) Ueno, K.; Muraoka, T. *Bull. Jpn. Soc. Coord. Chem.* **2007**, *50*, 18.

(2) (a) Cowley, A. H.; Lomeli, V.; Voigt, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401. (b) Coombs, D. L.; Aldridge, S.; Jones, C.; Willock, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6356. (c) Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911. (d) Braunschweig, H.; Kollann, C.; Englert, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 3179. (e) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H. G.; Neumann, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2298. (f) Braunschweig, H.; Colling, M.; Kollann, C.; Merz, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4198. (g) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 205. (h) Kays, D. L.; Day, J. K.; Ooi, L.-L.; Aldridge, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7457. (i) Aldridge, S.; Jones, C.; Gans-Eichler, T.; Stasch, A.; Kays, D. L.; Coombs, N. D.; Willock, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6118.

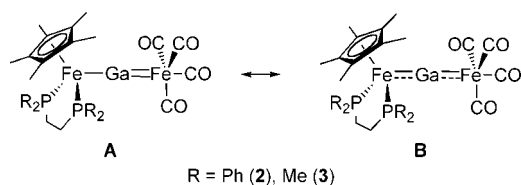
(3) (a) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70. (b) Yu, Q.; Purath, A.; Donchev, A.; Schnöckel, H. *J. Organomet. Chem.* **1999**, *584*, 94. (c) Weiss, D.; Steinke, T.; Winter, M.; Fischer, R. A.; Fröhlich, N.; Uddin, J.; Frenking, G. *Organometallics* **2000**, *19*, 4583. (d) Steinke, T.; Gemel, C.; Cokoja, M.; Winter, M.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2299. (e) Steinke, T.; Cokoja, M.; Gemel, C.; Kempter, A.; Krapp, A.; Frenking, G.; Zenneck, U.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2943.

(4) (a) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511. (b) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305. (c) Uhl, W.; Benter, M.; Melle, S.; Saak, W.; Frenking, G.; Uddin, J. *Organometallics* **1999**, *18*, 3778. (d) Jutzi, P.; Neumann, B.; Schebaum, L. O.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4462. (e) Leiner, E.; Scheer, M. J. *Organomet. Chem.* **2002**, *646*, 247. (f) Weiss, D.; Winter, M.; Merz, K.; Knüfer, A.; Fischer, R. A.; Fröhlich, N.; Frenking, G. *Polyhedron* **2002**, *21*, 535. (g) Cokoja, M.; Steinke, T.; Gemel, C.; Welzel, T.; Winter, M.; Merz, K.; Fischer, R. A. *J. Organomet. Chem.* **2003**, *684*, 277. (h) Cadenbach, T.; Gemel, C.; Schmid, R.; Block, S.; Fischer, R. A. *Dalton Trans.* **2004**, 3171. (i) Yang, X.-J.; Quillian, B.; Wang, Y.; Wei, P.; Robinson, G. H. *Organometallics* **2004**, *23*, 5119. (j) Cokoja, M.; Gemel, C.; Steinke, T.; Schröder, F.; Fischer, R. A. *Dalton Trans.* **2005**, 44. (k) Steinke, T.; Gemel, C.; Cokoja, M.; Winter, M.; Fischer, R. A. *Dalton Trans.* **2005**, 55. (l) Yang, X.-J.; Wang, Y.; Quillian, B.; Wei, P.; Chen, Z.; Schleyer, P. v. R.; Robinson, G. H. *Organometallics* **2006**, *25*, 925.

(5) (a) Uhl, W.; Pohlmann, M.; Wartchow, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 961. (b) Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202. (c) Jutzi, P.; Neumann, B.; Reumann, G.; Schebaum, L. O.; Stammler, H.-G. *Organometallics* **1999**, *18*, 2550. (d) Uhl, W.; Melle, S. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2043. (e) Steinke, T.; Gemel, C.; Cokoja, M.; Winter, M.; Fischer, R. A. *Chem. Commun.* **2003**, 1066.

