Halide Abstraction as a Route to Cationic Transition-Metal Complexes Containing Two-Coordinate Gallium and Indium Ligand Systems

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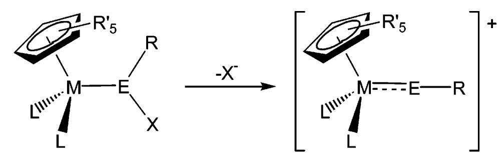
Halide abstraction chemistry offers a viable synthetic route to the cationic two-coordinate complexes $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+$ (**7**, E = Ga; **8**, E = In) featuring linear bridging gallium or indium atoms. Structural, spectroscopic, and computational studies undertaken on **7** are consistent with appreciable Fe–Ga π-bonding character; in contrast, the indium-bridged complex **8** is shown to feature a much smaller π component to the metal–ligand interaction. Analogous reactions utilizing the supermesityl-substituted gallyl or indyl precursors of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$, on the other hand, lead to the synthesis of halide-bridged species of the type $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)\}_2(\mu\text{-}X)]^+$, presumably by trapping of the highly electrophilic putative cationic diyl complex $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)]^+$.

Introduction

Compounds offering the potential for multiple bonding involving the heavier group 13 elements have attracted considerable attention in recent years, with studies reporting examples of both homo- and heteronuclear multiple bonds having appeared in the literature.[1] Within this sphere, the transition-metal diyl complexes $L_nM(EX)$ have been the subject of considerable debate,[2,3] primarily concerning the nature of the interaction between the group 13 and transition-metal centers. The description of superficially similar complexes as being bound via multiple bonds (e.g. $L_nM{=}EX$ or $L_nM{\equiv}EX$) or via donor/acceptor interactions ($L_nM{\leftarrow}EX$) reflects not only the fundamental questions of structure and bonding posed by such systems but also the lack of definitive experimental verification of potential bonding models.[4]

Scheme 1. Halide Abstraction Methodology for 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)



In an attempt to broaden the scope of synthetic methodologies available for unsaturated group 13 systems, we have been examining the use of halide abstraction chemistry to generate cationic derivatives (Scheme 1).[5] A series of preliminary computational analyses has suggested that the positive charge in cationic terminal diyl species, $[L_nM(EX)]^+$, resides primarily at the group 13 center (e.g. Mulliken charges of +0.438, +0.680, and +0.309 for $[Cp^*Fe(CO)_2E(Mes)]^+$; E = B, Al, Ga) and that M→E back-bonding may

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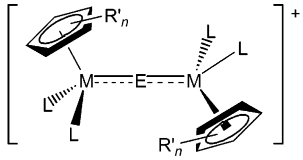
Chart 1. Cationic Trimetallic Systems Featuring Naked Group 13 Atoms as Bridging Ligands (E = Group 13 Element; L = Generic Ligand Coordinated to Transition Metal M)



II

contribute appreciably to the overall metal−ligand interaction (e.g., a 38% π contribution to the FeB bonding density in $[Cp^*Fe(CO)_2B(Mes)]^+$).[6] Hence, the Fe═B double bond in $[Cp^*Fe(CO)_2B(Mes)]^+$ can be described simplistically as being comprised of B→Fe σ-donor and Fe→B π-acceptor components. Recently we have been seeking to extend this synthetic approach from boron to the heavier group 13 elements and from isolated metal−ligand bonds (i.e. **I**) to delocalized trimetallic systems featuring naked group 13 atoms as ligands (i.e. **II**; Chart 1).[7]

Herein we report an extended investigation into the use of halide abstraction chemistry in heavier group 13 systems, leading to the synthesis of cationic derivatives containing gallium and indium donors. This has allowed for comparative spectroscopic, structural, and computational probes of M−E bond character as a function of the element E, thereby probing the controversial subject of multiple bonding involving the heavier group 13 elements. In addition, preliminary studies of the fundamental reactivity of the trimetallic systems $[L_nM(\mu\text{-}E)ML_n]^+$ (E = Ga, In) are reported.

