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Synthesis and Structure of the First Dinuclear Complex Bridged by a Substituent-Free Gallium Atom

Keiji Ueno,*,† Takahito Watanabe,‡ Hiromi Tobita,‡ and Hiroshi Ogino§

Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu 376-8515, Japan, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan, and Miyagi Study Center, The University of the Air, Sendai 980-8577, Japan

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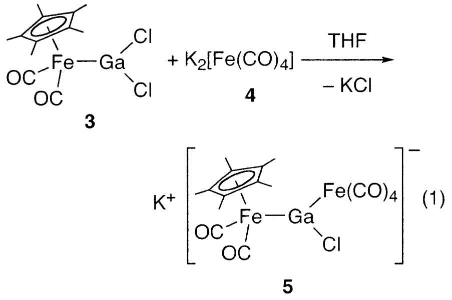
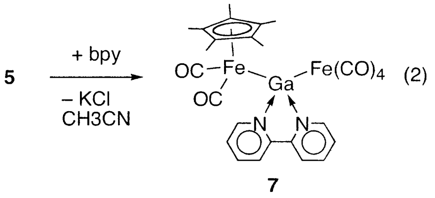
*Summary: The first dinuclear complex bridged by a substituent-free gallium atom, $Cp^*Fe(dppe)(\mu\text{-}Ga)Fe(CO)_4$ (**1**; $Cp^* = \eta\text{-}C_5Me_5$, dppe $= Ph_2PCH_2CH_2PPh_2$), was synthesized by the reaction of $Cp^*Fe(dppe)GaCl_2$ with $K_2[Fe(CO)_4]$. A crystal structure analysis of complex **1** revealed that the geometry around the gallium atom is essentially linear and the Fe−Ga bonds are significantly shorter than that of usual single bonds. These structural features indicate that the Fe−Ga bonds bear significantly unsaturated character.*

Transition-metal complexes with metal−gallium unsaturated bonding have excited much recent interest from a structure/bonding viewpoint.[1,2] Isolation of the first terminal gallyleneiron complex, $(OC)_4FeGaAr^*$ (**2**; $Ar^* = 2{,}6\text{-}(2{,}4{,}6\text{-}Pr^iC_6H_2)_2C_6H_3$), by Robinson et al. triggered an extensive discussion.[2a] A recent theoretical study suggests that the M−ER (M = metal, E = group 13 element) bond in transition-metal complexes with terminal group 13 diyl ligands is mainly ionic but is significantly affected by the π-back-donation from the metal to the ER group.[3] However, systematic studies to clarify the effect of π-bonding have been hampered by the paucity of complexes containing a metal−gallium unsaturated bond.[2] Herein we report the synthesis of the first dinuclear complex bridged by a substituent-free gallium atom, $[Cp^*(dppe)Fe{-}Ga{-}Fe(CO)_4]$ (**1**). The bonding in complex **1** can be 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 $Fe(CO)_4$ on the basis of the 18-electron rule. In contrast to expectations, a structural determination revealed that the former is even shorter than the latter, which is attributable to the contribution of strong π-back-donation in the former bond.

To synthesize the complex in question, we initially examined the salt elimination reaction between the (dichlorogallyl)iron complex $Cp^*(OC)_2FeGaCl_2$ (**3**)[4] and $K_2[Fe(CO)_4]$ (**4**) in THF, which afforded an extremely unstable orange solid of complex **5** (eq 1).[5] The product is soluble in THF but insoluble in nonpolar solvents such as benzene and toluene, indicating the ionic nature of complex **5**. The ^{13}C NMR spectrum shows two CO signals at 217.2 and 220.5 ppm. The IR spectrum gives six ν_{CO} bands in the range of 1890−1994 cm^{-1}, whose positions are comparable to those of **3** (1930 and 1981 cm^{-1}), the gallyleneiron complex **2** (1929−2032 cm^{-1}),[2a] the Cp*Ga complex $(OC)_4FeGaCp^*$ (**6**; 1942−2037 cm^{-1}),[6] and base-stabilized gallyleneiron complexes $(OC)_4FeGaR(L_2)$ (R = halogen, alkyl, L = Lewis donor; 1870−2010 cm^{-1}).[7] Thus, complex **5** was tentatively assigned to $K[\{Cp^*(OC)_2Fe\}(\mu\text{-}GaCl)\{Fe(CO)_4\}]$.



