Organometallics **2000,** *19,* 5679−5682

Synthesis of Cationic Diiron Complexes Bridged by a Base-Stabilized Gallium Atom $[Fp_2(\mu\text{-}Ga\cdot Do_2)]^+X^-$ (Fp = $(\eta\text{-}C_5H_5)Fe(CO)_2$, Do_2 = 2,2′-Bipyridine, *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine, 1,10-Phenanthroline, (4-(Dimethylamino)pyridine)$_2$, X^- = $[Fp_2GaCl_2]^-$, BPh_4^-)

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Addition of 2,2′-bipyridine (bpy) to an acetonitrile solution of Fp_2GaCl (**1**: Fp = CpFe(CO)$_2$; Cp = η-C_5H_5) afforded quantitatively a salt consisting of a diiron cation bridged by a Ga·bpy fragment $[Fp_2(\mu\text{-}Ga\cdot bpy)]^+$ ([**2a**]$^+$) and a μ-$GaCl_2$ diiron anion $[Fp_2(\mu\text{-}GaCl_2)]^-$ ([**3**]$^-$). The reaction of **1** with Do_2 (Do_2 = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), 1,10-phenanthroline (phen), and (4-(dimethylamino)pyridine)$_2$ (= dmap$_2$)) in the presence of 1 equiv of $NaBPh_4$ in acetonitrile afforded $[Fp_2(\mu\text{-}Ga\cdot Do_2)]^+BPh_4^-$ (Do_2 = tmeda (**2b**), phen (**2c**), and (dmap)$_2$ (**2d**)). Cation [**2a**−**d**]$^+$ is the first example of a dinuclear complex bridged by a base-coordinated gallium atom Ga·Do_2 (Do = Lewis base). X-ray crystal structure analysis of [**2a**][**3**]·CH_3CN revealed that the Fe−Ga bond lengths (2.3969(16) and 2.4037(14) Å) in [**2a**]$^+$ are shorter than those of [**3**]$^-$ (2.4234(13) and 2.4359(15) Å), but within the range previously observed for Fp−gallyl complexes (2.36−2.46 Å). The Ga−Cl bonds in [**3**]$^-$ (2.3259(19) and 2.3537(19) Å) are longer than those of known chlorogallyl complexes (2.18−2.29 Å).

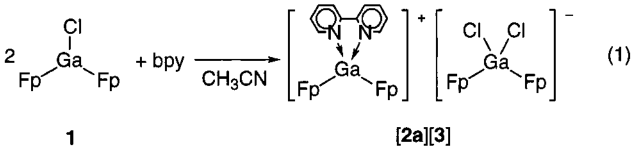
Introduction

Chemistry of the transition metal complex with metal−gallium bonding is an actively investigated field.[1] The isolation of a terminal gallylene (gallanediyl) complex L_nMGaR (L_nM = metal fragment) is of particular interest. Terminal gallylene complexes have been isolated by stabilizing the unsaturated gallium center using a bulky substituent R or by introducing Lewis bases on the gallium atom $L_nMGaR\cdot Do_2$ (Do = Lewis base).[2]

Dinuclear complexes bridged by a "naked" gallium atom $[L_nM]_2(\mu\text{-}Ga)$ (**A**) are an interesting synthetic target. However, complexes of type **A** as well as their base-stabilized form $[L_nM]_2(\mu\text{-}Ga\cdot Do_2)$ (**B**) in which the electron-deficient Ga atom is stabilized by coordination of Lewis base molecule(s) have hitherto defied isolation, though analogous complexes of type **A** have been known for thallium[3] and those of type **B**, for thallium[4] and indium.[5] We report here the first example of dinuclear complexes of type **B**, namely, $[Fp_2(\mu\text{-}Ga\cdot Do_2)]^+$ (Fp = CpFe(CO)$_2$, Do_2 = 2,2′-bipyridine (bpy), *N*,*N*,*N*′*N*′-tetramethylethylenediamine (tmeda), 1,10-phenanthroline (phen), (4-(dimethylamino)pyridine)$_2$ (= dmap$_2$)).