(6) (a) Bickelhaupt, F. M.; Radius, U.; Ehlers, A. W.; Hoffmann, R.; Baerends, E. J. *New J. Chem.* **1998**, *1*. (b) Cotton, F. A.; Feng, X. *Organometallics* **1998**, *17*, 128. (c) Ehlers, A. W.; Baerends, E. J.; Bickelhaupt, F. M.; Radius, U. *Chem.-Eur. J.* **1998**, *4*, 210. (d) Boehme, C.; Frenking, G. *Chem.-Eur. J.* **1999**, *5*, 2184. (e) Chen, Y.; Frenking, G. *J. Chem. Soc., Dalton Trans.* **2001**, 434.

Scheme 1



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**.

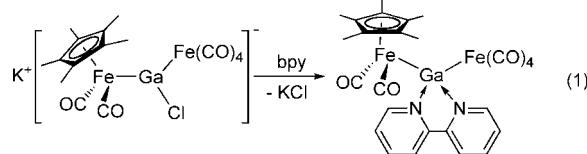
Several types of E atom-bridged complexes M^1-E-M^2 as well as terminal group 13 diyl complexes $M-ER$ have been synthesized so far; however, their reactivity remains largely unexplored. Cationic terminal borylene complexes are rare examples whose reactivity has been investigated extensively, which includes 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 nucleo-

phile 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 $Cp^*(P_2)FeGaFe(CO)_3L$ 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 $Cp^*(OC)_2FeGa(2,2'-bpy)-Fe(CO)_4$ by the reaction of anionic chlorogallylene-bridged diiron complex $K[Cp^*(OC)_2FeGa(Cl)Fe(CO)_4]$ 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 $[Cp^*(OC)_2Fe]_2Ga(4-picoline)]^+$, 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.



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 $HBFA$.¹⁴

(7) (a) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717. (b) Cundari, T. R. *Chem. Rev.* **2000**, *100*, 807. (c) Boehme, C.; Uddin, J.; Frenking, G. *Coord. Chem. Rev.* **2000**, *197*, 249. (d) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238–239*, 55. (e) Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12113. (f) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571. (g) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683. (h) Aldridge, S.; Rossin, A.; Coombs, D. L.; Willock, D. J. *Dalton Trans.* **2004**, 2649. (i) Coombs, N. D.; Clegg, W.; Thompson, A. L.; Willock, D. J.; Aldridge, S. *J. Am. Chem. Soc.* **2008**, *130*, 5449.

(8) (a) Schiemenz, B.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1772. (b) Usón, R.; Forníes, J.; Tomás, M.; Garde, R. *J. Am. Chem. Soc.* **1995**, *117*, 1837. (c) Jeffery, J. C.; Jelliss, P. A.; Liao, Y.-H.; Stone, F. G. A. *J. Organomet. Chem.* **1998**, *551*, 27. (d) Ueno, K.; Watanabe, T.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4375. (e) Bunn, N. R.; Aldridge, S.; Coombs, D. L.; Rossin, A.; Willock, D. J.; Jones, C.; Ooi, L. *Chem. Commun.* **2004**, 1732. (f) Braunschweig, H.; Radacki, K.; Schesckewitz, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1658. (g) Bunn, N. R.; Aldridge, S.; Kays, D. L.; Coombs, N. D.; Rossin, A.; Willock, D. J.; Day, J. K.; Jones, C.; Ooi, L. *Organometallics* **2005**, *24*, 5891. (h) Coombs, N. D.; Bunn, N. R.; Kays, D. L.; Day, J. K.; Ooi, L.; Aldridge, S. *Inorg. Chim. Acta* **2006**, *359*, 3693. (i) Buchin, B.; Gemel, C.; Cadenbach, T.; Fernández, I.; Frenking, G.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 5207. (j) Ueno, K.; Hirotsu, M.; Hatori, N. *J. Organomet. Chem.* **2007**, *692*, 88.