(1)



(2)

The structure of **5** was further supported by the fact that addition of bpy (2,2′-bipyridine) to an acetonitrile solution of **5** caused KCl elimination to give a diiron complex bridged by a base-stabilized gallium atom, $[Cp^*(OC)_2Fe](\mu\text{-}Ga{\cdot}bpy)[Fe(CO)_4]$ (**7**), in 43% yield (eq 2).[8] Base-stabilized complexes related to this have been previously reported by us.[9] An X-ray crystal structure analysis of **7** (Figure 1) revealed that the gallium atom adopts a distorted-tetrahedral geometry with an Fe(1)−

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* To whom correspondence should be addressed. Tel +81-277-30-1261. Fax: +81-277-30-1263. E-mail: ueno@chem.gunma-u.ac.jp.

† Gunma University.

‡ Tohoku University.

§ The University of the Air.

(1) (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1882. (b) Fischer, R. A.; Weiss, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2830. (c) Linti, G.; Schnockel, H. *Coord. Chem. Rev.* **2000**, *206*, 285. (d) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.

(2) (a) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511. (b) Uhl, W.; Benter, M.; Melle, S.; Saak, W. *Organometallics* **1999**, *18*, 3778.

(3) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571.

(4) Ueno, K.; Watanabe, T.; Ogino, H. *Appl. Organomet. Chem.* **2003**, *17*, 403.

(5) **5**: ^1H NMR (300 MHz, THF-d_8) δ 1.91 (s, 15H, C_5Me_5); ^{13}C NMR (75.5 MHz, THF-d_8) δ 10.2 ($C_5\mathit{Me}_5$), 94.6 (C_5Me_5), 217.2 (CO), 220.5 (CO); IR (KBr) ν_{CO} 1890, 1911, 1928, 1967, 1982, 1994 cm^{-1}.

(6) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305.

10.1021/om034073d CCC: $25.00

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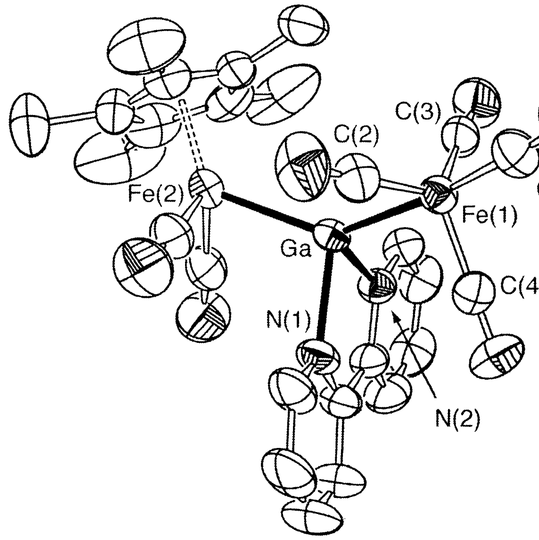


Figure 1. ORTEP drawing of **7** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ga−Fe(1) = 2.4026(5), Ga−Fe(2) = 2.4221(5), Ga−N(1) = 2.121(2), Ga−N(2) = 2.128(2), Fe(1)−C(1) = 1.766(4), Fe(1)−C(2) = 1.774(4), Fe(1)−C(3) = 1.757(3), Fe(1)−C(4) = 1.765(3); Fe(1)−Ga−Fe(2) = 136.676(19), N(1)−Ga−N(2) = 76.05(10).

Ga−Fe(2) angle of 136.676(19)°.[10] The Fe(1)−Ga bond length (2.4026(5) Å) is much longer than the corresponding bond lengths of **2** (2.2248(7) Å) and **6** (2.2731(4) Å) and is within the range of those of the base-stabilized gallyleneiron complexes $(OC)_4Fe{-}GaR(L_2)$ (2.32−2.42 Å).[7] The Fe(2)−Ga bond (2.4221(5) Å) is also within the range of usual Fe−Ga single bonds (2.36−2.46 Å).[1b] These structural features indicate that the unsaturated bonding character between the iron and gallium atoms is negligible.

Attempts to remove chloride from the gallium atom in complex **5** without coordination of bases always led to decomposition. This suggests that it is essential to stabilize the complex electronically by increasing back-donation from the metal center to the unsaturated gallium atom using electron-rich metal fragments. It seems to be also essential to protect sterically the two-coordinate gallium center with bulky metal fragments. Indeed, reaction of the dppe-substituted (dichlorogallyl)iron complex $Cp^*Fe(dppe)GaCl_2$ (**8**) with $K_2[Fe(CO)_4]$ (**4**) in THF afforded the first dinuclear complex bridged by a substituent-free gallium atom, $Cp^*Fe(dppe)(\mu\text{-}Ga)Fe(CO)_4$ (**1**), where dppe denotes bis(diphenylphosphino)ethane (eq 3).[11] Among group 13 elements, only dinuclear complexes containing substituent-free thallium atom have been reported.[12] Complex **1** was isolated as orange crystals in 77% yield and fully characterized by NMR, IR, and mass spectroscopy, elemental analysis, and crystal structure analysis.