Results and Discussion

Reaction of Fp_2GaCl (**1**: Fp = CpFe(CO)$_2$) with $AgPF_6$ in acetonitrile gave a complex mixture that contained AgCl. This suggests that a diiron complex bridged by a gallium atom, even if it formed, is unstable under the reaction conditions. Surprisingly, the addition of bpy to an acetonitrile solution of **1** afforded quantitatively a salt consisting of a cationic diiron complex bridged by a μ-Ga·bpy fragment [**2a**]$^+$ and an anionic μ-$GaCl_2$ diiron complex [**3**]$^-$ (eq 1). The product was isolated as orange crystals [**2a**][**3**]·CH_3CN in 86% yield and fully characterized by NMR, IR, and mass spectroscopy, elemental



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[1] Fischer, R. A.; Weiss, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2830.

[2] (a) Schulte, M. M.; Herdtweck, E.; Raudaschl-Sieber, G.; Fischer, R. A. *Angew. Chem.* **1996**, *108*, 489; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 424. (b) Harakas, G. N.; Whittlesey, B. R. *Inorg. Chem.* **1997**, *36*, 2704. (c) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511. (d) 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. (e) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305. (f) Jutzi, P.; Neumann, B.; Schebaum, L. O.; Stammler, A.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4462. (g) Uhl, W.; Benter, M.; Melle, S.; Saak, W.; Frenking, G.; Uddin, J. *Organometallics* **1999**, *18*, 3778.

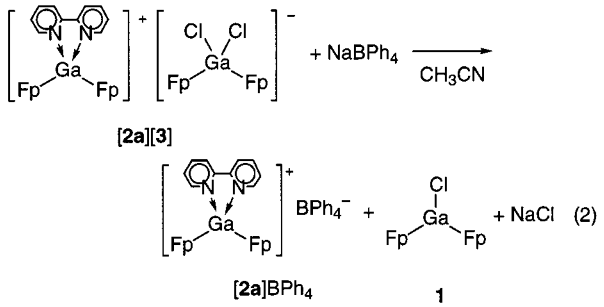
[3] Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4123. Schiemenz, B.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1772.

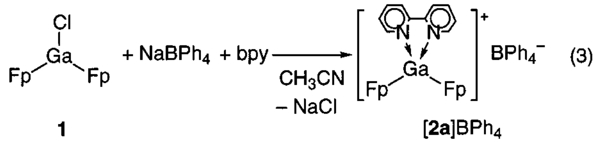
[4] Cassidy, J. M.; Whitmire, K. H. *Inorg. Chem.* **1989**, *28*, 1435.

[5] Cassidy, J. M.; Whitmire, K. H. *Acta Crystallogr.* **1990**, *C46*, 1781.

10.1021/om000673q CCC: $19.00

analysis, and crystal structure analysis (vide infra). The reaction shown in eq 1 corresponds to a disproportionation reaction induced by coordination of a bpy molecule. To our knowledge, base-induced disproportionation of transition-metal-substituted halogallanes has not been reported so far, although such reactions of organohalogallanes were reported almost 70 years ago.[6,7] In the disproportionation reaction, complex **1** behaves not only as a Cl^- donor but also as an acceptor. Reaction of **1** with an excess of bpy did not afford [**2a**]Cl but gave [**2a**][**3**] quantitatively. The [**2a**][**3**] salt reacts in CH_3CN with $NaBPh_4$ to give [**2a**]BPh_4 quantitatively, together with **1** and NaCl (eq 2). This synthesis of [**2a**]BPh_4 can be carried out directly starting with **1**, bpy, and $NaBPh_4$ in 59% yield (eq 3).





Diiron complexes bridged by a Ga·Do_2 fragment bearing various donors (Do_2 = tmeda (**2b**), phen (**2c**), and $(dmap)_2$ (**2d**)) can also be synthesized in moderate yields by the reaction of **1** with $NaBPh_4$ in the presence of bidentate donors, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and 1,10-phenanthroline, as well as a monodentate donor, 4-(dimethylamino)pyridine. The chelating effect is therefore not essential for the formation of a Ga·Do_2 bridged diiron complex.