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 and 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. $Na[BPh_4]$, $[^nBu_4N]I$, and [PPN]Cl were dried in vacuo prior to use; the compounds $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$ (Mes* = supermesityl = $C_6H_2{}^tBu_3$-2,4,6; **1**, E = Ga, R = H, X = Cl; **2**, E = Ga, R = Me, X = Cl; **3**, E = In, R = H, X = Br), $[Cp^*Fe(CO)_2]_2EX$ (**4**, E = Ga, X = Cl; **5**, E = In, X = Br; **6**, E = In, X = I), and $Na[BAr^f_4]$ ($Ar^f = C_6H_3(CF_3)_2$-3,5) were prepared by literature methods.[8,9]

NMR spectra were measured on a Bruker AM-400 or JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual signals of the solvent were used for reference for ^{1}H and ^{13}C NMR, while a sealed tube containing a solution of $[^nBu_4N][B_3H_8]$ in $CDCl_3$ was used as an external reference for ^{11}B NMR and $CFCl_3$ was used as a reference for ^{19}F NMR. 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, Wales. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Despite repeated attempts, satisfactory elementary microanalyses for the new cationic gallium and indium complexes were frustrated by their extreme air and moisture sensitivity. 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 **7**, **8**, **10**, and **14**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95% (see the Supporting Information). Abbreviations: br = broad, s = singlet, q = quartet, m = multiplet.

(ii) Syntheses. $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}Ga)][BAr^f_4]$ (7). To a suspension of $Na[BAr^f_4]$ (0.067 g, 0.075 mmol) in dichloromethane (10 mL) at −78 °C was added a solution of **4** (0.045 g, 0.075 mmol) in dichloromethane (10 mL), and the reaction mixture was warmed to 20 °C over 30 min. Further stirring for 20 min, filtration, and removal of volatiles in vacuo yielded **7** as a golden yellow powder (0.050 g, 46%). X-ray-quality crystals were grown by layering a dichloromethane solution with hexanes at −30 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.93 (s, 30H, Cp*), 7.54 (s, 4H, para CH of $BAr^f_4{}^-$), 7.70 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.3 (CH_3 of Cp*), 97.5 (quaternary of Cp*), 117.5 (para CH of $BAr^f_4{}^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 160.8 (q, $^1J_{CB}$= 53 Hz, ipso C of $BAr^f_4{}^-$), 211.4 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). IR (CH_2Cl_2): ν(CO) 2016, 1994, 1963 cm^{-1}. MS: ES−, *m/z* 863 (100%) $[BAr^f4]^-$; ES+, *m/z* 563 (5%) $[M]^+$, correct isotope distribution for 2 Fe and 1 Ga atoms. Exact mass: calcd for $[M]^+$ 563.0093, found 563.0092.

$[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)][BAr^f_4]$ (8). To a suspension of $Na[BAr^f_4]$ (0.057 g, 0.064 mmol) in dichloromethane (4 mL) at −78 °C was added a solution of **5** (0.044 g, 0.064 mmol) in dichloromethane (4 mL), and the reaction mixture was warmed to 20 °C over 30 min. Further stirring for 90 min, filtration, and layering with hexanes and storage at −30 °C yielded **8** as orange crystals suitable for X-ray diffraction (0.060 g, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.85 (s, 30H, Cp*), 7.44 (s, 4H, para CH of $BAr^f_4{}^-$), 7.64 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.4 (CH_3 of Cp*), 96.5 (quaternary of Cp*), 117.8 (para CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 35 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 161.8 (q, $^1J_{CB}$ = 50 Hz, ipso C of $BAr^f_4{}^-$), 211.9 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.7 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f_4{}^-$). IR (CD_2Cl_2): ν(CO) 2005, 1983, 1951 cm^{-1}. MS: ES−, *m/z* 863 (100%) $[BAr^f_4]^-$; ES+, *m/z* 609 (6%) $[M]^+$, correct isotope distribution for 2 Fe and 1 In atoms, significant fragment ions at *m/z* 581 (weak) $[M - CO]^+$, 553 (5%) $[M - 2CO]^+$. Exact mass: calcd for $[M]^+$ 608.9876, found 608.9884.