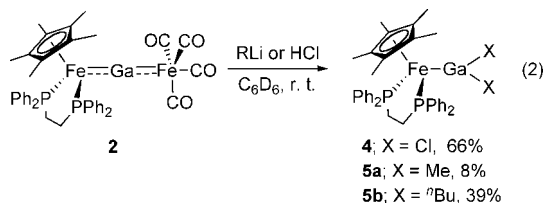
(9) (a) Braunschweig, H.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 3763. (b) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Organometallics* **2006**, *25*, 5159.

(10) (a) Braunschweig, H.; Herbst, T.; Rais, D.; Seeler, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 7461. (b) Braunschweig, H.; Forster, M.; Radacki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2132.

(11) Chemical shift of hydride resonance on $H_2Fe(CO)_4$ has never been reported. (a) Blanchard, A. A.; Coleman, G. W. *Inorg. Synth.* **1946**, *2*, 243. (b) Farmery, K.; Kilner, M. J. *Chem. Soc. (A)* **1970**, 634. (c) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551. (d) Vancea, L.; Graham, W. A. G. *J. Organomet. Chem.* **1977**, *134*, 219. (e) Nagorski, H.; Mirbach, M. J. *J. Organomet. Chem.* **1985**, *291*, 199. (f) Zybilla, C.; Müller, G. *Organometallics* **1988**, *7*, 1368.

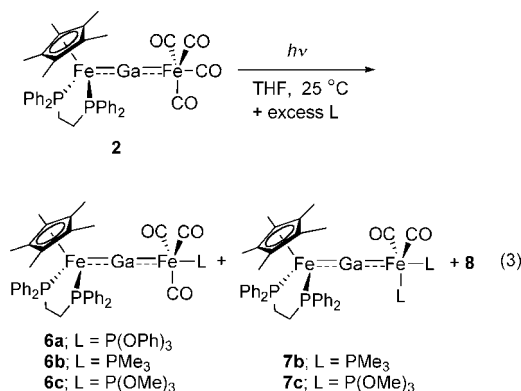
(12) (a) Rogers, W. N.; Baird, M. C. *J. Organomet. Chem.* **1979**, *182*, C65. (b) Basallote, M. G.; Durán, J.; Fernández-Trujillo, J.; Mániz, M. A.; Torre, J. R. *J. Chem. Soc., Dalton Trans.* **1998**, 745. (c) Basallote, M. G.; Durán, J.; Fernández-Trujillo, J.; Mániz, M. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2205.

(13) (a) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185. (b) Shima, T.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5537.



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 ⁿBuLi in C₆D₆ at ambient temperature afforded dialkylgallyliron complex Cp*(dppe)-FeGaR₂ (R = Me (**5a**) and ⁿBu (**5b**)) in 8% and 39% yield, respectively (eq 2). The reactions also formed a white precipitate, which is tentatively assigned to Li₂Fe(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 ⁿBuLi, respectively.

Photolysis of 2. Irradiation of **2** in the presence of P(OPh)₃, PMe₃, and P(OMe)₃ resulted in the substitution of CO to give monosubstituted complex Cp*(dppe)FeGaFe(CO)₃L (L = P(OPh)₃ (**6a**), PMe₃ (**6b**), and P(OMe)₃ (**6c**)), disubstituted complex Cp*(dppe)FeGaFe(CO)₂L₂ (L = PMe₃ (**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 PMe₃ 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 PMe₃. 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}(PR₃)_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.