X-ray crystal structure analysis of [**2a**][**3**]·CH_3CN revealed that the gallium centers in cation [**2a**]$^+$ and anion [**3**]$^-$ adopt highly distorted tetrahedral geometry (Figure 1, Table 1). The Fe–Ga–Fe angles for [**2a**]$^+$ and [**3**]$^-$ are 132.81(5)° and 127.81(4)°, respectively. The Fe–Ga bond lengths (2.3969(16) and 2.4037(14) Å) in [**2a**]$^+$ are shorter than those in [**3**]$^-$ (2.4234(13) and 2.4359(15) Å), but within the range previously observed for Fp–gallyl complexes (2.36–2.46 Å).[1] The Ga–N bond lengths in [**2a**]$^+$ (2.074(5) and 2.091(5) Å) are close to the lower limit of those of the reported amino-coordinated gallylmetal complexes (1.97–2.40 Å),[8,9] which suggests strong coordination of the bpy molecule to the gallium atom. The Ga–Cl bonds in [**3**]$^-$ (2.3251(19) and 2.3537(19) Å) are longer than those of known chlorogallyl complexes (2.18–2.29 Å).[9,10] This shows that the bonding between Ga and Cl in [**3**]$^-$ is weaker than the usual Ga–Cl single bond.

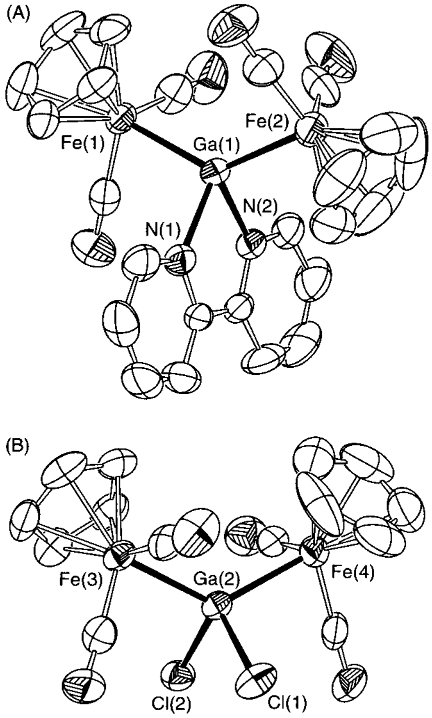


Figure 1. ORTEP drawing of [**2a**][**3**]·CH_3CN. Thermal ellipsoids are depicted at 50% probability level. A and B represent the cationic ([**2a**]$^+$) and the anionic fragments ([**3**]$^-$), respectively.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for [2a][3]·CH_3CN

Ga(1)–N(2)	2.074(5)	Ga(1)–N(1)	2.091(5)
Ga(1)–Fe(2)	2.3969(16)	Ga(1)–Fe(1)	2.4037(14)
Ga(2)–Cl(1)	2.3251(19)	Ga(2)–Cl(2)	2.3537(19)
Ga(2)–Fe(3)	2.4234(13)	Ga(2)–Fe(4)	2.4359(15)
N(2)–Ga(1)–N(1)	77.4(2)	N(2)–Ga(1)–Fe(2)	104.81(14)
N(1)–Ga(1)–Fe(2)	112.16(15)	N(2)–Ga(1)–Fe(1)	108.84(15)
N(1)–Ga(1)–Fe(1)	106.78(14)	Fe(2)–Ga(1)–Fe(1)	132.81(5)
Cl(1)–Ga(2)–Cl(2)	100.04(7)	Cl(1)–Ga(2)–Fe(3)	108.00(6)
Cl(2)–Ga(2)–Fe(3)	105.29(6)	Cl(1)–Ga(2)–Fe(4)	105.02(7)
Cl(2)–Ga(2)–Fe(4)	107.37(6)	Fe(3)–Ga(2)–Fe(4)	127.81(4)

The ^1H NMR spectrum of complex [**2a**]$^+$ shows the Cp signal at δ 4.98 ppm, which is comparable with that of **1** (δ 4.87 ppm). This suggests that the positive charge in [**2a**]$^+$ is mainly localized on the gallium fragment rather than the iron fragments. This is also supported by the fact that the ν_{CO} frequencies of [**2a**]BPh_4 (1986, 1967, and 1926 cm^{-1} in Nujol) are comparable to those of $Fp_2(\mu\text{-}GaBu^t)$ (ν_{CO} 1978, 1967, 1927, and 1915 cm^{-1} in Nujol);[11] that is, the electron density on the iron fragments in cationic complex [**2a**]$^+$ is comparable with that in the neutral gallylene-bridged complex $Fp_2(\mu\text{-}GaBu^t)$. Therefore, complex [**2a**]$^+$ can be regarded as a result of the interaction between two neutral 17 VE Fp fragments and a cationic base-coordinated gallium atom, Ga·bpy$^+$.

