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Toward Cationic Gallane- and Indanediyl Complexes: Synthetic Approaches to Three-Coordinate Halogallyl and -indyl Precursors

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Transition metal complexes containing ligands featuring three-coordinate, halide-functionalized gallium or indium donors represent key precursors to unsaturated cationic species of the type $[L_nM(EX)]^+$ via halide abstraction chemistry. Two routes to these three-coordinate systems have been demonstrated: (i) salt elimination, such as the reaction between Na[Cp*Fe(CO)$_2$] and Mes*GaCl$_2$ or Mes*InBr$_2$ (Mes* = $C_6H_2{}^tBu_3$-2,4,6, supermesityl) to generate Cp*Fe(CO)$_2$E(Mes*)X (**3a**, E = Ga, X = Cl; **5**, E = In, X = Br), and (ii) insertion of a gallium(I) or indium(I) halide into a metal−halogen or metal−metal bond followed, where necessary, by substitution by a sterically bulky anionic nucleophile. Crystallographic studies have confirmed the presence of the target trigonal planar ligand systems both in gallyl/indyl complexes of the type L_nM-E(Aryl)X and in halide-functionalized gallane- and indanediyl systems of the type $(L_nM)_2EX$.

Introduction

The chemistry of low-coordinate or multiply bonded group 13 ligand systems continues to attract considerable research effort,[1−3] due, at least in part, to a desire to resolve fundamental questions of structure and bonding.[4,5] Despite this, a systematic appraisal of both structural and reaction chemistry, e.g., for terminal diyl systems, $L_nM(EX)$ (E = B, Al, Ga, In), lags behind that of analogous group 14 systems (such as carbenes and silylenes),[6] reflecting the relatively small number of authenticated complexes in the literature. To date, such species have predominantly been derived from either salt elimination or ligand substitution chemistries (Scheme 1).[1−3]

Scheme 1. Ligand Substitution and Salt Elimination Routes to Group 13 Diyl Complexes [E = group 13 element; R = bulky substituent (e.g., amino or aryl group); X = halide; L, L′ = generic ligands coordinated to transition metal M]

$$1/n\,(\mathrm{RE})_n + \mathrm{L}_n\mathrm{ML'} \xrightarrow{-\mathrm{L'}} \mathrm{L}_n\mathrm{M(ER)} \xleftarrow{-2\,\mathrm{X}^-} \mathrm{REX}_2 + [\mathrm{L}_n\mathrm{M}]^{2-}$$

Recently we have been successful in developing a halide abstraction methodology for the synthesis of the first base-free *cationic* group 13 diyl systems (Scheme 2).[7,8] The predominant localization of the positive charge at the group 13 center (E) in such complexes has been demonstrated by density functional theory (DFT) and in the case of $[\mathrm{Cp^*Fe(CO)_2(BMes)}]^+$ (**1**, Mes = mesityl, 2,4,6-Me$_3$C$_6$H$_2$), for example, leads to an appreciable M→E π back-bonding component.[7] Thus a bonding description as an Fe═B double bond, comprised of B→Fe σ and Fe→B π contributions has been proposed.[7]

We have been seeking to expand this abstraction methodology to the heavier group 13 elements,[9] with a

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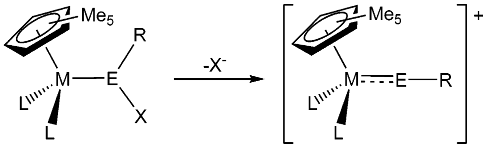
Scheme 2. Halide Abstraction Route to Cationic Transition Metal Complexes Containing Two-Coordinate Group 13 Ligands (E = group 13 element; R = bulky substituent; X = halide; L = generic ligand coordinated to transition metal M)



view to exploring the structural and reaction chemistry of cationic diyl complexes featuring, for example, gallium and indium donors. Central to this approach is ready access to a range of halo-substituted precursors featuring *three-coordinate* gallium or indium centers (Scheme 3). Given the propensity of halogallium and -indium systems in general to augment the coordination number at the group 13 center through bridging halide ligands,[10] it is not surprising that, to date, there have been almost no literature reports of neutral three-coordinate systems of the type $L_nM\text{-}E(X)(E'R'_x)$ (E = Ga, In; X = halide).[9,11,12] From a synthetic standpoint, sterically bulky metal (L_nM) and/or gallyl/indyl substituents ($E'R'_x$) are therefore likely to be key factors in enforcing a trigonal planar ligand geometry.[13]

During the course of this study two parallel approaches to these key halogallyl and -indyl precursors have been examined: (i) direct substitution of a gallium- or indium-bound halide by an organometallic anion[11] and (ii) a two-step process involving initial insertion of a gallium(I) or indium(I) halide into a metal−halogen (or metal−metal) bond,[2a,14,15] followed by substitution at the group 13 center by an appropriately bulky anionic nucleophile. On paper at least, the latter route offers much greater versatility in the nature of the metal fragment (L_nM) by employing a metal halide (or M−M bonded dimer) rather than an organometallic anion as the metal-containing precursor. However, given the likely importance of sterically bulky gallyl/indyl substituents ($E'R'_x$), a significant synthetic challenge lies in the second (substitution) step; previous reports of substitution chemistry at existing group 13 ligand systems (e.g., boryls, gallyls etc.) that proceed with retention of the M−E bond are very rare.[7c,8b]

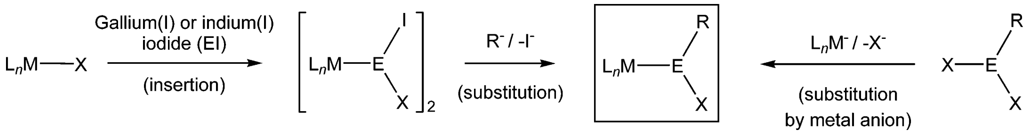
Experimental Section

(i) General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or drybox techniques. Solvents were predried over sodium wire (hexanes, toluene, thf) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation from the appropriate drying agent (hexanes: potassium, toluene; thf: sodium; dichloromethane: CaH_2). Benzene-d_6 and dichloromethane-d_2 (both Goss) were degassed and dried over the appropriate drying agent (potassium or molecular sieves) prior to use. InI, InCl, $InBr_3$, and $GaCl_3$ were used as received without further purification; Li[Mes*] (Mes* = $C_6H_2{}^tBu_3$-2,4,6, supermesityl), Li[tmp] (tmp = $\overline{NCMe_2CH_2CH_2CH_2CMe_2}$ tetramethylpiperamide), Mes*$GaCl_2$, Mes*$InBr_2$, GaI, $CpFe(CO)_2X$ (X = Br, I), $[Cp^*Fe(CO)_2]_2$, and $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ (R = H, Me) were prepared by literature methods.[14a,16−20]

NMR spectra were measured on a Bruker AM-400 or JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual signals of solvent were used for reference for ^1H and ^{13}C NMR spectroscopy. Infrared spectra were measured for each compound either pressed into a disk with excess dry KBr or as a solution in the appropriate solvent, on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Despite repeated attempts, satisfactory elementary microanalysis for new gallium and indium complexes was often frustrated by their extreme air, moisture, and (in some cases) thermal instability. With the exceptions of compounds **6a**, **6b**, **8**, **11**, and **12** (for which satisfactory analyses could be obtained), characterization of the new compounds is therefore based upon multinuclear NMR, IR, and mass spectrometry data (including accurate mass measurement), supplemented by single-crystal X-ray diffraction studies in the cases of **2**, **3a**, and **5**−**16**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95% (see Supporting Information). Abbreviations: b = broad, s = singlet, d = doublet, t = triplet, m = multiplet.

(ii) Syntheses. $(\eta^5\text{-}C_5R_5)Fe(CO)_2Ga(Mes^*)Cl$ (2: R = H; 3a: R = Me). The two compounds were prepared using an identical method, exemplified for **2**. To a solution of $Na[CpFe(CO)_2]$ (0.052 g, 0.26 mmol) in diethyl ether (10 mL) was added a solution of Mes*$GaCl_2$ (0.100 g, 0.26 mmol) in diethyl ether (10 mL), and the reaction mixture was stirred at 20 °C for 12 h. Filtration, concentration of the reaction mixture, and cooling to −50 °C yielded pale yellow crystals suitable for X-ray diffraction. Yields: 0.040 g, 29% (for **2**); 0.100 g, 30% (for **3a**). Characterizing data for **2**: ^1H NMR (300 MHz, CD_2Cl_2): δ 1.25 (s, 9H, para ^{t}Bu), 1.52 (s, 18H, ortho ^{t}Bu), 4.75 (b s, 5H, Cp), 7.34 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 31.0 (CH_3 of para ^{t}Bu), 34.0 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.3 (quaternary of ortho ^{t}Bu), 82.8 (Cp), 119.5 (aryl CH), 142.1 (aryl ipso), 150.1 (aryl para), 154.8 (aryl ortho), 214.6 (CO). IR (KBr): ν(CO) 2004, 1948 cm^{-1}; (C_6D_6) ν(CO) 1996, 1951; (CD_2Cl_2) ν(CO) 1999, 1952. MS (EI): *m/z* 526.1 (weak) $[M]^+$, correct isotope distribution for 1 Fe, 1 Ga, and 1 Cl atom, significant fragment ion peaks at *m/z* 498.1 (5%) $[M - CO]^+$, 470.1 (8%) $[M - 2CO]^+$; exact mass calc for $[M]^+$ 526.0847, found 526.0845. Characterizing data for **3a**: ^1H NMR (300 MHz, CD_2Cl_2): δ 1.27 (s, 9H, para ^{t}Bu), 1.53 (s, 18H, ortho ^{t}Bu), 1.74 (s, 15H, CH_3 of Cp*), 7.33 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.0 (CH_3 of Cp*), 31.0 (CH_3 of para ^{t}Bu), 33.9 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.6 (quaternary of ortho ^{t}Bu), 94.1 (quaternary of Cp*), 122.6 (aryl CH), 151.0 (aryl para), 154.7 (aryl ortho), 212.9 (CO), ipso carbon of Mes* not observed. IR (KBr): ν(CO) 1983, 1931 cm^{-1}. MS (EI): *m/z* 596.1 (3%) $[M]^+$, correct isotope distribution for

Scheme 3. Insertion/Substitution and Direct Metal Anion Substitution Routes to Key Halogallyl and -indyl Precursors (E = group 13 element; R = bulky substituent; X = halide; L generic ligand coordinated to transition metal M)



1 Fe, 1 Ga, and 1 Cl atom, significant fragment ion peaks at *m/z* 568.1 (22%) [M − CO]$^+$, 540.1 (40%) [M − 2CO]$^+$; exact mass calc for [M]$^+$ 596.1630, found 596.1634.

Cp*Fe(CO)$_2$Ga(Mes*)I, 3b. To a solution of [Cp*Fe(CO)$_2$GaI$_2$]$_2$ (**12**, 0.100 g, 0.088 mmol) in diethyl ether (20 mL) was added dropwise a solution of Mes*Li (0.044 g, 0.17 mmol) in diethyl ether (15 mL), and the resulting mixture stirred at 20 °C for 12 h. The reaction mixture was filtered and concentrated; hexane (30 mL) was then added and the solution cooled to −30 °C for 12 h to yield **3b** as a pale yellow powder. Yield: 0.040 g, 33%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.24 (s, 9H, para ^{t}Bu), 1.78 (s, 18H, ortho ^{t}Bu), 1.89 (s, 15H, CH$_3$ of Cp*), 7.10 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 9.4 (CH$_3$ of Cp*), 25.0 (CH$_3$ of para ^{t}Bu), 31.4 (CH$_3$ of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 37.9 (quaternary of ortho ^{t}Bu), 95.2 (quaternary of Cp*), 119.5 (aryl CH), 150.1 (aryl para), 155.6 (aryl ortho), 211.8 (CO), ipso carbon of Mes* not observed. IR (CD$_2$Cl$_2$): ν(CO) 1982, 1932 cm^{-1}. MS (EI): *m/z* 688.1 (weak) [M]$^+$, correct isotope distribution for 1 Fe, 1 Ga, and 1 I atom, significant fragment ion peaks at *m/z* 660.1 (weak) [M − CO]$^+$, 632.1 (10%) [M − 2CO]$^+$; exact mass calc for [M]$^+$ 688.0986, found 688.0999; calc for [M − CO]$^+$ 660.1037, found 660.1043.