Reaction of $[Cp^*Fe(CO)_2]_2InI$ (6) with $Na[BAr^f_4]$: Isolation of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}I)][BAr^f_4]$ (9). To a suspension of $Na[BAr^f_4]$ (0.111 g, 0.13 mmol) in dichloromethane (6 mL) at −78 °C was added a solution of **6** (0.092 g, 0.13 mmol) in dichloromethane (8 mL), and the reaction mixture was warmed to 20 °C over 30 min. Further stirring for 3 h, filtration, and layering with hexanes yielded orange crystals of **9** (0.028 g, 15%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.84 (s, 30H, Cp*), 7.48 (s, 4H, para CH of $BAr^f_4{}^-$), 7.64 (s, 8H, ortho CH of $BAr^f_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.4 (CH_3 of Cp*), 96.1 (quaternary of Cp*), 117.5 (para CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 274 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 31 Hz, meta C of $BAr^f_4{}^-$), 134.8 (ortho CH of $BAr^f_4{}^-$), 161.8 (q, $^1J_{CB}$ = 49 Hz, ipso C of $BAr^f_4{}^-$), 212.8 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ

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−62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6. IR (CH_2Cl_2): ν(CO) 2003, 1984, 1952 cm^{-1}. MS: ES−, 863 (100%) [BAr$^f_4$]$^-$; ES+, 621 (50%) [M]$^+$, correct isotope distribution for 2 Fe and 1 I atoms, significant fragment ions at *m/z* 593 (weak) [M − CO]$^+$, 565 (20%) [M − 2CO]$^+$, 537 (45%) [M − 3CO]$^+$, 509 (5%) [M − 4CO]$^+$. Exact mass: calcd for [M]$^+$ 620.9882, found 620.9872.

Reaction of [Cp*Fe(CO)$_2$]$_2$InI (6) with Na[BPh$_4$]. To a suspension of Na[BPh$_4$] (0.074 g, 0.22 mmol) in dichloromethane (10 mL) at −78 °C was added a solution of **6** (0.080 g, 0.11 mmol) in dichloromethane (10 mL), and the reaction mixture was warmed slowly to 20 °C. Monitoring the reaction mixture by IR spectroscopy over a period of 72 h led to the gradual disappearance of the peaks due to the starting material (1969, 1957, and 1922 cm^{-1}) and the growth of bands at 2016, 1995, 1970, and 1940 cm^{-1}. Monitoring by ^{11}B NMR spectroscopy also revealed the growth of a strong broad signal at δ_B 67.0. Filtration of the supernatant solution, removal of volatiles in vacuo, and recrystallization from hexanes at −30 °C led to the formation of crops of colorless and dark red microcrystalline material, which were identified as BPh_3 (δ_B 67.0) and a mixture of Cp*Fe(CO)$_2$I (ν(CO) 2016 and 1970 cm^{-1}) and Cp*Fe(CO)$_2$Ph (ν(CO) 1995 and 1940 cm^{-1}), respectively, by comparison of multinuclear NMR, IR, and mass spectrometric data with those reported previously.[10] A similar procedure was adopted to monitor the reaction of [Cp*Fe(CO)$_2$]$_2$GaCl (**4**) with Na[BPh$_4$]; in this case both BPh_3 and Cp*Fe(CO)$_2$Ph were isolated and identified by comparison with literature data.[10]