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(6) Kraus, C. A.; Toonder, F. E. *Proc. Natl. Acad. Sci., U.S.A.* **1933**, *19*, 292.

(7) Shriver, D. F.; Parry, R. W. *Inorg. Chem.* **1962**, *1*, 835.

(8) Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9*, 2763. Fischer, R. A.; Behm, J.; Priermeier, T. *J. Organomet. Chem.* **1992**, *429*, 275. Fischer, R. A.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *459*, 65. Olazábal, C. A.; Gabbai, F. P.; Cowley, A. H.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *Organometallics* **1994**, *13*, 421.

(9) Fischer, R. A.; Miehr, A.; Priermeier, T. *Chem. Ber.* **1995**, *128*, 831.

(10) Fischer, R. A.; Behm, J.; Priermeier, T.; Scherer, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 746.

(11) He, X.; Bartlett, R. A.; Power, P. P. *Organometallics* **1994**, *13*, 548.

It is noteworthy that the cationic fragment $\mathrm{Ga\cdot Do_2^+}$ is isolobal to the neutral silylene and germylene $\mathrm{E'R_2}$ (E′ = Si, Ge) and the cationic base-coordinated silylyne and germylyne $\mathrm{E'R\cdot Do^+}$. In contrast with complex [**2a**]$^+$ reported here, significantly short Fe−E′ bond lengths have been observed for the cationic diiron complexes bridged by a base-coordinated silylyne and germylyne ligand $\{\mathrm{[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}E'R\cdot Do)}\}^+$.[12] This shortening of the Fe−E′ bonds would be attributable to the partial double bond character in the Fe−E′ bonding which is derived from the back-donation of electron in a filled Fe d orbital toward the E′−Do σ* orbital, based on the interpretation reported for the base-stabilized terminal silylene complexes $\mathrm{L}_n\mathrm{M{=}SiR_2\cdot Do}$.[13] For the gallium complex, however, the σ* Ga−Do orbitals lie too high to interact efficiently with the filled d orbital of the iron atom. Therefore, double bond character is insignificant in complex [**2**]$^+$.[14,15]

Experimental Section

General Procedures. All manipulations were performed using either standard Schlenk tube techniques under nitrogen or argon atmosphere, vacuum line techniques, or a drybox under a nitrogen atmosphere. Toluene was dried by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere. Acetonitrile and acetonitrile-d_3 were dried over $\mathrm{CaH_2}$ and distilled prior to use. 2,2′-Bipyridine (bpy), 1,10-phenanthroline (phen), and 4-(dimethylamino)pyridine were purified by recrystallization from a hexane or toluene solution. *N,N,N′,N′*-Tetramethylethylenediamine was distilled from KOH prior to use. $\mathrm{Fp_2GaCl}$ were prepared by the literature procedure.[16] NMR spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer at room temperature unless otherwise noted. IR spectra were obtained on a HORIBA FT-200 spectrometer at room temperature. Mass spectra were recorded on a JEOL HX-110 spectrometer at the Instrumental Analysis Center for Chemistry, Tohoku University. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Tohoku University.

Synthesis of [Fp$_2$(μ-Ga·bpy)][Fp$_2$(μ-GaCl$_2$)] ([2a][3]). An acetonitrile (5 mL) solution of 2,2′-bipyridine (0.035 g, 0.22 mmol) was added to $\mathrm{Fp_2GaCl}$ (0.20 g, 0.44 mmol) in acetonitrile (10 mL) at room temperature with vigorous stirring. The solvent was removed from the reaction mixture under reduced pressure. The residual solid was washed with toluene (5 mL) and dried under reduced pressure to give orange crystals of [**2a**][**3**]·$\mathrm{CH_3CN}$. Yield: 0.21 g (0.19 mmol, 86%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ/ppm 4.80 (s, 10H, $\mathrm{C_5}H_5$), 4.98 (s, 10H, $\mathrm{C_5}H_5$), 7.93 (m, 2H, bpy), 8.43 (m, 2H, bpy), 8.68 (m, 2H, bpy), 8.87 (m, 2H, bpy). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ/ppm 83.8 ($C_5\mathrm{H_5}$), 84.0 ($C_5\mathrm{H_5}$), 124.6, 128.9, 143.8, 147.8 (bpy), 216.6 (CO), 219.2 (CO). IR (acetonitrile solution): ν_{CO} 1925, 1961, 1973 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m/z* 579 ([Fp$_2$Ga(bpy)]$^+$, 100), 423([Fp$_2$Ga]$^+$, 65), 225 (Ga(bpy)$^+$, 65). Anal. Calcd for $\mathrm{C_{40}H_{31}Cl_2Fe_4Ga_2N_3O_8}$: C, 43.07; H, 2.80; N, 3.77. Found: C,43.19; H, 2.80; N, 3.85.