(η^5-C$_5$R$_5$)Fe(CO)$_2$In(Mes*)Br (4: R = H; 5: R = Me). The two compounds were prepared using an identical method, exemplified for **4**. To a solution of Na[CpFe(CO)$_2$] (0.183 g, 0.90 mmol) in diethyl ether (5 mL) was added a solution of Mes*InBr$_2$ (0.499 g, 0.96 mmol) in diethyl ether (10 mL), yielding a dark yellow solution and pale white precipitate. The reaction mixture was stirred at 20 °C for 16 h, then filtered to yield a dark yellow solution. Volatiles were then removed in vacuo, yielding a dark yellow solid. The solid was washed with hexane (3 × 10 mL) and dried in vacuo, yielding a yellow powder. Crystalline samples could be obtained by slow diffusion of hexanes into a solution in toluene at −30 °C. Yields: 0.135 g, 22% (for **4**); 0.124 g, 25% (for **5**). Characterizing data for **4**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.25 (s, 9H, para ^{t}Bu), 1.50 (s, 18H, ortho ^{t}Bu), 4.89 (s, 5H, Cp), 7.34 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): 31.1 (CH$_3$ of para ^{t}Bu), 33.5 (CH$_3$ of ortho ^{t}Bu), 34.8 (quaternary of para ^{t}Bu), 37.9 (quaternary of ortho ^{t}Bu), 82.7 (Cp), 122.0 (aryl CH), 150.3 (aryl para), 155.4 (aryl ortho), 213.9 (CO), ipso carbon of Mes* not observed. IR (CD$_2$Cl$_2$): ν(CO) 1996, 1945 cm^{-1}. MS (EI): *m/z* 616.1 (weak) [M]$^+$, correct isotope distribution for 1 Fe, 1 In, and 1 Br atom, significant fragment ions at *m/z* 588.1 (7%) [M − CO]$^+$, 560.1 (5%) [M − 2CO]$^+$, 537.1 (6%) [M − Br]$^+$; exact mass calc for [M − CO]$^+$ 588.0176, found 588.0163. Characterizing data for **5**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.26 (s, 9H, para ^{t}Bu), 1.48 (s, 18H, ortho ^{t}Bu), 1.87 (s, 15H, CH$_3$ of Cp*), 7.28 (s, 2H, aryl CH). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): 9.6 (CH$_3$ of Cp*), 30.3 (CH$_3$ of para ^{t}Bu), 32.8 (CH$_3$ of ortho ^{t}Bu), 33.9 (quaternary of para ^{t}Bu), 37.3 (quaternary of ortho ^{t}Bu), 94.3 (quaternary of Cp*), 121.2 (aryl CH), 150.7 (aryl para), 154.9 (aryl ortho), 215.4 (CO), ipso carbon of Mes* not observed. IR (CD$_2$Cl$_2$): ν(CO) 1977, 1928 cm^{-1}. MS (EI): *m/z* 686.1 (weak) [M]$^+$, correct isotope distribution for 1 Fe, 1 In, and 1 Br atom, significant fragment ions at *m/z* 658.1 (4%) [M − CO]$^+$, 630.1 (7%) [M − 2CO]$^+$, 607.2 (9%) [M − Br]$^+$; exact mass calc for [M]$^+$ 686.0907, found 686.0889.

[Cp*Fe(CO)$_2$]$_2$GaCl, 6a. To a solution/suspension of Na[Cp*Fe(CO)$_2$] (0.500 g, 1.85 mmol) in diethyl ether (30 mL) was added a solution of GaCl$_3$ (0.163 g, 0.93 mmol) in diethyl ether (20 mL), and the reaction mixture stirred at 20 °C for 12 h, during which time **6a** precipitated out of solution as a yellow powder. Filtration and recrystallization from dichloromethane/hexane at −30 °C led to the isolation of microcrystalline **6a** (yield: 0.320 g, 58%). A lower yield is obtained if toluene is used as the reaction solvent, rather than diethyl ether (0.200 g, 36%). X-ray quality crystals could be grown by slow diffusion of hexanes into a solution in thf at −50 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.68 (s, 30H, Cp*); (CD$_2$Cl$_2$): δ 1.85 (s, 30H, Cp*). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 9.7 (CH$_3$ of Cp*), 94.4 (quaternary of Cp*), 217.2 (CO). IR (KBr): ν(CO) 1955, 1932, 1919; (CH$_2$Cl$_2$) 1960, 1925, 1910. MS (EI): *m/z* 598 (5%) [M]$^+$, correct isotope distribution for 2 Fe, 1 Ga, and 1 Cl atom, significant fragment ions at *m/z* 570 (35%) [M − CO]$^+$, 542 (25%) [M − 2CO]$^+$; exact mass calc for [M]$^+$ 597.9782, found 597.9780. Anal Calc for C$_{24}$H$_{30}$ClFe$_2$GaO$_4$: C 48.09, H 5.05. Found: C 47.82, H 5.33.

[Cp*Fe(CO)$_2$]$_2$GaI, 6b. To a solution/suspension of Na[Cp*Fe(CO)$_2$] (0.040 g, 0.148 mmol) in diethyl ether (10 mL) was added dropwise a solution of [Cp*Fe(CO)$_2$GaI$_2$]$_2$ (**12**, 0.085 g, 0.074 mmol) in diethyl ether (20 mL), and the reaction mixture stirred at 20 °C for 12 h, during which time **6b** precipitated out of solution as a yellow powder. Filtration, washing with hexanes, and drying in vacuo led to the isolation of **6b** (yield: 0.060 g, 61%). Crystalline samples could be obtained by slow diffusion of hexanes into a solution in thf at −30 °C. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.77 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 9.2 (CH$_3$ of Cp*), 94.1 (quaternary of Cp*), 217.4 (CO). IR (CD$_2$Cl$_2$): ν(CO) 2003, 1964, 1928 cm^{-1}. MS (EI): *m/z* 662 (45%) [M − CO]$^+$, correct isotope distribution for 2 Fe, 1 Ga, and 1 I atom, significant fragment ion at *m/z* 634 (30%) [M − 2CO]$^+$; exact mass calc for [M − CO]$^+$ 661.9189, found 661.9191. Anal. Calc for C$_{24}$H$_{30}$Fe$_2$GaIO$_4$: C 41.73, H 4.38. Found: C 41.67, H 4.21.

[Cp*Fe(CO)$_2$]$_2$InBr, 7a. To a suspension of Na[Cp*Fe(CO)$_2$] (0.201 g, 0.74 mmol) in diethyl ether (20 mL) was added a solution of InBr$_3$ (0.131 g, 0.37 mmol) in diethyl ether (10 mL), and the reaction mixture stirred at 20 °C for 16 h. Filtration of the supernatant solution, removal of volatiles in vacuo, and recrystallization from toluene (60 mL) at −30 °C yielded **7a** as an orange microcrystalline solid (0.121 g, 47%). X-ray quality crystals could be grown by slow diffusion of hexanes into a solution in toluene at −30 °C. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.83 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD$_2$Cl$_2$): δ 10.0 (CH$_3$ of Cp*), 94.2 (quaternary of Cp*), 216.1 (CO). IR (CD$_2$Cl$_2$): ν(CO) 1979, 1946, 1925 cm^{-1}. MS (EI): *m/z* 687.9 (5%) [M]$^+$, correct isotope distribution for 2 Fe, 1 In, and 1 Br atom, significant fragment ion peaks at *m/z* 661.9 (100%) [M − CO]$^+$, 663.9 (20%) [M − 2CO]$^+$; exact mass calc for [M]$^+$ 687.9060, found 687.9066.

[Cp*Fe(CO)$_2$]$_2$InI, 7b. To a suspension of InI (0.245 g, 1.01 mmol) in toluene (10 mL) was added a solution of [Cp*Fe(CO)$_2$]$_2$ (0.501 g, 1.01 mmol) in toluene (50 mL), and the reaction mixture refluxed for 144 h. Filtration, concentration, and cooling of the solution to −30 °C yielded **7b** as a microcrystalline solid (0.396 g, 53%). Single crystals suitable for X-ray diffraction could be obtained by slow diffusion of

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hexanes into a toluene solution at −30 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 9.6 (CH_3 of Cp*), 93.7 (quaternary of Cp*), 216.3 (CO). IR (CH_2Cl_2): ν(CO) 1969, 1957, 1922 cm^{-1}. MS (EI): *m/z* 736 (weak) [M]$^+$, correct isotope distribution for 2 Fe, 1 In, and 1 I atom, significant fragment ions at *m/z* 708 (100%) [M − CO]$^+$, 680 (8%) [M − 2CO]$^+$; exact mass calc for [M − CO]$^+$ 707.8972, found 707.8961.

[CpFe(CO)$_2$Ga(I)Br]$_2$, 8. To a suspension of GaI, prepared by sonicating gallium (0.136 g, 1.95 mmol) and iodine (0.247 g, 0.97 mmol) in toluene (50 mL), was added a solution/suspension of CpFe(CO)$_2$Br (0.500 g, 1.95 mmol) in toluene (30 mL), and the reaction mixture was stirred at 20 °C for 12 h. Filtration, concentration, and standing at 20 °C for 12 h yielded pale orange crystals suitable for X-ray diffraction (0.425 g, 48%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.91 (s, 5H, Cp). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 84.3 (Cp), 213.3 (CO). IR (CD_2Cl_2): ν(CO) 2015, 1968 cm^{-1}. MS (EI): *m/z* 499.7 (5%) [CpFe(CO)$_2$GaI$_2$]$^+$, 471.7 (38%) [CpFe(CO)$_2$GaI$_2$ − CO]$^+$, 443.7 (25%) [CpFe(CO)$_2$GaI$_2$ − 2CO]$^+$, 454 (3%) [CpFe(CO)$_2$Ga(I)Br]$^+$, 425.7 (28%) [CpFe(CO)$_2$Ga(I)Br − CO]$^+$, 397.7 (30%) [CpFe(CO)$_2$Ga(I)Br − 2CO]$^+$, 406 (2%) [CpFe(CO)$_2$GaBr$_2$]$^+$, 378 (18%) [CpFe(CO)$_2$GaBr$_2$ − CO]$^+$, 349.7 (13%) [CpFe(CO)$_2$GaBr$_2$ − 2CO]$^+$; exact mass calc for [CpFe(CO)$_2$GaI$_2$]$^+$ 499.6979, found 499.6973. Anal. Calc for $C_{14}H_{10}Br_2Fe_2Ga_2I_2O_4$: C 18.54, H 1.11. Found: C 18.22, H 0.99.

[CpFe(CO)$_2$In(I)Br]$_2$, 9. To a suspension of InI (0.247 g, 1.0 mmol) in toluene (5 mL) was added a solution/suspension of CpFe(CO)$_2$Br (0.262 g, 1.0 mmol) in toluene (40 mL), and the reaction mixture stirred at 20 °C for 144 h, during which time **9** precipitated out of solution as a yellow powder. Recrystallization by slow diffusion of hexanes into a toluene solution at −30 °C yielded orange crystals of **9** suitable for X-ray diffraction (0.407 g, 80%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.96 (s, 10H, Cp). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 82.8 (Cp), carbon of CO ligands not observed. IR (CH_2Cl_2): ν(CO) 2012, 1969 cm^{-1}. MS (EI): 916 (25%) [M − Br]$^+$, 870 (30%) [M − I]$^+$, 546 (10%) [CpFe(CO)$_2$InI$_2$]$^+$, 518 (6%) [CpFe(CO)$_2$InI$_2$ − CO]$^+$, 498 (2%) [CpFe(CO)$_2$In(I)Br]$^+$, 490 (23%) [CpFe(CO)$_2$InI$_2$ − 2CO]$^+$, 470 (2%) [CpFe(CO)$_2$In(I)Br − CO]$^+$, 442 (20%) [CpFe(CO)$_2$In(I)Br − 2CO]$^+$, 419 (100%) [CpFe(CO)$_2$InI]$^+$, 391 (8%) [CpFe(CO)$_2$InI − CO]$^+$, 371 (60%) [CpFe(CO)$_2$InBr]$^+$, 363 (7%) [CpFe(CO)$_2$InI − 2CO]$^+$, 343 (7%) [CpFe(CO)$_2$InBr − CO]$^+$, 315 (3%) [CpFe(CO)$_2$InBr − 2CO}$^+$, 3%]; exact mass calc for [CpFe(CO)$_2$InI$_2$]$^+$ 545.6762, found 545.6760.

CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp, 10. To a suspension of GaI, prepared by sonicating gallium (0.138 g, 1.97 mmol) and iodine (0.250 g, 0.98 mmol) in toluene (50 mL), was added dropwise a solution/suspension CpFe(CO)$_2$I (0.600 g, 1.97 mmol) in toluene (20 mL), and the reaction mixture stirred at 20 °C for 12 h. Filtration, layering with hexanes, and cooling to −30 °C yielded dark red crystals suitable for X-ray diffraction (0.570 g, 72%). ^{1}H NMR (300 MHz, C_6D_6): δ 4.24 (s, 5H, Cp), 4.25 (s, 5H, Cp). ^{13}C NMR (76 MHz, C_6D_6): δ 83.8 (Cp), 84.2 (Cp), 212.0 (CO), 215.1 (CO). IR (C_6D_6): ν(CO) 2037, 2003, 2000, 1957. MS (EI): *m/z* 499.7 (5%) [CpFe(CO)$_2$GaI$_2$]$^+$, 471.7 (75%) [CpFe(CO)$_2$GaI$_2$ − CO]$^+$, 443.7 (52%) [CpFe(CO)$_2$GaI$_2$ − 2CO]$^+$, all with correct isotope distribution for 1 Fe, 1 Ga, and 2 I atom, 303.8 (45%) [CpFe(CO)$_2$I]$^+$, 275.8 (47%) [CpFe(CO)$_2$I − CO]$^+$, 247.8 (80%) [CpFe(CO)$_2$I − 2CO]$^+$; exact mass calc for [CpFe(CO)$_2$GaI$_2$ − CO]$^+$ 471.7030, found 471.7030.

[CpFe(CO)$_2$GaI$_2$]$_2$, 11. To a suspension of GaI, prepared by sonicating gallium (0.205 g, 2.94 mmol) and iodine (0.373 g, 1.47 mmol) in toluene (50 mL), was added a solution/suspension of CpFe(CO)$_2$I (0.300 g, 0.98 mmol) in toluene (20 mL), and the reaction mixture stirred at 20 °C for 48 h. Filtration, layering with hexanes, and cooling to −30 °C yielded crystals suitable for X-ray diffraction (0.300 g, 27%). ^{1}H NMR (300 MHz, C_6D_6): δ 4.12 (s, 5H, Cp). ^{13}C NMR (76 MHz, C_6D_6): δ 84.0 (Cp), 213.4 (CO). IR (C_6D_6): ν(CO) 2012, 1970 cm^{-1}. MS (EI): *m/z* 500 (5%) [CpFe(CO)$_2$GaI$_2$]$^+$, correct isotope distribution for 1 Fe, 1 Ga, and 2 I atom, significant fragment ions at *m/z* 472 (100%) [CpFe(CO)GaI$_2$]$^+$, 444 (75%) [CpFeGaI$_2$]$^+$, 373 (50%) [CpFe(CO)$_2$GaI]$^+$; exact mass calc for [CpFe(CO)$_2$GaI$_2$]$^+$ 499.6979, found 499.6975. Anal. Calc for $C_{14}H_{10}Fe_2Ga_2I_4O_4$: C 16.80, H 1.01. Found: C 16.48, H 0.91.

[Cp*Fe(CO)$_2$GaI$_2$]$_2$, 12. To a suspension of GaI, prepared by sonicating gallium (0.169 g, 2.42 mmol) and iodine (0.307 g, 1.21 mmol) in toluene (50 mL), was added a solution of [Cp*Fe(CO)$_2$]$_2$ (0.300 g, 0.61 mmol) in toluene (30 mL), and the reaction mixture stirred at 20 °C for 120 h, during which time **12** precipitated out of solution as a yellow powder. Recrystallization from dichloromethane at −30 °C yielded pale yellow crystals suitable for X-ray diffraction (0.324 g, 47%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.60 (s, 30H, Cp*). ^{13}C NMR (76 MHz, C_6D_6): δ 9.8 (CH_3 of Cp*), 95.4 (quaternary of Cp*), 216.4 (CO). IR (C_6D_6) ν(CO) 2001, 1954 cm^{-1}. MS (EI): *m/z* 569.8 (15%) [Cp*Fe(CO)$_2$GaI$_2$]$^+$, 541.8 (100%) [Cp*Fe(CO)$_2$GaI$_2$ − CO]$^+$, 513.8 (60%) [Cp*Fe(CO)$_2$GaI$_2$ − 2CO]$^+$; exact mass calc For [Cp*Fe(CO)$_2$GaI$_2$]$^+$ 569.7761; found 569.7753. Anal. Calc for $C_{24}H_{30}Fe_2Ga_2I_4O_4$: C 25.26, H 2.65. Found: C 24.98, H 2.43.

[Cp*Fe(CO)$_2$]$_2$In(μ-Cl)$_2$InCl[Fe(CO)$_2$Cp*], 13. To a suspension of InCl (0.182 g, 1.22 mmol) in toluene (10 mL) was added a solution of [Cp*Fe(CO)$_2$]$_2$ (0.298 g, 0.60 mmol) in toluene (40 mL), and the reaction mixture refluxed for 36 h. Filtration, concentration, and cooling of the solution to −30 °C yielded **13** as single crystals suitable for X-ray diffraction (0.065 g, 20%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.81 (s, 15H, Cp*), 1.87 (s, 30H, Cp*). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.0 (CH_3 of Cp*), 10.2 (CH_3 of Cp*), 94.1 (quaternary of Cp*), 94.3 (quaternary of Cp*), 215.4 (CO), 216.5 (CO). IR (CD_2Cl_2): ν(CO) 1987, 1967, 1954, 1939, 1919 cm^{-1}. MS (EI): *m/z* 616 (13%) [{Cp*Fe(CO)$_2$}$_2$InCl − CO]$^+$, correct isotope distribution for 2 Fe, 1 In, and 1 Cl atom, significant fragment ions at *m/z* 588 (5%) [{Cp*Fe(CO)$_2$}$_2$InCl − 2CO]$^+$, 397 (12%) [Cp*Fe(CO)$_2$InCl]$^+$; exact mass calc for [{Cp*Fe(CO)$_2$}$_2$InCl − CO]$^+$ 615.9616; found 615.9616.

Reaction of [CpFe(CO)$_2$Ga(I)Br]$_2$ (8) with 4-Picoline. To a solution of **8** (0.100 g, 0.11 mmol) in toluene (15 mL) was added dropwise a solution of 4-picoline in toluene (10 mL containing 0.020 g, 0.22 mmol of 4-picoline), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration, addition of hexane (40 mL), and cooling to −30 °C yielded a pale yellow microcrystalline material (0.030 g, 25%). Crystals of CpFe(CO)$_2$GaI$_2$·(4-pic) (**14**) suitable for X-ray diffraction could be obtained by slow diffusion of hexanes into a benzene solution. Characterizing data for crude (microcrystalline) product: ^{1}H NMR (300 MHz, C_6D_6): δ 1.35 (b, 3H, CH_3), 4.27, 4.29, 4.31 (s, 5H, Cp), 6.13 (b, 2H, CH of pic), 8.62 (b, 2H, CH of pic). ^{13}C NMR (76 MHz, C_6D_6): δ 20.6, 20.8 (CH_3), 83.4, 84.0, 84.6 (Cp), 125.8, 125.9 (CH of pic), 145.9, 146.0 (CH of pic), 153.5, 153.6 (quaternary of pic), 215.6, 216.1 (CO). IR (C_6D_6): ν(CO) 1985, 1979, 1950, 1934 cm^{-1}. MS (EI): *m/z* 500 (weak) [CpFe(CO)$_2$GaI$_2$]$^+$, 472 (10%) [CpFe(CO)$_2$GaI$_2$ − CO]$^+$, 454 (2%) [CpFe(CO)$_2$Ga(I)Br]$^+$, 444 (8%) [CpFe(CO)$_2$GaI$_2$ − 2CO]$^+$, 426 (25%) [CpFe(CO)$_2$Ga(I)Br − CO]$^+$, 406 (2%) [CpFe(CO)$_2$GaBr$_2$]$^+$, 398 (25%) [CpFe(CO)$_2$Ga(I)Br − 2CO]$^+$, 378 (18%) [CpFe(CO)$_2$GaBr$_2$ − CO]$^+$, 350 (30%) [CpFe(CO)$_2$GaBr$_2$ − 2CO]$^+$, 93.1 (100%) [4-pic]$^+$. Characterizing data for the crystalline product **14** were identical to those of a crystalline sample prepared independently from [CpFe(CO)$_2$GaI$_2$]$_2$ (**11**) and 4-picoline and recrystallized from toluene/hexanes: ^{1}H NMR (300 MHz, C_6D_6): δ 1.34 (s, 3H, CH_3), 4.33 (s, 5H, Cp), 6.09 (b m, 2H, CH of pic), 8.82 (b, 2H, CH of pic). ^{13}C NMR (76 MHz, C_6D_6): δ 20.3 (CH_3), 84.6 (Cp), 125.5, (CH of pic), 146.2 (CH of pic), 153.3 (quaternary of pic), 216.1 (CO). IR (C_6D_6): ν(CO) 1985, 1933 cm^{-1}. MS (EI): *m/z* 565 (weak) [M − CO]$^+$, correct isotope distribution for 1 Fe, 1 Ga, and 2 I atom, significant fragment ions at *m/z* 500 (4%) [M − pic]$^+$, 472 (75%) [M − pic − CO]$^+$, 444 (60%) [M − pic − 2CO]; exact mass calc for [M − CO]$^+$ 564.7608, found 564.7611.

Table 1. Details of Data Collection, Structure Solution and Refinement for Compounds 2, 3a, 5, 6a, and 7b