Reactions of (η^5-C$_5$R$_5$)Fe(CO)$_2$E(Mes*)X (1, R = H, E = Ga, X = Cl; 2, R = Me, E = Ga, X = Cl; 3, R = H, E = In, X = Br) with Na[BAr$^f_4$]: Syntheses of [{(η^5-C$_5$R$_5$)Fe(CO)$_2$E(Mes*)}$_2$(μ-X)][BAr$^f_4$] (10, R = H, E = Ga, X = Cl; 11, R = Me, E = Ga, X = Cl; 12, R = H, E = In, X = Br). The three reactions were carried out in a similar manner, exemplified for **1**. To a suspension of Na[BAr$^f_4$] (0.042 g, 0.047 mmol) in dichloromethane-d_2 (1 mL) at −78 °C was added dropwise a solution of CpFe(CO)$_2$Ga(Mes*)Cl (**1**; 0.025 g, 0.047 mmol) in dichloromethane-d_2 (5 mL), and the reaction mixture was warmed to 20 °C over 30 min. At this point, the reaction was judged to be complete by ^{1}H NMR spectroscopy; filtration and layering with hexanes led to the isolation of **10** as crystals suitable for X-ray diffraction (yield: 0.021 g, 24%). **11** and **12** were isolated as pale yellow microcrystalline materials in yields of 31 and 28%, respectively.

Data for **10** are as follows. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.25 (s, 9H, para ^{t}Bu), 1.46 (s, 18H, ortho ^{t}Bu), 4.88 (s, Cp), 7.34 (s, 2H, aryl CH of Mes*), 7.55 (s, 4H, para CH of BAr$^f_4$$^-$), 7.71 (s, 8H, ortho CH of BAr$^f_4$$^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 30.9 (CH_3 of para ^{t}Bu), 34.0 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.2 (quaternary of ortho ^{t}Bu), 83.5 (Cp), 117.4 (para CH of BAr$^f_4$$^-$), 119.4 (meta CH of Mes*), 122.9 (q, $^1J_{CF}$ = 273 Hz, CF_3 of BAr$^f_4$$^-$), 128.8 (q, $^2J_{CF}$ = 31 Hz, meta C of BAr$^f_4$$^-$), 134.9 (ortho CH of BAr$^f_4$), 154.9 (para C of Mes*), 155.0 (ortho C of Mes*), 212.7 (CO), ipso carbons undetected. ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 (BAr$^f_4$$^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.7 (CF_3). IR (CD_2Cl_2): ν(CO) 2016, 2002, 1972, 1954 cm^{-1}. MS (EI): *m/z* 963.7 (5%) [M − 2CO]$^+$, correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms, significant fragment ions at *m/z* 527.1 (5%) [CpFe(CO)$_2$Ga(Mes*)Cl]$^+$, 491.1 (20%) [CpFe(CO)$_2$Ga(Mes*)]$^+$.

Data for **11** are as follows. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.25 (s, 18H, para ^{t}Bu), 1.42 (s, 36H, ortho ^{t}Bu), 1.76 (s, 30H, Cp*), 7.30 (s, 4H, aryl CH of Mes*), 7.50 (s, 4H, para CH of BAr$^f_4$$^-$), 7.66 (s, 8H, ortho CH of BAr$^f_4$$^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.0 (CH_3 of Cp*), 30.9 (CH_3 of para ^{t}Bu), 33.9 (CH_3 of ortho ^{t}Bu), 34.7 (quaternary of para ^{t}Bu), 38.5 (quaternary of ortho ^{t}Bu), 95.5 (quaternary of Cp*), 117.5 (para CH of BAr$^f_4$$^-$), 123.4 (meta CH of Mes*), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF_3 of BAr$^f_4$$^-$), 128.9 (q, $^2J_{CF}$ = 31 Hz, meta C of BAr$^f_4$$^-$), 134.9 (ortho CH of BAr$^f_4$$^-$), 137.9 (ipso C of Mes*), 151.6 (para C of Mes*), 155.4 (ortho C of Mes*), 161.8 (q, $^1J_{CB}$ = 50 Hz, ipso C of BAr$^f_4$$^-$), 214.5 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 (BAr$^f_4$$^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.8 (CF_3). ν(CO) 1996, 1986, 1954, 1932 cm^{-1}. MS (EI): *m/z* 1131.1 (weak) [M − CO]$^+$, correct isotope distribution for 2 Fe, 2Ga and 1 Cl atoms, significant fragment ions at *m/z* 723.0 (25%) [Cp*Fe(CO)$_2$GaAr$^f_2$Cl − 2CO]$^+$, 650.1 (100%) [BAr$^f_3$]$^+$, 631.1 (80%) [BAr$^f_3$ − F]$^+$.