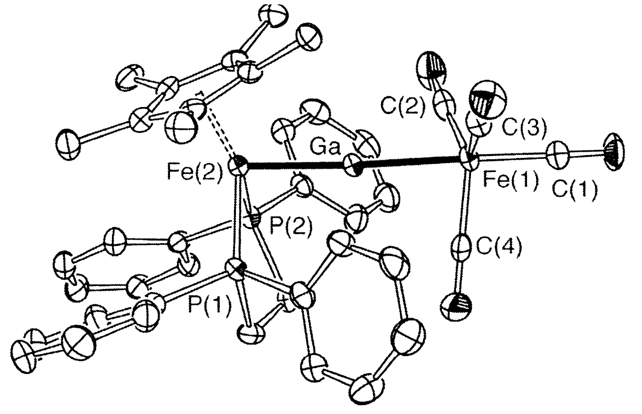
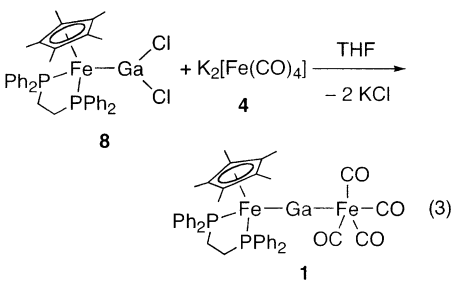


Figure 2. ORTEP drawing of **1** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ga−Fe(1) = 2.2931(10), Ga−Fe(2) = 2.2479(10), Fe(1)−C(1) = 1.792(6), Fe(1)−C(2) = 1.783(8), Fe(1)−C(3) = 1.769(7), Fe(1)−C(4) = 1.769(7); Fe(1)−Ga−Fe(2) = 176.01(4).



An X-ray crystal structure analysis of **1** revealed that the two-coordinate gallium atom is effectively covered by two phenyl groups of the dppe ligand and the Cp* ligand on Fe(2) (Figure 2).[13] The geometry around the gallium atom is essentially linear (176.01(4)°), indicating sp hybridization of the gallium atom. The Fe(2)−Ga bond (2.2479(10) Å) is markedly shorter than those of complex **7** and usual Fe−Ga single bonds (2.36−2.46

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(7) (a) Folsing, H.; Segnitz, O.; Bossek, U.; Merz, K.; Winter, M.; Fischer, R. A. *J. Organomet. Chem.* **2000**, *606*, 132. (b) Fischer, R. A.; Schulte, M. M.; Weiss, J.; Zsolnai, L.; Jacobi, A.; Huttner, G.; Frenking, G.; Boehme, C.; Vyboishchikov, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 1237. (c) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667. (d) Reger, D. L.; Graza, D. G.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3624.

(8) **7**: ^1H NMR (300 MHz, C_6D_6) δ 1.79 (s, 15H, C_5Me_5), 6.45 (m, 2H, bpy), 6.80 (m, 2H, bpy), 7.04 (m, 2H, bpy), 8.95 (m, 2H, bpy); ^{13}C NMR (75.5 MHz, THF-d_8) δ 10.6 (C_5*Me*$_5$), 96.1 (*C*$_5$Me$_5$), 123.3, 127.3, 142.1, 147.8, 148.0 (bpy), 220.9 (CO); IR (KBr) ν_{CO} 1858, 1901, 1951, 1982 cm^{-1}. Anal. Calcd for $C_{26}H_{23}Fe_2GaN_2O_6$: C, 48.73; H, 3.62; N, 4.37. Found: C, 48.53; H, 3.78; N, 4.33.

(9) Ueno, K.; Watanabe, T.; Ogino, H. *Organometallics* **2000**, *19*, 5679.

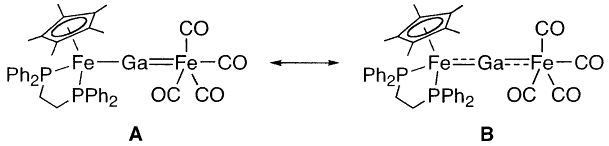
(10) Crystallographic data for **7**: formula $C_{26}H_{23}Fe_2GaN_2O_6$, fw = 640.88, monoclinic, space group $P2_1/a$, $a = 14.8574(6)$ Å, $b = 10.9612(4)$ Å, $c = 17.2178(5)$ Å, $\beta = 107.7229(12)°$, $V = 2670.93(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.594$ g cm^{-3}, $\mu = 2.166$ mm^{-1}, $F(000) = 1296$, θ range 1.24−27.41°, 339 variables refined with 5158 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0418 and wR2 = 0.1093 with GOF = 1.099.