	2	**3a**	**5**	**6b**	**7b**
empirical formula	$C_{25}H_{34}ClFeGaO_2$	$C_{30}H_{44}ClFeGaO_2$	$C_{30}H_{44}BrFeInO_2$	$C_{24}H_{30}Fe_2GaIO_4$	$C_{24}H_{30}Fe_2IInO_4$
fw	527.54	597.67	687.23	690.80	735.90
temperature (K)	150(2)	150(2)	180(2)	150(2)	150(2)
CCDC deposit number	271129	271128	272450	271131	271132
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*Pcab*	*Cmca*	*Cmca*	$P2_1/c$	$P2_1/c$
unit cell dimens (Å, deg) *a*	16.8447(3)	15.2046(4)	15.0781(4)	13.4340(2)	13.4349(3)
b	17.0707(4)	19.8952(5)	20.5262(6)	11.2410(2)	11.5133(3)
c	17.7094(4)	20.2595(7)	20.4631(8)	17.0130(3)	17.0644(5)
α	90	90	90	90	90
β	90	90	90	94.1360(10)	94.3400(10)
γ	90	90	90	90	90
volume ($Å^3$)	5092.35(19)	6128.5(3)	6333.2(4)	2562.47(4)	2631.95(12)
density (calcd, Mg m^{-3})	1.376	1.296	1.422	1.791	1.857
Z	8	8	8	4	4
absorp coeff (mm^{-1})	1.750	1.463	2.470	3.393	3.156
F(000)	2192	2512	2800	1368	1440
cryst size (mm^3)	0.50 × 0.30 × 0.20	0.20 × 0.15 × 0.15	0.35 × 0.22 × 0.10	0.25 × 0.25 × 0.20	0.18 × 0.15 × 0.10
θ range (deg)	2.91 to 27.48	3.52 to 26.37	3.59 to 26.37	3.54 to 26.37	2.98 to 27.47
index ranges *h*	−21 to 21	−18 to 18	−18 to 18	−16 to 16	−17 to 17
k	−21 to 22	−20 to 24	−25 to 25	−14 to 14	−14 to 14
l	−22 to 23	−25 to 25	−25 to 25	−21 to 21	−21 to 22
no. of reflns collected	38 720	21 350	20 540	29 428	18 768
no. of indep reflns	5780 [R(int) = 0.1282]	3245 [R(int) = 0.0981]	3356 [R(int) = 0.1051]	5232 [R(int) = 0.0774]	5991 [R(int) = 0.0778]
completeness to θ max	99.0%	99.5%	99.6%	99.8%	99.5%
absorp corr	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min. transmn	0.7210 and 0.4748	0.8104 and 0.7585	0.7902 and 0.4785	0.5502 and 0.4842	0.7432 and 0.6004
refinement method	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)
no. of data/restraints/params	5780/0/280	3245/6/183	3356/0/168	5232/0/299	5991/0/299
goodness-of-fit on F^2	1.031	1.057	1.030	1.025	1.036
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0532, wR2 = 0.1076	R1 = 0.0735, wR2 = 0.1880	R1 = 0.0517, wR2 = 0.1071	R1 = 0.0321, wR2 = 0.0651	R1 = 0.0401, wR2 = 0.0782
R indices (all data)	R1 = 0.1327, wR2 = 0.1304	R1 = 0.1121, wR2 = 0.2062	R1 = 0.0935, wR2 = 0.1206	R1 = 0.0448, wR2 = 0.0701	R1 = 0.0586, wR2 = 0.0846
largest diff pk and hole (e $Å^{-3}$)	0.623 and −0.916	2.393 and −1.046	0.730 and −0.672	0.542 and −0.720	0.697 and −1.096

$\{[CpFe(CO)_2]_2InI\}_2$, 15. To a suspension of $Na[CpFe(CO)_2]$ (0.023 g, 0.12 mmol) in toluene (10 mL) was added a solution of **9** (0.057 g, 0.06 mmol) in toluene (10 mL), and the reaction mixture stirred at 20 °C for 16 h. Filtration and crystallization by slow diffusion of hexanes into a toluene solution at −30 °C led to the formation of orange-yellow crystals suitable for X-ray diffraction (0.055 g, 77%). ^1H NMR (400 MHz, C_6D_6): δ 4.34 (s, 20H, Cp). ^{13}C NMR (76 MHz, C_6D_6): δ 82.8 (Cp), 215.5 (CO). IR (C_6D_6): ν(CO) 1997, 1972, 1927 cm^{-1}. MS (EI): 596 (2%) $[\{CpFe(CO)_2\}_2InI]^+$, correct isotope distribution for 2 Fe, 1 In, and 1 I atom, 568 (33%) $[\{CpFe(CO)_2\}_2InI - CO]^+$, 540 (20%) $[\{CpFe(CO)_2\}_2InI - 2CO]^+$, 419 (53%) $[CpFe(CO)_2InI]^+$, 391 (8%) $[CpFe(CO)_2InI - CO]^+$, 363 (35%) $[CpFe(CO)_2InI - 2CO]^+$; exact mass calc for $[\{CpFe(CO)_2\}_2InI]^+$ 595.7356, found 595.7364.

$[tmpH_2]^+[Cp^*Fe(CO)_2GaI_3]^-$, 16. To a solution of $[Cp^*Fe(CO)_2GaI_2]_2$ (**12**, 0.100 g, 0.088 mmol) in toluene (20 mL) was added dropwise a solution of Li[tmp] (0.026 g, 0.18 mmol) in toluene (20 mL), and the reaction mixture stirred at 20 °C for 12 h. Filtration, concentration, and cooling to −30 °C led to the formation of pale yellow crystals suitable for X-ray diffraction (0.041 g, 28%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.57 (b, 12H, CH_3 of tmp), 1.66 (b, 4H, CH_2CMe_2 of tmp), 1.76 (s, 15H, CH_3 of Cp*), 1.89 (b, 2H, CH_2 of tmp), 6.49 (b, 2H, NH_2). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 8.4 (CH_3 of Cp*), 15.2 (CH_3 of tmp), 27.6 (CH_2CMe_2 of tmp), 35.2 (CH_2 of tmp), 59.1 (quaternary of tmp), 93.6 (quaternary of Cp*), 217.0 (CO). IR (C_6D_6): ν(CO) 1980, 1933 cm^{-1}. MS (ES−): 696.7 (10%) $[Cp^*Fe(CO)_2GaI_3]^-$, 668.7 (1%), $[Cp^*Fe(CO)_2GaI_3 - CO]^-$, 569.7 (5%) $[Cp^*Fe(CO)_2GaI_3 - I]^-$; exact mass calc for $[Cp^*Fe(CO)_2GaI_3]^-$ (^{69}Ga): 696.6817, found 696.6815. MS (ES+): 142.1 (100%) $[tmpH_2]^+$.

(iii) Crystallographic Method. Data for compounds **2**, **3a**, and **5**−**16** were collected on an Bruker Nonius Kappa CCD diffractometer. Data collection and cell refinement were carried out using DENZO and COLLECT; structure solution and refinement used DIRDIFF-99 (Patterson methods), SIR-92 (direct methods), and SHELXL-97, respectively; absorption corrections were performed using SORTAV.[21] Details of each data collection, structure solution, and refinement can be found in Tables 1 and 2. Relevant bond lengths and angles are included in the figure captions, and complete details of each structure have been deposited with the CCDC (numbers as listed in Table 1). In addition, complete details for each structure (including CIF files) have been included in the Supporting Information. The crystal structure of compound **6a** has been reported in a preliminary communication;[9] the structures of **7a**, **8**, **14**, and **16** were obtained predominantly for compound verification and show geometric features very similar to related derivatives. Hence these three structures, together with those of $[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$ and

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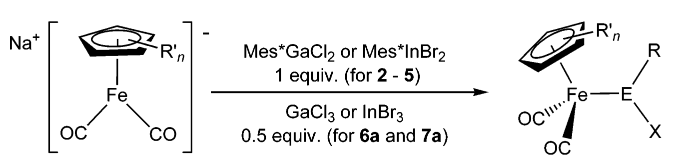
Table 2. Details of Data Collection, Structure Solution, and Refinement for Compounds 9−13 and 15

	9	**10**	**11**	**12**	**13**·1/4(C_6H_6)	**15**
empirical formula	$C_{14}H_{10}Br_2Fe_2I_2In_2O_4$	$C_{14}H_{10}Fe_2GaI_3O_4$	$C_{14}H_{10}Fe_2Ga_2I_4O_4$	$C_{24}H_{30}Fe_2Ga_2I_4O_4$	$C_{37.5}H_{46.5}Cl_3Fe_3In_2O_6$	$C_{28}H_{20}Fe_4I_2In_2O_8$
fw	997.18	804.34	1000.96	1141.22	1096.79	1191.28
temperature (K)	150(2) K	150(2)	150(2)	150(2)	150(2)	150(2)
CCDC deposit number	271135	271136	271137	271138	271139	271141
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	triclinic	orthorhombic	orthorhombic
space group	$P21/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pcab*	*Pcab*
unit cell dimens (Å, deg) *a*	7.6338(3)	7.9200(3)	8.9422(3)	8.4507(2)	14.9810(2)	7.5598(2)
b	14.8212(6)	9.8960(3)	8.7431(3)	9.6929(3)	21.5210(3)	18.7946(5)
c	9.9594(5)	15.2600(6)	14.4917(6)	11.4642(3)	29.8390(4)	23.1101(6)
α	90	100.5820(10)	90	75.9390(10)	90	90
β	90.796(2)	97.6700(10)	90.301(1)	74.028(2)	90	90
γ	90	113.333(2)	90	67.5600(10)	90	90
volume ($Å^3$)	1126.72(9)	1050.98(7)	1132.98(7)	824.33(4)	9620.3(2)	3283.56(15)
density (calcd, Mg m^{-3})	2.939	2.542	2.934	2.299	1.515	2.410
Z	2	2	2	1	8	4
absorp coeff (mm^{-1})	9.585	7.054	9.073	6.250	2.031	5.028
F(000)	904	736	904	532	4372	2240
cryst size (mm^3)	0.30 × 0.13 × 0.10	0.15 × 0.10 × 0.05	0.35 × 0.28 × 0.25	0.15 × 0.15 × 0.13	0.18 × 0.15 × 0.10	0.25 × 0.08 × 0.03
θ range (deg)	3.00 to 27.42	3.52 to 26.37	3.54 to 26.37	2.93 to 27.47	3.53 to 26.37	3.04 to 27.47
index ranges *h*	−9 to 9	−9 to 9	−11 to 11	−10 to 10	−18 to 18	−9 to 9
k	−19 to 19	−12 to 12	−9 to 10	−12 to 12	−26 to 26	−24 to 24
l	−12 to 12	−19 to 19	−17 to 18	−14 to14	−35 to 37	−29 to 30
no. of reflns collected	9748	14 311	7086	13 459	47 982	24 421
no. of indep reflns	2554 [*R*(int) = 0.0807]	4287 [*R*(int) = 0.0907]	2302 [*R*(int) = 0.0594]	3761 [*R*(int) = 0.0878]	9794 [*R*(int) = 0.1115]	3757 [*R*(int) = 0.1148]
completeness to *θ* max	99.4%	99.7%	99.4%	99.7%	99.5%	99.9%
absorp corr	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min. transmn	0.4474 and 0.1611	0.7193 and 0.4176	0.2101 and 0.1434	0.4971 and 0.4541	0.8227 and 0.7113	0.8638 and 0.3662
refinement method	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)
no. of data/restraints/params	2554/30/137	4287/12/217	2302/0/118	3761/0/168	9794/0/484	3757/0/200
goodness-of-fit on F^2	1.142	1.021	1.148	1.031	1.023	1.031
final R indices [$I > 2\sigma(I)$]	R1 = 0.0491, wR2 = 0.1179	R1 = 0.0503, wR2 = 0.1174	R1 = 0.0424, wR2 = 0.1049	R1 = 0.0408, wR2 = 0.0902	R1 = 0.0527, wR2 = 0.1356	R1 = 0.0465, wR2 = 0.0852
R indices (all data)	R1 = 0.0592, wR2 = 0.1241	R1 = 0.0851, wR2 = 0.1331	R1 = 0.0492, wR2 = 0.1087	R1 = 0.0571, wR2 = 0.0977	R1 = 0.0835, wR2 = 0.1499	R1 = 0.0888, wR2 = 0.0980
largest diff pk and hole (e $Å^{-3}$)	1.336 and −2.099	1.405 and −1.667	0.948 and −2.532	1.100 and −1.586	1.626 and −0.620	1.106 and −1.357

Scheme 4. Direct Substitution by Organometallic Anions as a One-Step Route to Three-Coordinate Halogallium and -indium Ligand Systems



2: E = Ga, X = Cl, R = Mes*, R'_n = H_5
3a: E = Ga, X = Cl, R = Mes*, R'_n = Me_5
4: E = In, X = Br, R = Mes*, R'_n = H_5
5: E = In, X = Br, R = Mes*, R'_n = Me_5
6a: E = Ga, X = Cl, R = (η^5-C_5Me_5)Fe(CO)$_2$, R'_n = Me_5
7a: E = In, X = Br, R = (η^5-C_5Me_5)Fe(CO)$_2$, R'_n = Me_5

$[CpFe(CO)_3]^+[CpFe(CO)_2Ga(I)Br_2]^-$, are included only in the Supporting Information. The halide ligands in $[CpFe(CO)_2In(I)Br]_2$, **9**, are disordered between bridging and terminal positions. This disorder was successfully modeled (summing to unity in each position) giving refined occupancies of 70:30 Br:I for the bridging positions and 30:70 for the terminal positions.