Data for **12** are as follows. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.18 (s, 18H, para ^{t}Bu), 1.32 (s, 36H, ortho ^{t}Bu), 4.81 (s, 10H, Cp), 7.29 (s, 4H, aryl CH of Mes*), 7.37 (s, 4H, para CH of BAr$^f_4$$^-$), 7.57 (s, 8H, ortho CH of BAr$^f_4$$^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 31.0 (CH_3 of para ^{t}Bu), 33.6 (CH_3 of ortho ^{t}Bu), 34.9 (quaternary of para ^{t}Bu), 37.7 (quaternary of ortho ^{t}Bu), 82.5 (Cp), 117.4 (para CH of BAr$^f_4$$^-$), 122.2 (meta CH of Mes*), 123.5 (q, $^1J_{CF}$ = 273 Hz, CF_3 of BAr$^f_4$$^-$), 128.7 (q, $^2J_{CF}$ = 29 Hz, meta C of BAr$^f_4$$^-$), 134.8 (ortho CH of BAr$^f_4$$^-$), 151.2 (para C of Mes*), 155.3 (ortho C of Mes*), 161.5 (q, $^1J_{CB}$ = 49 Hz, ipso C of BAr$^f_4$$^-$), 212.4 (CO), ipso carbon of Mes* not detected. ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 (BAr$^f_4$$^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ_F −62.7 (CF_3). IR (CD_2Cl_2): ν(CO) 2013, 1977, 1968 cm^{-1}. MS (EI): *m/z* 1140.8 (5%) [M − Me]$^+$, correct isotope distribution for 2 Fe, 2 In, and 1 Br atoms, significant fragment ions at *m/z* 1127.8 [M − 2CO]$^+$, 650 (100%) [BAr$^f_3$]$^+$, 631 (80%) [BAr$^f_3$ − F]$^+$.

Reaction of 7 with [PPN]Cl: Synthesis of [Cp*Fe(CO)$_2$]$_2$GaCl (4). To a solution of [PPN]Cl (0.020 mg, 0.035 mmol) in dichloromethane-d_2 (1 mL) was added a solution of **7** (0.050 g, 0.035 mmol) in dichloromethane-d_2 (3 mL) at room temperature. The reaction mixture was sonicated for 1 h, after which time ^{1}H NMR spectroscopy revealed complete conversion to **4** (quantitative conversion by NMR). Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample of **4** confirmed the identity of **4** as the sole organometallic product.[7,8]

Reaction of 8 with [^{n}Bu$_4$N]I: Synthesis of [Cp*Fe(CO)$_2$]$_2$InI (6). To a solution of [^{n}Bu$_4$N]I (0.010 g, 0.03 mmol) in dichloromethane-d_2 (1 mL) was added a solution of **8** (0.021 g, 0.01 mmol) in dichloromethane-d_2 (2 mL) at room temperature. The reaction mixture was sonicated for 1 h, after which time ^{1}H NMR spectroscopy revealed complete conversion to **6** (quantitative conversion by NMR). Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample confirmed the identity of **6** as the sole organometallic product.[8]

Reactions of 7 and 8 with thf: Syntheses of [{Cp*Fe(CO)$_2$}$_2${μ-E(thf)}][BAr$^f_4$] (13, E = Ga; 14, E = In). The two reactions were carried out in a similar manner, exemplified for **7**. To a solution of **7** in dichloromethane (12 mL), prepared in situ from Na[BAr$^f_4$] (0.059 g, 0.067 mmol) and [Cp*Fe(CO)$_2$]$_2$GaCl (**4**; 0.040 g, 0.067 mmol) at −78 °C, was added thf (2 mL), and the reaction mixture warmed to 20 °C over 30 min. After the mixture was stirred for a further 1 h at 20 °C, the reaction was judged to be complete by IR spectroscopy; filtration and cooling to −30 °C led to the isolation of [{Cp*Fe(CO)$_2$}$_2${μ-Ga(thf)}][BAr$^f_4$] (**13**) as a pale yellow microcrystalline solid (yield: 0.035 g, 35%). **14** was isolated in a similar manner as single crystals suitable for X-ray diffraction (0.030 g, 41%).