As described later, crystal structure analysis of **6a** and **6b** revealed that the substituted PR₃ ligand occupied the position

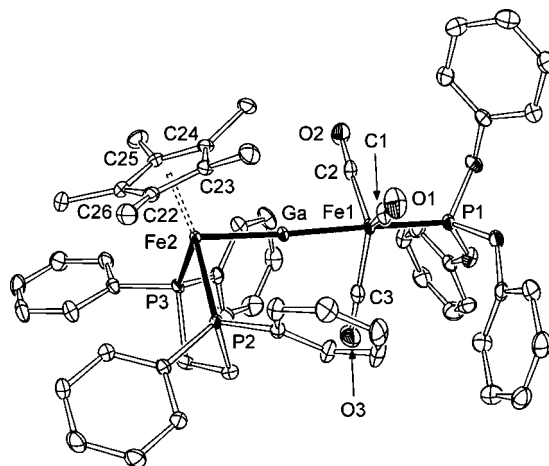
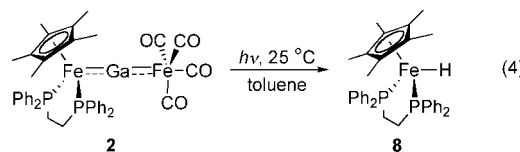


Figure 1. ORTEP drawing of **6a** (thermal ellipsoids at the 50% probability level).

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, ³¹P and ¹H NMR showed only one signal for the two PR₃ ligands. Furthermore, ³¹P NMR signals for dppe and PR₃ ligands appeared as a singlet. Observation of only one signal for the two PR₃ ligands as well as disappearance of the ⁴J_{pp} coupling indicates the rapid scrambling of the two phosphines on the NMR time scale.

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 ¹H 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 C₆D₆.



Structures of 6a and 6b. ORTEP drawings of **6a** and **6b** are shown in Figures 1 and 2, and selected 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 PR₃ 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)₄Fe–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).

(14) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4056. (c) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (d) Hamon, J.-R.; Hamon, P.; Toupet, L.; Costuas, K.; Saillard, J.-Y. *C. R. Chim.* **2002**, *5*, 89.

(15) (a) Roger, C.; Marseille, P.; Salus, C.; Hamon, J.-R.; Lapinte, C. *J. Organomet. Chem.* **1987**, *336*, C13. (b) Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045. See also: (c) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429. (d) Hamon, P.; Hamon, J.-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1602. (e) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1994**, 931.

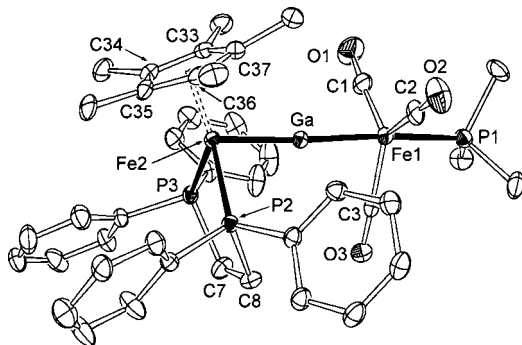


Figure 2. ORTEP drawing of **6b** (thermal ellipsoids at the 50% probability level).

Table 1. Selected Bond Lengths [Å] and Angles [deg] for $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3[\text{P}(\text{OPh})_3]$ (**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 $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3(\text{PMe}_3)$ (**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 $\nu(\text{CO})$ 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 $\text{P}(\text{OPh})_3$ elongates the $\text{Cp}^*(\text{dppe})\text{Fe–Ga}$ bond and shortens the $\text{Ga–Fe}(\text{CO})_3\text{L}$ bond (complex **6a**). This is attributable to the fact that the increased electron density on the $\text{Fe}(\text{CO})_3\text{L}$ fragment enhances the π -back-donation from the $\text{Fe}(\text{CO})_3\text{L}$ fragment to the Ga center and, consequently, suppresses that from the $\text{Cp}^*(\text{dppe})\text{Fe}$ fragment. The red shift of the $\nu(\text{CO})$ frequencies also suggests the increase of π -basicity in the $\text{Fe}(\text{CO})_{4-n}\text{L}_n$ fragment. This explanation is also supported