Results and Discussion

(i) Synthesis from Metal Anions. Synthesis from anionic organometallic precursors has been applied to two classes of three-coordinate gallium- or indium-containing ligand system, namely, (i) asymmetric halogallyl and -indyl systems of the type L_nM-E(Mes*)X (Mes* = supermesityl, 2,4,6-^{t}Bu$_3$C$_6$H$_2$) and (ii) bridging halogallanediyl and -indanediyl complexes $(L_nM)_2EX$. The former class of compound is exemplified by complexes **2**−**5**, which can be synthesized by the reaction of Na[(η^5-C_5R_5)Fe(CO)$_2$] (R = H, Me) with Mes*GaCl$_2$ or Mes*InBr$_2$ (Scheme 4).

Given the observation for boron-based systems that subsequent halide abstraction chemistry leads to tractable cationic diyl derivatives *only* in the presence of bulky aryl or amino groups,[7] the supermesityl substituent was employed in complexes **2**−**5**.[11] Although Mes*BBr$_2$ is itself inert to boron-centered substitution chemistry with anions of the type [(η^5-C_5R_5)Fe(CO)$_2$]$^-$, presumably on steric grounds,[22c] substitution at the larger group 13 centers in Mes*EX$_2$ (E = Ga, In) has previously been shown to offer a viable route of generating monomeric, three-coordinate group 13 systems [e.g., Mes*Ga(Cl)N(SiMe$_3$)$_2$ and (OC)$_5$MnGa(Mes*)Cl[11,23]]. For complexes **2** and **3a**, Mes*GaCl$_2$ represents a convenient,

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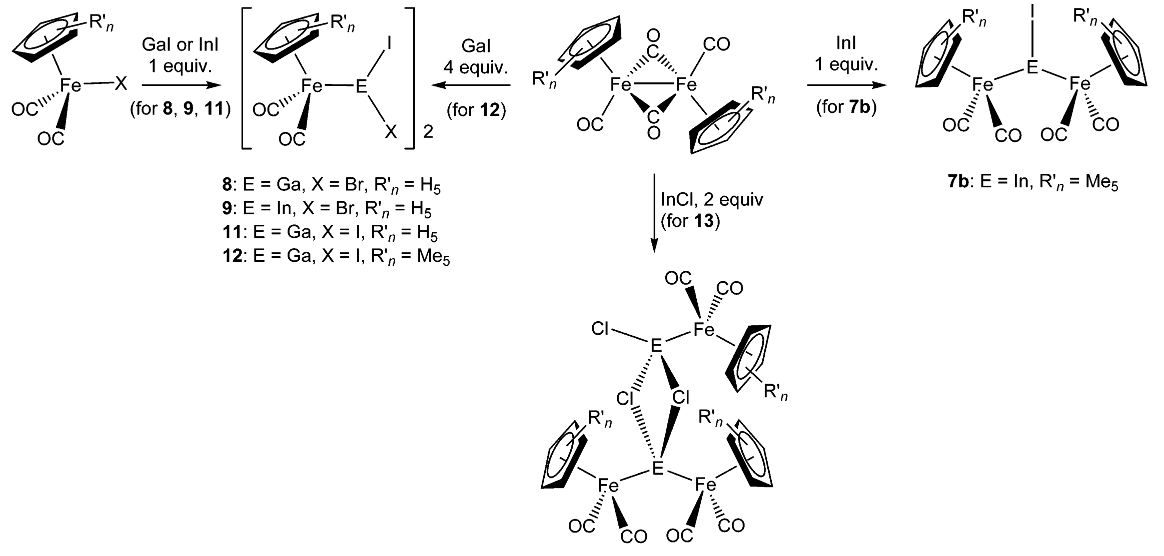
(22) (a) Aldridge, S.; Coombs, D. L.; Jones, C. *Chem. Commun.* **2002**, 856. (b) Coombs, D. L.; Aldridge, S.; Jones, C. *Dalton Trans.* **2002**, 3851. (c) Coombs, D. L.; Aldridge, S.; Jones, C. *Appl. Organomet. Chem.* **2003**, *6*−*7*, 356.

Scheme 5. Insertion Chemistry as a Route to Gallium- and Indium-Based Ligand Systems Containing Pendant Halides



8: E = Ga, X = Br, R'$_n$ = H$_5$
9: E = In, X = Br, R'$_n$ = H$_5$
11: E = Ga, X = I, R'$_n$ = H$_5$
12: E = Ga, X = I, R'$_n$ = Me$_5$

7b: E = In, R'$_n$ = Me$_5$

13: E = In, R'$_n$ = Me$_5$

readily synthesized precursor, with the corresponding bromide Mes*InBr$_2$ being employed for indyl complexes **4** and **5** because of reported difficulties obtaining Mes*InCl$_2$ free from InCl$_3$.[16b,c] Complexes **2**–**5** are pale yellow crystalline solids, which have been characterized by multinuclear NMR and IR spectroscopies, by mass spectrometry (including exact mass determination), and, in the cases of **2**, **3a** and **5**, by single-crystal X-ray diffraction. Similar chemistry can also be employed in the synthesis of bridging gallanediyl and indanediyl complexes **6a** and **7a** (Scheme 4). Thus, reaction of 2 equiv of the bulky [Cp*Fe(CO)$_2$]$^-$ anion with GaCl$_3$ or InBr$_3$ leads to selective substitution of two of the halide ligands to give the bridging halodiyl complexes [Cp*Fe(CO)$_2$]$_2$EX (**6a**: E = Ga, X = Cl; **7a**: E = In, X = Br) in isolated yields of 36 and 47%, respectively. A related salt elimination approach, albeit with *dianionic* organometallic reagents, has been exploited by Hüttner and co-workers in the synthesis of complexes of the type {[(OC)$_5$Cr]$_2$EX}$^{2-}$ (E = In, Tl; X = Cl, Br, I).[12]

Spectroscopic data for **6a** and **7a** are in accordance with the proposed formulations, which are confirmed in both cases by the results of a single-crystal X-ray diffraction study. In contrast to the corresponding complexes featuring the less bulky CpFe(CO)$_2$ fragment, **6a** and **7a** are monomeric in the solid state (vide infra) and can be recrystallized from coordinating solvents such as diethyl ether and thf without coordination at the group 13 center.[24,25]

(ii) Synthesis by Combined Insertion/Substitution Methodology. (a) Insertion Chemistry. An alternative approach to the synthesis of the requisite three-coordinate halo-gallium and -indium ligand systems involves initial insertion of EI (E = Ga, In) into a M–X or M–M bond to give a dihalogallyl or -indyl, [L$_n$M-E(I)X]$_n$, or halogallanediyl/indanediyl complex, (L$_n$M)$_2$EI. This approach offers a potentially more powerful route to such systems than the simple organometallic anion substitution methodology discussed above. By avoiding reliance on such anionic precursors, a much greater range of complexes is potentially accessible, leading ultimately to the possibility of cationic diyl systems [L$_n$M(EX)]$^+$ without competing ancillary π acidic ligands (i.e., carbonyls[26]). Relevant reaction chemistry of GaI and InX (X = Cl, I) toward metal–halogen and metal–metal bonds is shown in Scheme 5. The insertion of sonochemically generated GaI into M–I bonds (M = Fe, Mo) was originally demonstrated by Green and co-workers in 1990,[14a] and in similar fashion both GaI and InI readily insert into the Fe–Br bond of CpFe(CO)$_2$Br to give dimeric [CpFe(CO)$_2$E(I)Br]$_2$ (**8**: E = Ga; **9**: E = In) in yields of 48 and 80%, respectively. In each case IR and multinuclear NMR data are consistent with the proposed formulations, although the mass spectra reveal ready fragmentation into a mixture of monomeric species CpFe(CO)$_2$EBr$_2$, CpFe(CO)$_2$E(I)Br, and CpFe(CO)$_2$EI$_2$ under electron impact conditions. The halide-bridged dimeric structures of **8** and **9** were subsequently deduced from single-crystal X-ray diffraction studies (vide infra).

The reaction of CpFe(CO)$_2$I with GaI has also been investigated in some depth and provides some insight into the mechanism of the reaction, together with the reported tendency of similar systems under certain conditions to give salt-like transition metal/group 13 products (e.g., containing anions of the type [L$_n$M-GaX$_3$]$^-$).[24,27] Thus, under mild reaction conditions, reaction of CpFe(CO)$_2$I with GaI generates a deep red compound, **10**, which can be recrystallized from a

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[23] Leung, W.-P.; Chan, C. M. Y.; Wu, B. M.; Mak, T. C. W. *Organometallics* **1996**, *15*, 5179.

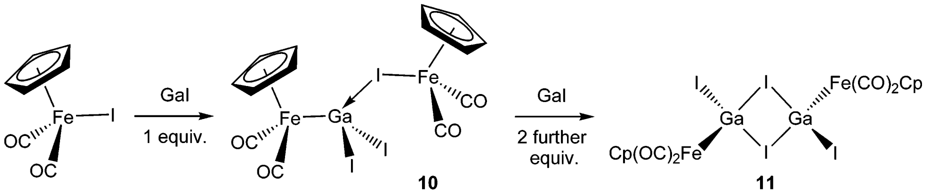
[24] Linti, G.; Li, G.; Pritzkow, H. *J. Organomet. Chem.* **2001**, *626*, 82.

[25] A previous report of the synthesis of **11** from GaI$_3$ and of its hydrolytic reactivity makes no comment as to its state of aggregation and reports slightly different spectroscopic data than those detailed in the present study: Borovik, A. S.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 2668.

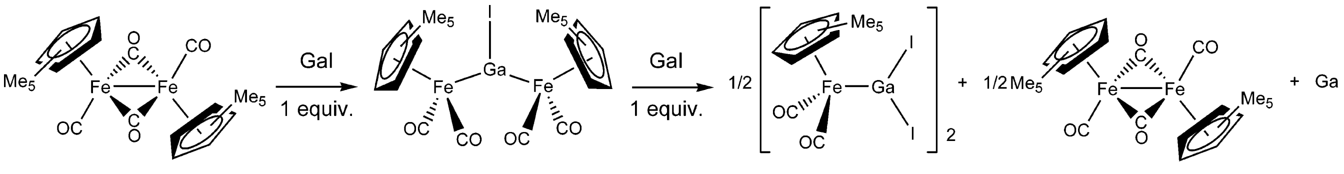
[26] Mork, B. V.; McMillan, A.; Yuen, H.; Tilley, T. D. *Organometallics* **2004**, *23*, 2855.

[27] Although the reaction of CpFe(CO)$_2$FeBr with GaI in toluene gives [CpFe(CO)$_2$Ga(I)Br]$_2$ in ca. 50% isolated yields, in the presence of traces of thf [CpFe(CO)$_3$]$^+$[CpFe(CO)$_2$Ga(I)Br$_2$]$^-$ is obtained. Details of the structure of this salt-like product are included in the Supporting Information.