Synthesis of [Fp$_2$(μ-Ga·bpy)]BPh$_4$ ([2a]BPh$_4$). An acetonitrile (2 mL) solution of 2,2′-bipyridine (0.068 g, 0.44 mmol) was added to $\mathrm{Fp_2GaCl}$ (0.20 g, 0.44 mmol) in acetonitrile (5 mL) at room temperature. A solution of $\mathrm{NaBPh_4}$ (0.149 g, 0.44 mmol) in acetonitrile (2 mL) was added to the mixture. The solution was stirred for 10 min at room temperature and was filtered. The filtrate was concentrated to 5 mL and cooled to −30 °C to give red crystals of [**2a**]BPh$_4$. Yield: 0.23 g (0.26 mmol, 59%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ/ppm 4.98 (s, 10H, $\mathrm{C_5}H_5$), 6.85 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 4H, BPh), 7.00 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 8H, BPh), 7.30 (m, 8H, BPh), 7.90 (m, 2H, bpy), 8.40 (m, 2H, bpy), 8.62 (m, 2H, bpy), 8.85 (m, 2H, bpy). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ/ppm 84.1 ($C_5\mathrm{H_5}$), 122.7, 126.6, 136.7 (BPh$_4$), 124.4, 128.8, 143.6, 147.6, 147.9 (bpy), 216.7 (CO). IR (acetonitrile solution): ν_{CO} 1927, 1973, 1988 cm^{-1}; (Nujol) ν_{CO} 1926, 1967, 1986 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m/z* 579 ([Fp$_2$Ga(bpy)]$^+$, 100), 423([Fp$_2$Ga]$^+$, 46). Anal. Calcd for $\mathrm{C_{48}H_{38}BFe_2GaN_2O_4}$: C, 64.13; H, 4.26; N, 3.12. Found: C, 64.17; H, 4.28; N, 3.13.

Synthesis of [Fp$_2$(μ-Ga·tmeda)]$^+$BPh$_4^-$ ([2b]BPh$_4$). [**2b**]BPh$_4$ was obtained as orange crystals by a procedure similar to that of [**2a**]BPh$_4$ using *N,N,N′,N′*-tetramethylethylenediamine (0.078 g, 0.67 mmol), $\mathrm{NaBPh_4}$ (0.150 g, 0.44 mmol), and $\mathrm{Fp_2GaCl}$ (0.20 g, 0.44 mmol). Yield: 0.12 g (0.14 mmol, 31%). ^{1}H NMR (300 MHz, acetonitrile-d_3, rt): δ/ppm 2.74 (s, 12H, $\mathrm{NCH_3}$), 3.02 (br, 4H, $\mathrm{CH_2}$), 5.07 (s, 10H, $\mathrm{C_5}H_5$), 6.85 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 4H, BPh), 7.01 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 8H, BPh), 7.28 (m, 8H, BPh). ^{1}H NMR (300 MHz, acetonitrile-d_3, 240 K): δ/ppm 2.65 (s, 6H, $\mathrm{NCH_3}$), 2.73 (s, 6H, $\mathrm{NCH_3}$), 2.79 (d, $^3J_{\mathrm{HH}}$ = 10.7 Hz, 2H, $\mathrm{CH_2}$), 3.23 (d, $^3J_{\mathrm{HH}}$ = 10.7 Hz, 2H, $\mathrm{CH_2}$), 5.05 (s, 10H, $\mathrm{C_5H_5}$), 6.84 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 4H, BPh), 7.01 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 8H, BPh), 7.27 (m, 8H, BPh). ^{13}C NMR (75.5 MHz, acetonitrile-d_3, rt): δ/ppm 50.4 ($\mathrm{NCH_3}$), 58.5 ($\mathrm{CH_2}$), 85.6 ($\mathrm{C_5H_5}$), 122.7, 126.6, 136.7, 164.7 (BPh$_4$). ^{13}C NMR (75.5 MHz, acetonitorile-d_3, 240 K): δ/ppm 49.8, 50.7($\mathrm{NCH_3}$), 58.3($\mathrm{CH_2}$), 85.6 ($\mathrm{C_5H_5}$), 122.9, 126.9, 136.5, 164.8 (BPh$_4$), 217.4, 220.7 (CO). IR (KBr pellet): ν_{CO} 1907, 1927, 1957, 1973 cm^{-1}. Anal. Calcd for $\mathrm{C_{44}H_{46}BFe_2GaN_2O_4}$: C, 61.52; H, 5.40; N, 3.26. Found: C, 61.67; H, 5.34; N, 3.21. Mass spectrum shows only the signals assignable to tmeda and its fragments, probably due to the thermal instability of complex [**2b**]$^+$.