by the fact that substitution of $\text{P}(\text{OPh})_3$ in **6a** by the more electron-releasing ligand PMe_3 in **6b** further shortens the $\text{Ga–Fe}(\text{CO})_3\text{L}$ bond and elongates the $\text{Cp}^*(\text{dppe})\text{Fe–Ga}$ bond. Substitution of dppe in **2** by the more electron-releasing ligand dmpe in **3**, in contrast, shortens the $\text{Cp}^*(\text{P2})\text{Fe–Ga}$ bond and elongates the $\text{Ga–Fe}(\text{CO})_4$ 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 $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**2**) and $\text{Cp}^*(\text{dppe})\text{FeGaCl}_2$ (**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. $[\text{PPN}]\text{Cl}$ 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_2O (1.20 M), $n\text{BuLi}$ in hexane (1.01 M), and HCl in Et_2O (0.92 M) were determined by standard titration techniques. $\text{P}(\text{OPh})_3$ and PMe_3 were used as received. $\text{P}(\text{OMe})_3$ 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_6D_6 solution (0.5 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**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_6D_6 (0.5 mL) and subjected to NMR measurements. Reaction of **2** with $n\text{BuLi}$ is also performed in a similar manner using **2** (1.6 mg, 1.9×10^{-3} mmol) and a hexane solution of $n\text{BuLi}$ (1.9 μL , 1.9×10^{-3} mmol).

Preparation of $\text{Cp}^*(\text{dppe})\text{FeGaR}_2$ ($\text{R} = \text{Me}$ (5a**), $n\text{Bu}$ (**5b**)).** Complex **5a** was prepared according to the following procedure: To a toluene solution (20 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaCl}_2$ (**4**) (90 mg, 1.2×10^{-4} mol) in a 50 mL round-bottomed flask was added a Et_2O 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 $\text{Cp}^*(\text{dppe})\text{FeGaMe}_2$ (**5a**) in 63% yield (52 mg, 7.5×10^{-5} mol). ^1H NMR (300 MHz, C_6D_6): δ /ppm 7.51–7.06 (m, 20H, PPh), 2.56 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.28 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.58 (s, 15H, C_5Me_5), –0.04 (s, 6H, GaMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7

(16) (a) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

Table 3. Fe–Ga Bond Lengths and $\nu(\text{CO})$ Frequencies of $\text{Cp}^*(\text{P}2)\text{Fe–Ga–Fe}(\text{CO})_{4-n}\text{L}_n$

complex	P2	L	<i>n</i>	$\text{Cp}^*(\text{P}2)\text{Fe–Ga}^a$	$\text{Ga–Fe}(\text{CO})_{4-n}\text{L}_n^a$	$\nu(\text{CO})^b$
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 ₂ GaO ₆ P ₃	C ₅₀ H ₆₄ Fe ₂ GaO ₅ P ₃
fw	1109.33	1019.34
temp (K)	150(2)	150(2)
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	<i>P</i> 1	<i>C</i> 2/ <i>c</i>
unit cell dimens		
<i>a</i> (Å)	11.3945(8)	25.3048(11)
<i>b</i> (Å)	14.6164(10)	21.5508(10)
<i>c</i> (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)
<i>Z</i>	2	8
<i>D</i> _{calc} (Mg/m ³)	1.477	1.378
absorp coeff (mm ^{−1})	1.259	1.269
<i>F</i> (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 ≤ <i>h</i> ≤ 14 −21 ≤ <i>k</i> ≤ 21 −23 ≤ <i>l</i> ≤ 23	−33 ≤ <i>h</i> ≤ 34 −31 ≤ <i>k</i> ≤ 29 −26 ≤ <i>l</i> ≤ 20
no. of reflns collected	24 989	35 211
no. of indep reflns [<i>R</i> (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 <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
no. of data/restraints/params	12 727/0/627	14 107/0/577
goodness-of-fit on <i>F</i> ²	1.136	1.213
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0908	<i>R</i> ₁ = 0.0618, <i>wR</i> ₂ = 0.1729
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0918	<i>R</i> ₁ = 0.0710, <i>wR</i> ₂ = 0.2141
largest diff in peak and hole (e Å ^{−3})	0.490 and −0.822	1.677 and −3.199