Scheme 6. Reaction of the Isolated Intermediate 10 with GaI via Further Insertion to Give Dimeric $[\mathrm{CpFe(CO)_2GaI_2}]_2$



Scheme 7. Proposed Mechanism for the Formation of $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{GaI}$ from $[\mathrm{Cp^*Fe(CO)_2}]_2$ and GaI



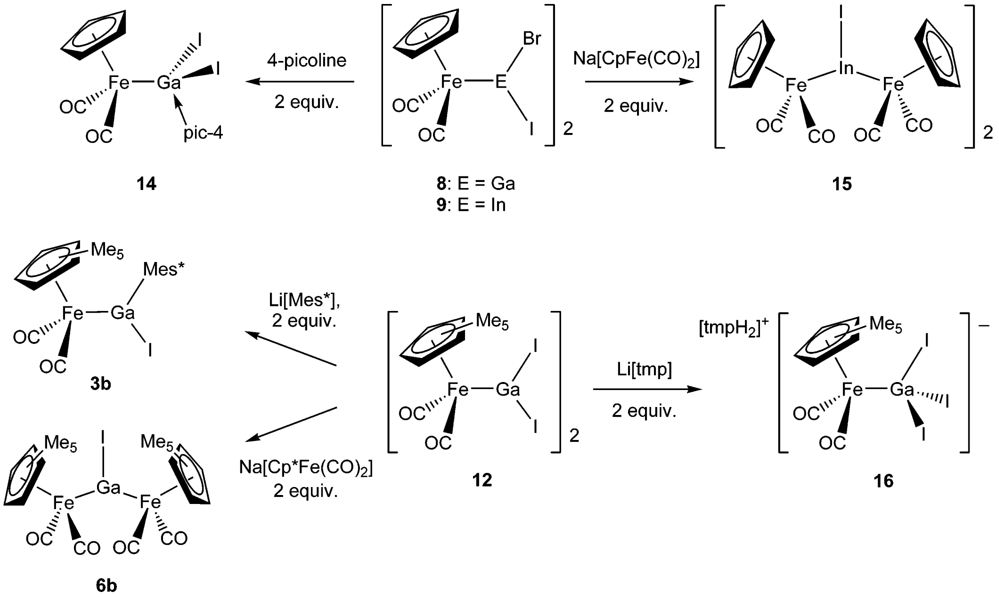
toluene/hexane mixture (ca. 1:2) as large block-like crystals. Spectroscopic and crystallographic studies indicate that **10** is a 1:1 adduct formed between $\mathrm{CpFe(CO)_2I}$ and $\mathrm{CpFe(CO)_2GaI_2}$ via an I→Ga donor/acceptor interaction (Scheme 6). It seems likely that **10** arises from the trapping of the initial product of GaI insertion [into the Fe−I bond of $\mathrm{CpFe(CO)_2I}$] by unreacted $\mathrm{CpFe(CO)_2I}$. From **10** two possible reaction pathways are plausible. First, in the presence of an excess of GaI, insertion into the remaining (and presumably weakened) Fe−I bond with concomitant formation of a further I→Ga interaction would create dimeric $[\mathrm{CpFe(CO)_2GaI_2}]_2$ (**11**). Indeed, under more forcing conditions (using 3 equiv of GaI) **11** is indeed the predominant product from this reaction and is shown from spectroscopic and structural data to possess the expected dimeric structure.[25] Alternatively, in the presence of a suitable nucleophile (L) substitution of the (Lewis acid activated) iodide ligand of the $\mathrm{CpFe(CO)_2I}$ fragment would generate a salt-like species of the type $[\mathrm{CpFe(CO)_2L}]^+[\mathrm{CpFe(CO)_2GaI_3}]^-$. Species containing similar $[\mathrm{CpFe(CO)_2GaX_3}]^-$ anions have been reported by Linti and co-workers from related GaI chemistry, and we have also isolated $[\mathrm{CpFe(CO)_3}]^+[\mathrm{CpFe(CO)_2Ga(I)Br_2}]^-$ as a minor product from the reaction of GaI with $\mathrm{CpFe(CO)_2Br}$ in the presence of traces of thf (see Supporting Information).[24,27]

Insertion of InI into *metal−metal* bonds can also be exploited to generate three-coordinate halo-indium ligand systems under appropriate conditions. Accordingly, reaction of InI with $[\mathrm{Cp^*Fe(CO)_2}]_2$ generates $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{InI}$, **7b** (in ca. 50% yield), which, unlike its Cp counterpart, has been shown to contain a trigonal planar indium center (vide infra). Thus, in the presence of sufficient steric bulk, subvalent metal halide insertion chemistry represents a direct one-step route to three-coordinate group 13 ligand systems. The reactions for GaI and InCl with $[\mathrm{Cp^*Fe(CO)_2}]_2$ have also been examined. In contrast to InI, however, the predominant products generated from reaction with these two reagents are not the simple products of EX insertion into the Fe−Fe bond. Instead $[\mathrm{Cp^*Fe(CO)_2GaI_2}]$ (**12**) and $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{In}(\mu\text{-Cl})_2\mathrm{InCl}[\mathrm{Fe(CO)_2Cp^*}]$ (**13**) are isolated in yields of 47 and 20%, respectively. In the reaction with GaI, **12** is the only Fe/Ga-containing product isolated, irrespective of reaction stoichiometry, and its formation contrasts markedly with the reactivity reported for $[\mathrm{CpFe(CO)_2}]_2$ toward the same reagent. Linti and co-workers have reported that this reaction generates a mixture of organometallic species, among which a $[\mathrm{CpFe(CO)_2GaI_3}]^-$ salt represents the only Fe/Ga/I-containing product.[24] In the case of **12**, at least 4 equiv of GaI are required to drive this reaction to completion, with substantial amounts of $[\mathrm{Cp^*Fe(CO)_2}]_2$ otherwise being retained; in addition 2 equiv of gallium metal are deposited during the reaction. Presumably the reaction mechanism involves initial insertion of GaI to give $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{GaI}$ in a manner analogous to the corresponding InI chemistry (which generates **7b**). Halide transfer from a second equivalent of GaI would then generate half an equivalent each of $[\mathrm{Cp^*Fe(CO)_2GaI_2}]_2$ and $[\mathrm{Cp^*Fe(CO)_2}]_2$, together with 1 equiv of gallium metal (Scheme 7). In this way, half of the original $[\mathrm{Cp^*Fe(CO)_2}]_2$ is consumed by reaction with 2 equiv of GaI, and the need for an overall 1:4 reaction stoichiometry is justified.

The reaction of InCl with $[\mathrm{Cp^*Fe(CO)_2}]_2$ finds a precedent of sorts in the chemistry of the corresponding Cp derivative; a mixture of the two halide-bridged dimers $[\mathrm{CpFe(CO)_2InCl_2}]_2$ and $\{[\mathrm{CpFe(CO)_2}]_2\mathrm{InCl}\}_2$ is thought to be formed in this case.[15e,f] ^{1}H and ^{13}C NMR analyses of the isolated crystalline product for the permethylated system are consistent with the formation of two Cp*- and carbonyl-containing moieties in a 2:1 ratio. In addition, the IR spectrum contains *five* carbonyl stretching bands (1987, 1967, 1954, 1939, 1919 cm^{-1}), the observed pattern appearing to correspond to the superposition of the two-band spectrum observed for derivatives of the type $[\mathrm{Cp^*Fe(CO)_2EX_2}]_2$ (e.g., 2001, 1954 cm^{-1} for **12**, E = Ga, X = I) with the three stretches observed for species of the type $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{EX}$ (e.g., 1979, 1946, 1925 cm^{-1} for **7a**, E = In, X = Br). The structure of the product $[\mathrm{Cp^*Fe(CO)_2}]_2\mathrm{In}(\mu\text{-Cl})_2\mathrm{InCl}[\mathrm{Fe(CO)_2Cp^*}]$, **13**, has been determined crystallographically (vide infra) and, consistent with the IR and NMR data, can be thought of as a chloride-bridged 1:1 adduct between $[\mathrm{Cp^*Fe(CO)}]_2\mathrm{InCl}$ and $\mathrm{Cp^*Fe(CO)_2InCl_2}$ fragments.

(b) Substitution Chemistry. Although direct insertion into metal−metal bonds, such as that demonstrated for InI with $[\mathrm{Cp^*Fe(CO)_2}]_2$, can in some cases be used to give access to the required three-coordinate ligand systems, analogous chemistry involving metal−halogen linkages invariably results in four-coordinate dihalogal-

Scheme 8. Substitution and Addition Chemistry at Gallium- and Indium-Based Ligands Containing Pendant Halides



lyl or -indyl systems. Thus, gallium- or indium-centered substitution chemistry with appropriately bulky nucleophiles is required to generate the desired three-coordinate group 13 center. Given this, and the scarcity of reports concerning substitution at existing group 13 ligand systems,[7c,8b] we have therefore examined the reactivity of **8**, **9**, and **12** toward a range of nucleophiles, with the results outlined in Scheme 8.

Simple adduct formation has been observed for dihalogallyl complexes in previous studies [e.g., $CpFe(CO)_2GaCl_2$·thf [24]], and the reaction of $[CpFe(CO)_2Ga(I)X]_2$ (**8**: X = Br; **11**: X = I) with neutral donors, exemplified by 4-picoline, appears to proceed along similar lines. Formation of the picoline adduct $CpFe(CO)_2GaI_2$·(4-pic) (**14**) can be demonstrated spectroscopically and has been confirmed by crystallographic study (see Supporting Information). In keeping with the necessity to effect halide *substitution* at gallium/indium, the reactivity of dihalogallyl and -indyl complexes toward *anionic* nucleophiles has also been examined. Thus, $[CpFe(CO)_2In(I)Br]_2$, **9**, reacts at room temperature with $Na[CpFe(CO)_2]$ via halide substitution to yield the bis-metalated species $[CpFe(CO)_2]_2InI$, **15**, which has been characterized spectroscopically and shown crystallographically to adopt an iodide-bridged dimeric structure $\{[CpFe(CO)_2]_2InI\}_2$ analogous to that reported for the corresponding chloride complex.[15f] Although this chemistry demonstrates the feasibility of substitution at existing gallyl/indyl ligand systems, it is apparent that a greater degree of steric bulk is required to generate three- rather than four-coordinate derivatives. Hence the corresponding reactivity of Cp*-substituted $[Cp^*Fe(CO)_2GaI_2]_2$ (**12**) was examined. Initial focus was centered upon the main group nucleophiles Li[tmp] and Li[Mes*] with a view to developing a route to amido(halo)gallyl species such as $Cp^*Fe(CO)_2Ga(tmp)I$[28] and an alternative (metal anion free) route to aryl(halo)gallyls [e.g., $Cp^*Fe(CO)_2Ga(Mes^*)I$]. Additionally, the reaction of **12** with $Na[Cp^*Fe(CO)_2]$ was examined as a possible route to the bridging iodogallylene $[Cp^*Fe(CO)_2]_2GaI$ (**6b**), given the lack of success in isolating this compound by direct insertion of GaI into the Fe–Fe bond of $[Cp^*Fe(CO)_2]_2$.

The reaction of **12** with Li[tmp] in toluene, however, proceeds not to the desired amidogallyl complex, but to the salt $[tmpH_2]^+[Cp^*Fe(CO)_2GaI_3]^-$ (**16**) in 28% yield. The same product is also isolated from the corresponding reaction in diethyl ether and has been characterized both spectroscopically and crystallographically. The origins of the protons of the $[tmpH_2]^+$ cation are unclear, but their location from X-ray diffraction data is supported by the results of mass spectrometry (ES+) and ^1H NMR experiments. Although the mechanism for the formation of **16** is not obvious, its formation is entirely reproducible and in accordance with the corresponding reaction of $[CpFe(CO)_2Ga(I)Br]_2$ (**8**) with Li[tmp], which generates the analogous salt $[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$ (see Supporting Information).

By contrast, the reaction of **12** with Li[Mes*] proceeds as expected, generating the aryl(iodo)gallyl complex $Cp^*Fe(CO)_2Ga(Mes^*)I$, **3b**, in 33% isolated yield. Although single crystals of **3b** suitable for X-ray diffraction could not be obtained, its identity was confirmed by mass spectrometry (including exact mass determination) and by multinuclear NMR and IR data, which are essentially identical to those for the structurally characterized chloride analogue **3a**. Thus by analogy with $(\eta^5\text{-}C_5R_5)Fe(CO)_2Ga(Mes^*)Cl$ (**2**: R = H; **3a**: R = Me) a mononuclear complex containing a three-coordinate gallyl ligand would be expected. In a similar fashion, the reaction of **12** with $Na[Cp^*Fe(CO)_2]$ generates $[Cp^*Fe(CO)_2]_2GaI$ (**6b**) in reasonable yield, with the identity of the product (and its tricoordinate geometry at gallium) being confirmed by a combination of spectroscopic and crystallographic data.