(11) **1**: ^1H NMR (300 MHz, C_6D_6) δ 1.43 (s, 15H, C_5Me_5), 1.97 (m, 2H, PCH_2), 2.39 (m, 2H, PCH_2), 6.96−7.19 (m, 12H, PPh), 7.41 (m, 4H, PPh), 7.79 (m, 4H, PPh); ^{13}C NMR (75.5 MHz, THF-d_8) δ 10.7 (C_5*Me*$_5$), 33.0 (PCH_2), 86.9 (*C*$_5$Me$_5$), 128.4, 129.5, 130.3, 130.5, 132.8, 134.1, 139.1, 140.5 (PPh), 218.7 (CO); ^{31}P NMR (121.5 MHz, C_6D_6) δ 92.9 ppm (dppe); IR (KBr) ν_{CO} 1878, 1890, 1923, 1998 cm^{-1}. Anal. Calcd for $C_{40}H_{39}Fe_2GaO_4P_2$: C, 58.09; H, 4.75. Found: C, 58.28; H, 4.89.

(12) (a) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 4123. (b) Schiemenz, B.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1772.

(13) Crystallographic data for **1**: formula $C_{40}H_{39}Fe_2GaO_4P_2$, fw = 827.07, monoclinic, space group $P2_1/c$, $a = 17.4600(12)$ Å, $b = 10.3435(7)$ Å, $c = 20.7597(19)$ Å, $\beta = 101.494(3)°$, $V = 3674.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.495$ g cm^{-3}, $\mu = 1.635$ mm^{-1}, $F(000) = 1696$, θ range 1.19−27.48°, 447 variables refined with 7807 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0725 and wR2 = 0.1722, with GOF = 1.166.

Scheme 1



Å).[1b] The Fe(1)−Ga bond (2.2931(10) Å) is also significantly shorter than the corresponding bonds of the base-stabilized gallyleneiron complexes (2.32−2.42 Å)[7] and slightly longer than those of the terminal gallyleneiron complex **2** (2.2248(7) Å)[2a] and the Cp*Ga iron complex **6** (2.2731(4) Å).[6] These structural features indicate that both Fe−Ga bonds in **1** bear significantly unsaturated character.

According to the 18-electron rule, **1** can be depicted as **A** in Scheme 1. However, the Fe(2)−Ga bond is shorter than the usual single bond and, surprisingly, even shorter than the Fe(1)−Ga bond. Thus, contribution of the canonical form **B** is dominant for complex **1**. The remarkable shortening of the Fe(2)−Ga bond is attributable to the strong π-basic character of the Cp*(dppe)Fe fragment compared to the $Fe(CO)_4$ fragment. The strong π-back-donation from the Cp*(dppe)-Fe fragment to the empty p orbitals of the Ga atom competes and, consequently, reduces the back-donation from $Fe(CO)_4$ to the Ga atom. This causes the elongation of the Ga−$Fe(CO)_4$ bond in **1** compared to that of **2** and **6**. The increasing order of the Ga−$Fe(CO)_4$ bond distances (**2** < **6** < **1**) indicates that the π-basicity of the substituent on the gallium atom increases in the order Ar* < Cp* < Cp*$(CO)_2$Fe. The strong π-donation from the Cp*$Fe(CO)_2$ fragment to the Ga atom also increases the electron density of the Ga atom and increases the σ-donor ability of the Ga fragment to the $Fe(CO)_4$ fragment. Indeed, the trans influence of the Cp*Fe(dppe)Ga fragment toward the $Fe(CO)_4$ fragment is larger than that of Ar*Ga in **2** and Cp*Ga in **6**. The Fe(1)−C(1) bond (1.792(6) Å) trans to the Ga atom in **1** is longer than the corresponding bonds of **2** (1.766(5) Å)[2a] and **6** (1.781(2) Å).[6] These data demonstrate the weak back-donation from $Fe(CO)_4$ fragment to the Ga atom in **1** and support the occurrence of strong back-donation from the Cp*(dppe)Fe fragment to the Ga atom. Our result clearly shows the importance of π-back-bonding in the metal−gallium bonding.

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Supporting Information Available: Text giving complete experimental details, including synthesis and characterization data of all new compounds, and tables giving crystal structure data; crystal structure data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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