MHz, C₆D₆): δ /ppm 133.2–127.3 (m, PPh), 86.1 (s, C₅Me₅), 33.4 (dd, ¹*J*_{PC} = 32 Hz, ²*J*_{PC} = 14 Hz, PCH₂), 11.9 (t, ³*J*_{PC} = 3.6 Hz, GaMe), 11.6 (s, C₅Me₅). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ /ppm 106.9 (s, dppe). Anal. Calc for C₃₈H₄₅FeGaP₂: 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.

$\text{Cp}^*(\text{dppe})\text{FeGa}^n\text{Bu}_2$ (**5b**) was prepared in a similar manner using $\text{Cp}^*(\text{dppe})\text{FeGaCl}_2$ (**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). ¹H NMR (300 MHz, C₆D₆): δ /ppm 7.07–7.57 (m, 20H, PPh), 2.67 (m, 2H, PCH₂CH₂P), 2.46 (m, 2H, PCH₂CH₂P), 1.59 (s, 15H, C₅Me₅), 1.33 (m, 4H, ^{*n*}Bu), 1.13 (m, 4H, ^{*n*}Bu), 0.95 (t, 6H, ^{*n*}Bu), 0.60 (m, 4H, ^{*n*}Bu). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ /ppm 127.2–145.8 (m, PPh), 86.4 (s, C₅Me₅), 34.0 (dd, ¹*J*_{PC} = 29.4 Hz, ²*J*_{PC} = 14.7 Hz, PCH₂), 29.6 (s, ^{*n*}Bu), 29.1 (s, ^{*n*}Bu), 27.5 (s, ^{*n*}Bu), 14.2 (s, ^{*n*}Bu), 11.7 (s, C₅Me₅). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ /ppm 108.7 (s, dppe). Anal. Calc for C₄₄H₅₇FeGaP₂: C, 68.33; H, 7.43. Found: C, 67.41; H, 7.32.

Reaction of 2 with HCl. To a C₆D₆ solution (0.5 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**2**) (3.5 mg, 4.2×10^{-3} mmol) in a NMR sample tube with a Teflon vacuum valve was added a Et₂O 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 ³¹P{¹H} and ¹H NMR. Yield of $\text{Cp}^*(\text{dppe})\text{FeGaCl}_2$ (**4**)^{8d} was determined from the ¹H NMR spectrum (66%).

$\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}$ (6a**).** A degassed THF solution (30 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**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 $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}$ (**6a**) in 50% yield (56 mg, 0.050 mmol). ¹H NMR (300 MHz, CD₂Cl₂): δ /ppm 7.63–7.15 (m, 35H, Ph), 2.22 (m, 4H, PCH₂), 1.46 (s, 15H, C₅Me₅). ¹³C{¹H} NMR (125.7 MHz, CD₂Cl₂): δ /ppm 216.4 (d, ²*J*_{PC} = 26 Hz, CO), 152.4–122.5 (m, Ph), 86.4 (s, C₅Me₅), 32.7 (m, PCH₂), 10.5 (s, C₅Me₅). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ /ppm 192.2 (t, ⁴*J*_{PP} = 7.8 Hz, P(OPh)₃), 92.6 (d, ⁴*J*_{PP} = 7.8 Hz, dppe). IR (KBr): ν/cm^{-1} 1872 (vs, C=O), 1851 (vs, C=O). Anal. Calc for C₅₇H₅₄Fe₂GaO₆P₃: C, 61.71; H, 4.91. Found: C, 61.22; H, 4.85.