Two routes to three-coordinate halogallium and -indium ligand systems have therefore been demonstrated: (i) simple salt elimination and (ii) insertion chemistry followed, where necessary, by halide substi-

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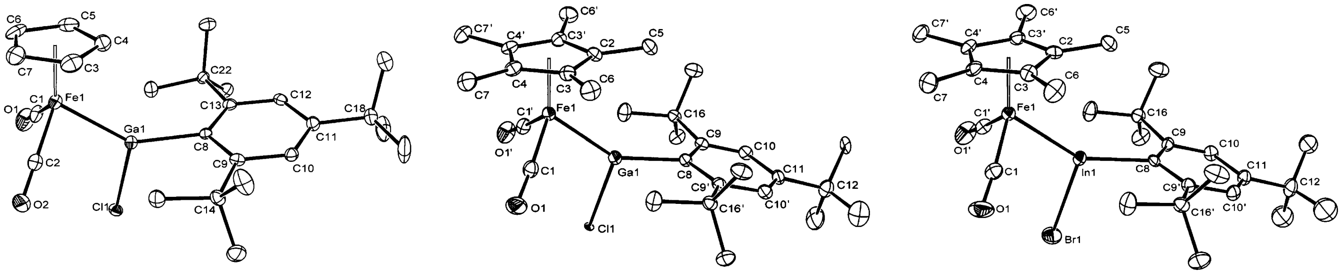
[28] For a previous example of a group 13 ligand system featuring a tmp substituent, see: Anand, B. N.; Crossing, I.; Nöth, H. *Inorg. Chem.* **1997**, *36*, 6, 1979.



(a) **(b)** **(c)**

Figure 1. Structures of (a) $CpFe(CO)_2Ga(Mes^*)Cl$, **2**; (b) $Cp^*Fe(CO)_2Ga(Mes^*)Cl$, **3a**; and (c) $Cp^*Fe(CO)_2In(Mes^*)Br$, **5**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): (for **2**) Fe(1)−Ga(1) 2.346(1), Fe(1)−Cp centroid 1.713(4), Fe(1)−C(1) 1.758(5), Ga(1)−Cl(1) 2.272(1), Ga(1)−C(8) 1.997(3), Fe(1)−Ga(1)−C(8) 139.18(10), Fe(1)−Ga(1)−Cl(1) 112.62(3), Cl(1)−Ga(1)−C(8) 108.21(10), Cp centroid−Fe(1)−Ga(1)−C(8) 2.40(10), Fe(1)−Ga(1)−C(8)−C(9) 97.51(18); (for **3a**) Fe(1)−Ga(1) 2.372(2), Fe(1)−Cp* centroid 1.729(7), Fe(1)−C(1) 1.749(7), Ga(1)−Cl(1) 2.358(2), Ga(1)−C(8) 2.025(8), Fe(1)−Ga(1)−C(8) 146.7(2), Fe(1)−Ga(1)−Cl(1) 111.5(1), Cl(1)−Ga(1)−C(8) 101.8(2), Cp* centroid−Fe(1)−Ga(1)−C(8) 0.0(1), Fe(1)−Ga(1)−C(8)−C(9) 93.6(3); (for **5**) Fe(1)−In(1) 2.509 (1), Fe(1)−Cp* centroid 1.719(5), Fe(1)−C(1) 1.747(6), In(1)−Br(1) 2.610(1), In(1)−C(8) 2.178(7), Fe(1)−In(1)−C(8) 148.9(2), Fe(1)−In(1)−Br(1) 111.4(1), Br(1)−In(1)−C(8) 100.7(2), Cp* centroid−Fe(1)−In(1)−C(8) 0.0(1), Fe(1)−In(1)−C(8)−C(9) 94.2(2).

tution. The latter route, although potentially more powerful, in terms of the range of complexes accessible, typically lacks the convenience inherent in the one-pot salt elimination methodology.

(iii) Structural Studies. Single-crystal X-ray diffraction studies were undertaken on compounds **2**, **3a**, and **5**−**16**; of these, the structures of **7a**, **8**, **14**, and **16** were obtained predominantly for compound verification and show geometric features very similar to related derivatives. Hence these three structures, together with those of $[tmpH_2]^+[CpFe(CO)_2GaBr_3]^-$ and $[CpFe(CO)_3]^+$-$[CpFe(CO)_2Ga(I)Br_2]^-$, are included only in the Supporting Information. The crystal structure of compound **6a** has been reported in a preliminary communication.[9] For the remaining compounds, details of data collection, structure solution, and refinement parameters are given in Table 1; relevant bond lengths and angles are included in the figure captions. Complete details of *all* structures are given in the Supporting Information and have been deposited with the Cambridge Structural Database.

Other than the complex $(OC)_5MnGa(Mes^*)Cl$ reported by Cowley and co-workers as a cocrystallite with $(OC)_5MnGa(Mes^*)(\mu_2\text{-}O)Ga(Mes^*)Mn(CO)_5$,[11] aryl(chloro)gallyl species **2** and **3a** (Figure 1) represent the only structurally authenticated three-coordinate halogallyl systems to be reported in the literature; **5** represents the first simple neutral haloindyl complex to be structurally characterized.[12,29] As expected, the gallium/indium center in each case is trigonal planar [sum of angles = 360.0(1)°, 360.0(6)°, and 360.0(2)° for **2**, **3a**, and **5**, respectively], and the orientation of the gallyl/indyl ligand is such that it lies essentially coplanar with the Cp centroid−Fe−Ga plane [∠Cp centroid−Fe−Ga−C_{ipso} = 2.40(10)°, 0.0(1)°, and 0.0(1)° for **2**, **3a**, and **5**, respectively, the latter two angles being enforced by a crystallographic mirror plane]. This ligand orientation and the near perpendicular alignment of the gallyl and supermesityl planes [∠Fe−Ga−C_{ipso}−C_{ortho} = 97.5(2)°, 93.6(3)° and 94.2(2)° for **2**, **3a** and **5**, respectively] mirror those seen for boryl complexes of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2B(Mes)X$ (Mes = $C_6H_2Me_3$-2,4,6)[7b,c,22] and are enforced largely to minimize steric interactions between the $(\eta^5\text{-}C_5R_5)$ and aryl substituents. The steric bulk of the supermesityl substituent is presumably also responsible for the relatively long Fe−Ga bonds [2.346(1) and 2.372(2) Å for **2** and **3a**, respectively], with that for **2**, for example, being significantly longer that those reported for $CpFe(CO)_2GaCl_2{\cdot}thf$ and $[CpFe(CO)_2GaCl_2]_2{\cdot}$dioxane [2.317(1) Å for both],[24] despite the reduction in coordination number at gallium from four to three. Differences *between* the structures of **2** and **3a** are presumably also primarily influenced by sterics, with the opening out of the Fe−Ga−C_{ipso} angle [146.7(2)° vs 139.2(1)°] and lengthening of the Fe−Ga bond reflecting the greater size of the Cp* substituent. Interestingly, there is also a pronounced lengthening of the Ga−Cl bond [2.358(2) vs 2.272(1) Å], which, with subsequent halide abstraction chemistry in mind, may be indicative of a thermodynamically more attractive target bond.

The molecular structures of the halodiyl complexes $[Cp^*Fe(CO)_2]_2GaI$ (**6b**), $[Cp^*Fe(CO)_2]_2InI$ (**7b**), and $\{[CpFe(CO)_2]_2InI\}_2$ (**15**) are depicted in Figure 2. **6b** and **7b** [together with the related species **6a** (reported in our preliminary communication[9]) and **7a** (included in the Supporting Information)] represent the first structurally characterized neutral complexes containing three-coordinate bridging halogallanediyl or -indanediyl ligands [sum of angles = 359.96(2)° and 359.89(2)° for **6b** and **7b**, respectively].[12,29] As such, these compounds represent potential precursors for the synthesis of cationic trimetallic systems via halide abstraction.[9] Three-coordinate gallium centers of the type seen in **6b** have previously been observed only with bulky gallylene substituents such as Mes, ^{t}Bu, or $CpFe(CO)_2$, and the smaller size of the iodide ligand is presumably responsible for the shorter Fe−Ga bonds and wider Fe−Ga−Fe angle in **6b** {2.354 Å (mean) and 140.14(2)° for **6b** vs 2.432(2) Å, 124.42(7)°; 2.411 Å (mean), 122.4(1)°; 2.444 Å (mean), 120.0° (mean) for $[Cp^*Fe(CO)_2]_2GaMes$, $[CpFe(CO)_2]_2Ga^tBu$, and $[CpFe(CO)_2]_3Ga$, respectively}.[13]

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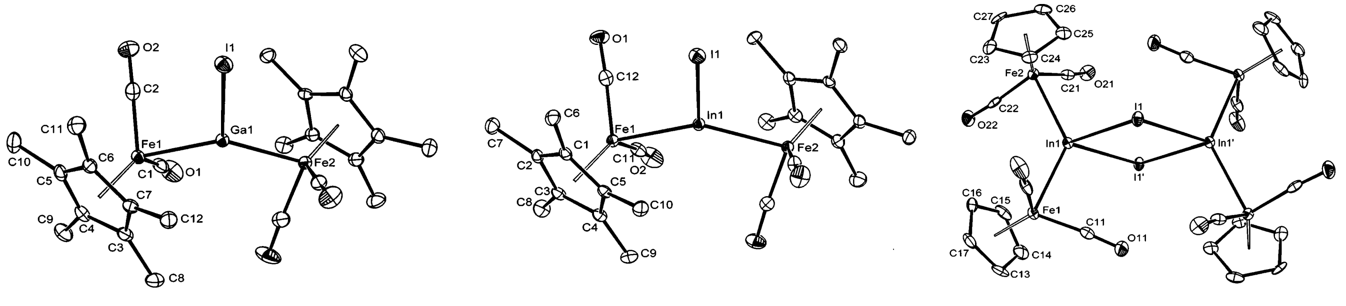
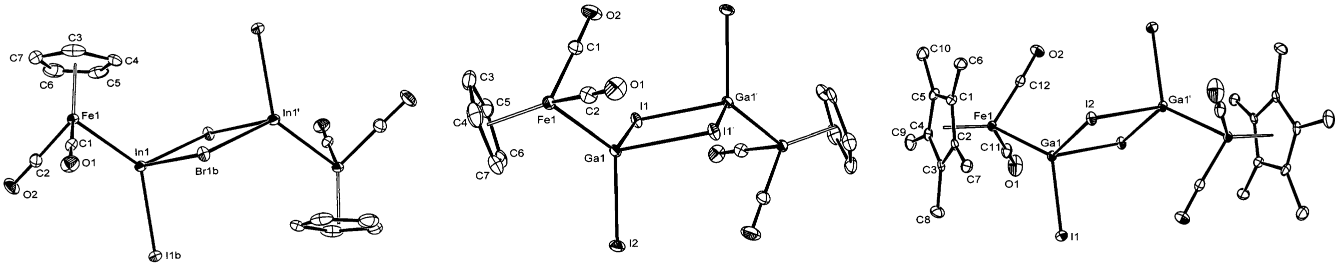
(29) For a related system containing an M−In(R)−halide unit in which the halide ligand bridges to a second group 13 center see: Steinke, T.; Gemel, C.; Cokoja, M.; Winter, M.; Fischer, R. A. *Chem. Commun.* **2003**, 1066.



(a) **(b)** **(c)**

Figure 2. Structures of (a) $[Cp^*Fe(CO)_2]_2GaI$, **6b**; (b) $[Cp^*Fe(CO)_2]_2InI$, **7b**; and (c) $\{[CpFe(CO)_2]_2InI\}_2$, **15**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): (for **6b**) Fe(1)−Ga(1) 2.357(1), Fe(2)−Ga(1) 2.351(1), Fe(1)−C(1) 1.749(4), Fe(1)−Cp* centroid 1.732(2), Ga(1)−I(1) 2.701(1), Fe(1)−Ga(1)−Fe(2) 140.14(2), Fe(1)−Ga(1)−I(1) 109.01(2); (for **7b**) Fe(1)−In(1) 2.513(1), Fe(2)−In(1) 2.519(1), Fe(1)−C(11) 1.754(5), Fe(1)−Cp* centroid 1.726(5), In(1)−I(1) 2.854(4), Fe(1)−In(1)−Fe(2) 141.98(2), Fe(1)−In(1)−I(1) 110.30(2), Fe(2)−In(1)−I(1) 107.61(2); (for **15**) Fe(1)−In(1) 2.549(1), Fe(2)−In(1) 2.554(1), Fe(1)−C(11) 1.755(8), Fe(1)−Cp centroid 1.723(6), In(1)−I(1) 3.081(1), In(1)−I(1′) 2.932(1), Fe(1)−In(1)−Fe(2) 130.36(3), Fe(1)−In(1)−I(1) 102.15(3), Fe(2)−In(1)−I(1) 106.47(3), I(1)−In(1)−I(1′) 86.59(2).