Synthesis of [Fp$_2$(μ-Ga·phen)]BPh$_4$ ([2c]BPh$_4$). [**2c**]BPh$_4$ was synthesized by a procedure similar to that of [**2a**]BPh$_4$ using 1,10-phenanthroline (0.080 g 0.44 mmol), $\mathrm{NaBPh_4}$ (0.150 g, 0.44 mmol), and $\mathrm{Fp_2GaCl}$ (0.20 g, 0.44 mmol). The title compound was obtained as red crystals of [Fp$_2$Ga(phen)]BPh$_4$·$\mathrm{CH_3CN}$. Yield: 0.27 g (0.28 mmol, 64%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ/ppm 5.00 (s, 10H, $\mathrm{C_5H_5}$), 6.85 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 4H, BPh), 7.00 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 8H, BPh), 7.28 (m, 8H, BPh), 8.18 (m, 2H, phen), 8.31 (s, 2H, phen), 8.94 (m, 2H, phen), 9.26 (m, 2H, phen). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ/ppm 84.0 ($\mathrm{C_5H_5}$), 122.7, 126.6, 136.7 (BPh$_4$), 127.2, 128.9, 130.9, 142.1, 148.8 (phen), 216.6 (CO). IR (acetonitrile solution): ν_{CO} 1927, 1973, 1988 cm^{-1}. MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m/z* 603 ([Fp$_2$Ga(phen)]$^+$, 67), 423 (Fp$_2$Ga$^+$, 16), 416 (Fe(phen)$_2^+$, 100), 249 (Ga(phen)$^+$, 44). Anal. Calcd for $\mathrm{C_{52}H_{41}BFe_2GaN_3O_4}$: C, 64.78; H, 4.29; N, 4.36. Found: C, 64.90; H, 4.28; N, 4.62.

Synthesis of [Fp$_2$(μ-Ga·(dmap)$_2$)]BPh$_4$ ([2d]BPh$_4$). [**2d**]BPh$_4$ was obtained as orange crystals by a procedure similar to that of [**2a**]BPh$_4$ using 4-(dimethylamino)pyridine (0.065 g 0.53 mmol), NaBPh4 (0.090 g, 0.26 mmol), and $\mathrm{Fp_2GaCl}$ (0.12 g, 0.26 mmol). Yield: 0.160 g (0.162 mmol, 62%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ/ppm 3.08 (s, 12H, $\mathrm{NCH_3}$), 4.83 (s, 10H,

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[12] Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843. Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575. Kawano, Y.; Sugawara, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1994**, *1994*, 293.

[13] Ueno, K.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *430*, 93. Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224. Braunstein, P.; Knorr, M.; Stern, C. *Coord. Chem. Rev.* **1998**, *178−180*, 903.