$\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3(\text{PMe}_3)$ (6b**).** A THF solution (20 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**2**) (103 mg, 0.124 mmol) and PMe₃ (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 $-35\text{ }^{\circ}\text{C}$ gave orange crystals of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3(\text{PMe}_3)$ (**6b**) in 65% yield (71 mg, 0.081 mmol). ^1H NMR (300 MHz, C_6D_6): δ/ppm 8.04–6.99 (m, 20H, Ph), 2.62 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.20 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.58 (s, 15H, C_5Me_5), 1.28 (d, $^2J_{\text{PH}} = 9\text{ Hz}$, 9H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ/ppm 220.7 (d, $^2J_{\text{PC}} = 22\text{ Hz}$, CO), 140.5–127.5 (m, PPh), 86.3 (s, C_5Me_5), 33.2 (dd, $^1J_{\text{PC}} = 29\text{ Hz}$, $^2J_{\text{PC}} = 8.9\text{ Hz}$, PCH_2), 22.0 (d, $^1J_{\text{PC}} = 29\text{ Hz}$, PMe_3), 10.8 (s, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): δ/ppm 94.7 (d, $^4J_{\text{PP}} = 3.4\text{ Hz}$, dppe), 36.4 (t, $^4J_{\text{PP}} = 3.4\text{ Hz}$, PMe_3). IR (KBr): ν/cm^{-1} 1831 (vs, $\text{C}=\text{O}$). Anal. Calc for $\text{C}_{42}\text{H}_{48}\text{Fe}_2\text{GaO}_3\text{P}_3$: C, 57.64; H, 5.53. Found: C, 57.38; H, 5.57.

$\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3\{\text{P}(\text{OMe})_3\}$ (6c**).** Complex **6c** was obtained as orange crystals according to a procedure similar to that for **6a** using $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**2**) (100 mg, 0.121 mmol) and $\text{P}(\text{OMe})_3$ (43.0 μL , 0.365 mmol) in 62% yield (69 mg, 0.075 mmol). ^1H NMR (300 MHz, C_6D_6): δ/ppm 7.98–6.99 (m, 20H, Ph), 3.64 (d, $^3J_{\text{PH}} = 12\text{ Hz}$, 9H, $\text{P}(\text{OMe})_3$), 2.57 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.11 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.57 (s, 15H, C_5Me_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ/ppm 218.1 (d, $^2J_{\text{PC}} = 26\text{ Hz}$, CO), 139.8–127.5 (m, PPh), 86.1 (s, C_5Me_5), 51.7 (s, $\text{P}(\text{OMe})_3$), 32.9 (m, PCH_2), 10.7 (s, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, C_6D_6): δ/ppm 204.3 (t, $^4J_{\text{PP}} = 7.5\text{ Hz}$, $\text{P}(\text{OMe})_3$), 93.9 (d, $^4J_{\text{PP}} = 7.5\text{ Hz}$, dppe). IR (KBr): ν/cm^{-1} 1853 (vs, $\text{C}=\text{O}$), 1837 (vs, $\text{C}=\text{O}$). Anal. Calc for $\text{C}_{42}\text{H}_{48}\text{Fe}_2\text{GaO}_6\text{P}_3$: C, 54.64; H, 5.24. Found: C, 54.19; H, 5.41.