Data for **13** are as follows. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.80 (br m, 4H, CH_2 of thf), 1.86 (s, 30H, Cp*), 3.65 (br m, 4H, CH_2 of thf), 7.48 (s, 4H, para CH of BAr$^f_4$$^-$), 7.65 (s, 8H, ortho CH of BAr$^f_4$$^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.2 (CH_3 of Cp*), 25.5 (CH_2 of thf), 69.0 (CH_2 of thf), 97.4 (quaternary of Cp*), 117.6 (para CH of BAr$^f_4$$^-$), 122.8 (q, $^1J_{CF}$ = 273 Hz, CF_3 of BAr$^f_4$$^-$), 129.1 (q, $^2J_{CF}$ = 34 Hz, meta C of BAr$^f_4$$^-$), 134.9 (ortho

(10) (a) Akita, M.; Terada, M.; Tanaka, M.; Morooka, Y. *J. Organomet. Chem.* **1996**, *510*, 255. (b) Odom, J. D.; Moore, T. F.; Goetze, R.; Nöth, H.; Wrackmeyer, B. *J. Organomet. Chem.* **1979**, *173*, 15. (c) Jacobsen, S. E.; Wojcicki, A. *J. Am. Chem. Soc.* **1973**, *95*, 6962.

Table 1. Details of Data Collection, Structure Solution, and Refinement for Compounds 8, 10, and 14

	8	10	14
empirical formula	$C_{56}H_{42}BF_{24}Fe_2InO_4$	$C_{82}H_{80}BClF_{24}Fe_2Ga_2O_4$	$C_{60}H_{50}BF_{24}Fe_2InO_5$
formula wt	1472.23	1882.86	1554.33
temp (K)	150(2)	150(2)	150(2)
CCDC deposit no.	276094	276095	276096
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
unit cell dimens			
a (Å)	14.533(1)	13.744(3)	16.0540(3)
b (Å)	14.644(1)	14.521(3)	16.2940(3)
c (Å)	16.268(1)	21.345(4)	24.2520(6)
α (deg)	65.829(3)	99.44(3)	90
β (deg)	68.927(3)	97.12(3)	90
γ (deg)	74.823(3)	95.59(3)	90
V (Å^3)	2920.5(4)	4139.6(14)	6343.9(2)
calcd density (Mg m^{-3})	1.674	1.511	1.617
Z	2	2	4
abs coeff (mm^{-1})	1.003	1.122	0.929
F(000)	1464	1912	3088
cryst size (mm^3)	0.05 × 0.28 × 0.35	0.15 × 0.20 × 0.25	0.10 × 0.15 × 0.23
θ range (deg)	3.53−26.37	1.50−26.03	3.55−26.37
index ranges			
h	−17 to +18	−16 to +16	−20 to +20
k	−16 to +18	−17 to +17	−20 to +20
l	−16 to +20	−26 to +26	−29 to +30
no. of rflns collected	28 114	52 550	26 498
no. of indep rflns	9917 (*R*(int) = 0.1035)	15 346 (*R*(int) = 0.0668)	12 739 (*R*(int) = 0.0692)
completeness to θ_{max} (%)	86.9	94.0	99.5
abs cor	semiempirical from equivs	Sortav	semiempirical from equivs
max and min transmissn	0.952 and 0.720	0.879 and 0.780	0.913 and 0.815
refinement method		full-matrix least squares (F^2)	
no. of data/restraints/params	9917/30/788	15346/18/1090	12739/150/857
goodness of fit on F^2	1.019	1.023	1.023
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0944, wR2 = 0.1918	R1 = 0.0512, wR2 = 0.1059	R1 = 0.0821, wR2 = 0.1815
R indices (all data)	R1 = 0.1812, wR2 = 0.2314	R1 = 0.0807, wR2 = 0.1175	R1 = 0.1226, wR2 = 0.2068
largest diff. peak and hole (e Å^{-3})	1.828 and −1.026	0.723 and −0.557	1.154 and −1.007