[14] The nature of metal−gallium unsaturated bonding in the terminal gallylene complex $\mathrm{L}_n\mathrm{MGaR}$ has been investigated extensively since the isolation of a gallyleneiron complex by Robinson et al.[2c] Recent theoretical studies indicated that the bonding is constructed mainly by the donation of lone pair electrons on the Ga center of the GaR ligand to an empty d orbital of the metal atom, i.e., $\mathrm{L}_n\mathrm{M}\leftarrow\mathrm{GaR}$, and the extent of the π-back-donation from the metal to Ga is relatively small mainly due to the high energy level of the 4p orbitals of the gallium atom.[15]

[15] Cotton, F. A.; Feng, X. *Organometallics* **1998**, *17*, 128. Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12213. Boehme, C.; Frenking, G. *Chem. Eur. J.* **1999**, *5*, 2184. Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571.

[16] Campbell, R. M.; Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Pickett, N. L.; Norman, N. C. *Chem. Ber.* **1992**, *125*, 55. Borovik, A. S.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 2668.

Table 2. Crystal Data and Structure Refinement for [2a][3]·CH_3CN

empirical formula	$C_{40}H_{31}Cl_2Fe_4Ga_2N_3O_8$
fw	1115.42
temp	293(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 13.816(6)$ Å, $\alpha = 93.54(3)°$ $b = 14.931(4)$ Å, $\beta = 99.38(4)°$ $c = 10.731(5)$ Å, $\gamma = 78.16(3)°$
volume	2136.7(15) $Å^3$
Z	2
density (calcd)	1.734 g/cm^3
abs coeff	2.744 mm^{-1}
$F(000)$	1112
cryst size	0.40 × 0.35 × 0.15 mm
θ range for data collection	1.52−27.50°
index ranges	$-17 \leq h \leq 0$, $-19 \leq k \leq 18$, $-13 \leq l \leq 13$
no. of reflns collected	10199
no. of ind reflns	9796 [R(int) = 0.0362]
no. of reflns with $I > 2\sigma(I)$	5299
completeness to $\theta = 27.50$	99.9%
abs corr	ψ-scan
max. and min. transm	0.9998 and 0.5406
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	9796/0/533
goodness-of-fit on F^2	1.011
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0506, wR2 = 0.1098
R indices[a] (all data)	R1 = 0.1330, wR2 = 0.1349
largest diff peak and hole	0.687 and −0.661 e $Å^{-3}$

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$, calc $w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.

C_5H_5), 6.74 (d, $^3J_{HH} = 6.5$ Hz, 4H, DMAP), 6.86 (d, $^3J_{HH} = 7.3$ Hz, 4H, BPh), 7.00 (t, $^3J_{HH} = 7.3$ Hz, 8H, BPh), 7.27 (m, 8H, BPh), 8.01 (d, $^3J_{HH} = 6.5$ Hz, 4H, DMAP). ^{13}C NMR (75.5 MHz, acetonitrile-d_3): δ/ppm 39.7 (NCH_3), 84.1 (C_5H_5), 108.0 (DMAP), 122.7, 126.5, 136.7, 164.4 (BPh_4), 146.9 (DMAP), 218.5 (CO). IR (KBr pellet): ν_{CO} 1909, 1959 cm^{-1}. Anal. Calcd for $C_{52}H_{50}BFe_2GaN_4O_4$: C, 63.27; H, 5.11; N, 5.68. Found: C, 63.37; H, 4.91; N, 5.79. Mass spectrum shows only signals assignable to dmap and its fragments, probably due to the thermal instability of complex [**2d**]$^+$.

X-ray Crystal Structure Determination of [2a][3]·CH_3CN. A single crystal of [**2a**][**3**]·CH_3CN was sealed in a glass capillary under an atmosphere of dry nitrogen. The intensity data for X-ray crystal structure analysis were collected on a RIGAKU AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation at 293 K. These data were corrected by Lorentz and polarization effects. Semiempirical absorption corrections were applied on the basis of ψ scans. Crystallographic data for [**2a**][**3**]·CH_3CN are listed in Table 2. The structures were solved by Patterson and Fourier transform methods (SHELXS-97).[17] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections (SHELXL-97).[18] All hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The final residue R1 and the weighted wR2 were R1 = 0.0506 and wR2 = 0.1098 for 5299 refractions with $I > 2\sigma(I)$, where $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. All calculations were performed on an Apple Macintosh computer.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, an ORTEP drawing (PDF), and an X-ray crystallographic file (CIF) for [**2a**][**3**]·CH_3CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

[18] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.