$\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_2(\text{PMe}_3)_2$ (7b**).** A THF solution (15 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**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_2O (10 mL). Cooling the extract to $-35\text{ }^{\circ}\text{C}$ gave red-orange crystals of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_2(\text{PMe}_3)_2$ (**7b**) in 40% yield (67 mg, 0.073 mmol). ^1H NMR (300 MHz, C_6D_6): δ/ppm 8.09–6.97 (m, 20H, Ph), 2.74 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.30 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.67 (s, 15H, C_5Me_5), 1.25 (d, $^2J_{\text{PH}} = 6.9\text{ Hz}$, 18H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ/ppm 226.4 (t, $^2J_{\text{PC}} = 15\text{ Hz}$, CO), 141.4–127.2 (m, PPh), 86.0 (s, C_5Me_5), 33.0 (m, PCH_2), 25.6 (dd, $^1J_{\text{PC}} = 15\text{ Hz}$, $^3J_{\text{PC}} = 7.3\text{ Hz}$, PMe_3), 10.9 (s, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): δ/ppm 94.9 (s, dppe), 20.9 (s, PMe_3). IR (KBr): ν/cm^{-1} 1837 (vs, $\text{C}=\text{O}$), 1782 (vs, $\text{C}=\text{O}$). Anal. Calc for $\text{C}_{44}\text{H}_{57}\text{Fe}_2\text{GaO}_2\text{P}_4$: 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.

$\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2$ (7c**).** A THF solution (20 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**2**) (100 mg, 0.121 mmol) and $\text{P}(\text{OMe})_3$ (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_2O (10 mL). The extract was concentrated to ca. 5 mL and cooled to $-35\text{ }^{\circ}\text{C}$. Red-orange crystals of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2$ (**7c**) were obtained in 48% yield (59 mg, 0.058 mmol). ^1H NMR (300 MHz, C_6D_6): δ/ppm 8.01–7.02 (m, 20H, Ph), 3.48 (t, $^2J_{\text{PH}} = 5.4\text{ Hz}$, 18H, $\text{P}(\text{OMe})_3$), 2.67 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.22 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.66 (s, 15H, C_5Me_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ/ppm 221.4 (t, $^2J_{\text{PC}} = 11\text{ Hz}$, CO), 141.5–127.4 (m, PPh), 86.7 (s, C_5Me_5), 50.6 (s, $\text{P}(\text{OMe})_3$), 33.2 (m, PCH_2), 10.9 (s, C_5Me_5).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): δ/ppm 197.3 (s, $\text{P}(\text{OMe})_3$), 95.9 (s, dppe). IR (KBr): ν/cm^{-1} 1872 (s, $\text{C}=\text{O}$), 1820 (vs, $\text{C}=\text{O}$). Anal. Calc for $\text{C}_{44}\text{H}_{57}\text{Fe}_2\text{GaO}_8\text{P}_4$: C, 51.85; H, 5.64. Found: C, 51.90; H, 5.64.

Photolysis of 2. A degassed toluene solution (15 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**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 $-30\text{ }^{\circ}\text{C}$ gave a small amount of red crystals of $\text{Cp}^*(\text{dppe})\text{FeH}$ (**8**). $^{15}\text{ }^1\text{H}$ NMR (300 MHz, C_6D_6): δ/ppm 7.82–7.12 (m, 20H, PPh), 1.74 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.69 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.62 (s, 15H, C_5Me_5), -16.8 (t, $^2J_{\text{PH}} = 68.0\text{ Hz}$, 1H, FeH).

$\text{Cp}^*(\text{dppe})\text{FeD}$ (8-D**).** 15b A degassed C_6D_6 solution (0.5 mL) of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_4$ (**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 ^1H NMR. ^1H NMR (300 MHz, C_6D_6): δ/ppm 7.82–7.12 (m, 20H, PPh), 1.74 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.69 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.69 (s, 15H, C_5Me_5).

X-ray Crystal Structure Determination of $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}$ (6a**) and $\text{Cp}^*(\text{dppe})\text{FeGaFe}(\text{CO})_3(\text{PMe}_3) \cdot 2\text{THF}$ (**6b** $\cdot$ 2THF).** A single crystal of **6a** or **6b** suitable for X-ray crystal structure determination was obtained by recrystallization from CH_2Cl_2 or THF, respectively. The intensity data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated Mo $\text{K}\alpha$ 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** $\cdot$ 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** $\cdot$ 2THF , respectively.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (Nos. 16033212 and 19027012) and for Scientific Research (No. 17655022) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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>.

OM800310H

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