(a) **(b)** **(c)**

Figure 3. Structures of (a) $[CpFe(CO)_2In(I)Br]_2$, **9**; (b) $[CpFe(CO)_2GaI_2]_2$, **11**; and (c) $[Cp^*Fe(CO)_2GaI_2]_2$, **12**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): (for **9**) Fe(1)−In(1) 2.480(1), Fe(1)−C(1) 1.770(9), Fe(1)−Cp centroid 1.730(8), In(1)−Br(1b) 2.974(10), In(1)−Br(1b′) 2.623(10), In(1)−I(1b) 2.704(3), Fe(1)−In(1)−I(1b) 130.71(6), Br(1b)−In(1)−Br(1b′) 82.7(3); (for **11**) Fe(1)−Ga(1) 2.321(1), Fe(1)−C(1) 1.757(8), Fe(1)−Cp centroid 1.717(8), Ga(1)−I(1) 2.799(1), Ga(1)−I(1′) 2.731(1), Ga(1)−I(2) 2.557(1), Fe(1)−Ga(1)−I(2) 126.48(4), I(1)−Ga(1)−I(1′) 91.59(2); (for **12**) Fe(1)−Ga(1) 2.314(1), Fe(1)−C(11) 1.746(6), Fe(1)−Cp* centroid 1.725(4), Ga(1)−I(1) 2.585(1), Ga(1)−I(2) 2.756(1), Ga(1)−I(2′) 2.789(1), Fe(1)−Ga(1)−I(1) 124.72(3), I(2)−Ga(1)−I(2′) 92.01(2).

In the cases of both **6a** and **7b**, the trigonal planar ligand geometries contrast with those observed for the corresponding complexes containing the less bulky (η^5-C_5H_5) ligand.[9] Thus, $[CpFe(CO)_2]_2GaCl$ is polymeric (featuring bridging Ga−Cl−Ga units)[25] and readily coordinates external bases such as thf, dioxane, or chloride.[24,31] As might be expected given the decreased coordination number at gallium in **6a**, the Fe−Ga distances are shorter and the Fe−Ga−Fe angle wider than those found in four-coordinate complexes {e.g., 2.365(1) Å, 135.58(4)°; 2.390 Å (mean), 129.51(4)°; 2.430 Å (mean), 127.81(4)° for $[CpFe(CO)_2]_2GaCl$, $[CpFe(CO)_2]_2GaCl{\cdot}thf$, $[CpFe(CO)_2]_2GaCl_2^-$, respectively}.[9,24,25,29] Similar steric influences are presumably responsible for the analogous differences between **7b** and **15** [d(Fe−In) = 2.513(1), 2.549(1) Å, ∠Fe−In−Fe = 141.98(2)°, 130.36(3)°, respectively], with the four-coordinate halide-bridged structure of the latter mirroring that of the corresponding chloride $\{[CpFe(CO)_2]_2InCl\}_2$.[15f]

The dimeric, halide-bridged structures of $[CpFe(CO)_2E(I)Br]_2$ (**8**: E = Ga; **9**: E = In) and $[(\eta^5$-$C_5R_5)Fe(CO)_2GaI_2]_2$ (**11**: R = H; **12**: R = Me) have been confirmed crystallographically (Figure 3). Although a similar $L_nME(X)(\mu\text{-}X)_2E(X)ML_n$ motif exists in the species $[CpFe(CO)_2GaCl_2]_2(GaCl_3)_2$, reported by Barron and co-workers,[25] complexes **8**, **9**, **11**, and **12** represent the first structurally characterized neutral base-free dihalogallyl or -indyl species to be reported.[32,33] Not unsurprisingly, these dimeric structures contrast with that reported by Braunschweig and co-workers for the related dihaloboryl system $CpFe(CO)_2BCl_2$, which is monomeric and features a trigonal planar group 13 center.[34] The disparate terminal and bridging Ga−X distances [e.g., 2.585(1) and 2.756(1) Å for **12** (X = I)] and narrow Ga(μ-X)$_2$ angles [e.g., 92.01(2)° for **12**] are reminiscent of the geometries found for related derivatives of the type Y(X)Ga(μ-X)$_2$Ga(X)Y [e.g., 2.714 (mean), 2.490(1) Å and 92.78(2)° for $(Cp^*GaI_2)_2$].[35]

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(30) For an example of a three-coordinate bridging halo-boranediyl complex see: Braunschweig, H.; Colling, M.; Chunhua, H.; Radacki, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1359.

(31) Ueno, W.; Watanabe, T.; Ogino, H. *Organometallics* **2000**, *19*, 5679.

(32) For examples of Lewis base adducts of the type $CpFe(CO)_2GaX_2{\cdot}L$, see for example, ref 24, and: Fischer, R. A.; Miehr, A.; Priermeier, T. *Chem. Ber.* **1995**, *128*, 831.

(33) For a report of the synthesis (but not the crystal structure) of a compound of empirical composition $Cp^*Fe(CO)_2GaCl_2$ see ref 8b and: Ueno, K.; Watanabe, T.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4375.

(34) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2004**, *23*, 4178.

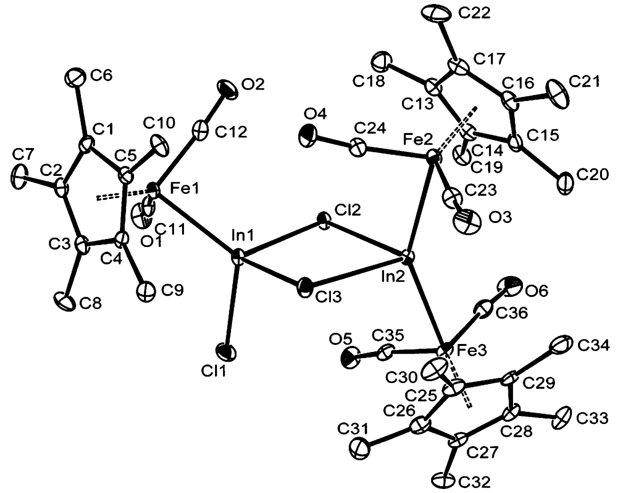

Figure 4. Structure of [Cp*Fe(CO)$_2$]$_2$In(μ-Cl)$_2$InCl[Fe(CO)$_2$Cp*], **13**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)–In(1) 2.488(1), Fe(2)–In(2) 2.546(1), Fe(3)–In(2) 2.540(1), In(1)–Cl(1) 2.403(2), In(1)–Cl(2) 2.527(2), In(1)–Cl(3) 2.503(2), In(2)–Cl(2) 2.754(2), In(2)–Cl(3) 2.782(2), Cl(2)–In(1)–Cl(3) 89.04(5), Cl(2)–In(2)–Cl(3) 79.15(5).

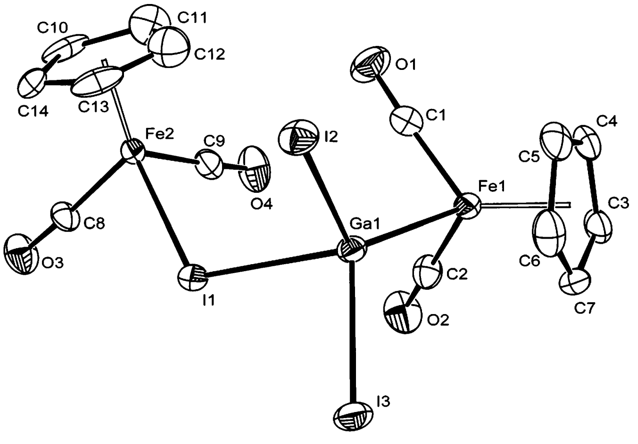

Figure 5. Structure of (a) CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp, **10**. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)–Ga(1) 2.331(2), Fe(1)–C(1) 1.740(11), Fe(1)–Cp centroid 1.726(9), Ga(1)–I(1) 2.788(1), Ga(1)–I(2) 2.596(1), Ga(1)–I(3) 2.605(1), Fe(2)–I(1) 2.589(1), Fe(2)–C(8) 1.760(8), Fe(2)–Cp centroid 1.727(8), Fe(1)–I(1)–Fe(2) 116.01(4), I(2)–Ga(1)–I(3) 106.60(4), Fe(1)–Ga(1)–I(2) 117.95(5), Fe(1)–Ga(1)–I(3) 117.98(5).

An interesting variation on the theme of dinuclear halide-bridged complexes is seen in the structure of [Cp*Fe(CO)$_2$]$_2$In(μ-Cl)$_2$InCl[Fe(CO)$_2$Cp*], **13**. This effectively represents a chloride-bridged 1:1 adduct between [Cp*Fe(CO)]$_2$InCl and Cp*Fe(CO)$_2$InCl$_2$ fragments and features a highly asymmetric In$_2$Cl$_2$ bridging unit. Unusually **13** shows the first indication of quaternization via a donor/acceptor interaction at a group 13 center bearing two bulky [Cp*Fe(CO)]$_2$ fragments. Although this structural motif is common for less bulky organometallic fragments (cf. the chloride-bridged structure of [{CpFe(CO)$_2$}$_2$InCl]$_2$[15f]), complexes of the type [Cp*Fe(CO)]$_2$EX examined in this study have typically shown little or no tendency toward coordination of external bases at E. As might be expected, given the differing steric requirements of the peripheral substituents, the bridging In–Cl bond lengths and Cl–In–Cl angle associated with In(2) are significantly different than those associated with In(1) [2.781(2), 2.754(2) Å, 79.14(5)° vs 2.503(2), 2.527(2) Å, 89.01(5)°].

The structure of CpFe(CO)$_2$GaI$_2$(μ-I)Fe(CO)$_2$Cp, **10**, an intermediate in the reaction pathway from CpFe(CO)$_2$I and GaI to [CpFe(CO)$_2$GaI$_2$]$_2$ (**11**), is shown in Figure 5 and consistent with its description as a donor/acceptor adduct between CpFe(CO)$_2$I and CpFe(CO)$_2$GaI$_2$. Thus the bridging Ga–I linkage is significantly longer than the terminal Ga–I bonds [2.788(1) vs 2.596(1) and 2.605(1) Å]. Somewhat surprisingly, however, the Fe–I distance [2.589(1) Å] is actually slightly *shorter* than that found in "free" CpFe(CO)$_2$I [2.607 Å (mean)].[36]

Conclusions

Transition metal complexes containing three-coordinate halogallium and -indium ligands represent the key precursors to unsaturated cationic species of the type [L$_n$M(EX)]$^+$ via halide abstraction chemistry. The application of two routes to these systems has been demonstrated: (i) simple salt elimination using organometallic anions and (ii) insertion chemistry followed, where necessary, by halide substitution. The latter route, although potentially more powerful, in terms of the range of complexes accessible, lacks the convenience inherent in the one-pot salt elimination methodology. Crystallographic studies have confirmed the presence of the target trigonal planar ligand systems both in gallyl/indyl complexes of the type L$_n$M-E(Aryl)X and in halodiyl systems of the type (L$_n$M)$_2$EX. Furthermore, the crucial role of steric factors in preventing halide-bridged oligomerization has been emphasized, e.g., by comparison of [(η^5-C$_5$R$_5$)Fe(CO)$_2$]$_2$InI (R = H, Me). Further studies utilizing these three-coordinate systems in the synthesis of unsaturated transition metal/group 13 cations are reported in a subsequent paper.[37]

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Supporting Information Available: Complete details of the crystal structures of compounds **2**, **3a**, **5**–**16**, [tmpH$_2$]$^+$[CpFe(CO)$_2$GaBr$_3$]$^-$, and [CpFe(CO)$_3$]$^+$[CpFe(CO)$_2$Ga(I)Br$_2$]$^-$ are included. NMR spectra for all compounds have also been included as evidence for bulk purity. This material is available free of charge via the Internet at http://pubs.acs.org.

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