CH of $BAr^f{}_4{}^-$), 160.8 (q, $^1J_{CB}$= 53 Hz, ipso C of $BAr^f{}_4{}^-$), 211.6 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($BAr^f{}_4{}^-$). ^{19}F NMR (283 MHz, CD_2Cl_2): δ − 62.8 (CF_3). IR (CH_2Cl_2/thf): ν(CO) 1978, 1962, 1927 cm^{-1}. MS: ES+, *m/z* 635.7 (weak) [M]$^+$, correct isotope distribution for 2Fe and 1 Ga atoms, significant fragment ions at *m/z* 563 (45%) [M − thf]$^+$, 535 (10%) [M − thf − CO]$^+$, 507 (5%) [M − thf − 2CO]$^+$. Exact mass: calcd for [M − thf]$^+$ 563.0093, found 563.0095.

Data for **14** are as follows. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.69 (br m, 4H, CH_2 of thf), 1.86 (s, 30H, Cp*), 3.63 (br m, 4H, CH_2 of thf), 7.48 (s, 4H, para CH of $BAr^f{}_4{}^-$), 7.64 (s, 8H, ortho CH of $BAr^f{}_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.5 (CH_3 of Cp*), 27.3 (CH_2 of thf), 59.1 (CH_2 of thf), 96.5 (quaternary of Cp*), 117.4 (para CH of $BAr^f{}_4{}^-$), 124.6 (q, $^1J_{CF}$ = 273 Hz, CF_3 of $BAr^f{}_4{}^-$), 128.9 (q, $^2J_{CF}$ = 34 Hz, meta C of $BAr^f{}_4{}^-$), 134.8 (ortho CH of $BAr^f{}_4{}^-$), ipso C of $BAr^f{}_4{}^-$ and CO signals not observed. IR (thf): ν(CO) 1974, 1958, 1922 cm^{-1}. MS (EI): *m/z* 609.0 (75%) [M − thf]$^+$, correct isotope distribution for 2 Fe and 1 In atoms. Exact mass: calcd for [M − thf]$^+$ 608.9876, found 608.9874.

(iii) Crystallographic and Computational Methods. Data for compounds **7**, **8**, **10**, and **14** were collected on an Enraf-Nonius Kappa CCD diffractometer; data collection and cell refinement were carried out using DENZO and COLLECT and structure solution and refinement using SIR-92, SHELXS-97, and SHELXL-97; absorption corrections were performed using SORTAV.[11] With the exception of compound **7**, the structure of which was communicated previously,[7] the details of each data collection, structure solution, and refinement can be found in Table 1. 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 quality of the diffraction data for compound **8** is less than optimal, although the final structure (R1 = 9.44%) is sufficient to corroborate the inferences made on the basis of spectroscopic measurements and to confirm the linear, two-coordinate geometry at indium.

The computational approaches utilized both for geometry optimization processes and for the calculation of σ and π contributions to bonding densities were as reported previously for analogous investigations of transition-metal diyl and boryl complexes.[6,12]

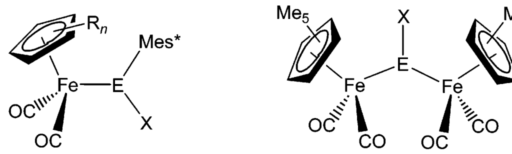
Results and Discussion

(i) Synthetic and Reaction Chemistry of Cationic Derivatives. Halide abstraction chemistry has been examined for a range of three-coordinate halogallium and -indium substrates (Chart 2), with a view to probing this route for the synthesis of cationic diyl and metalladiyl complexes. The success of this methodology in delivering tractable cationic derivatives containing gallium or indium donors can readily be demonstrated but is dependent both on the nature of the precursor complex and on the halide abstraction agent. Thus, Na[$BAr^f{}_4$] reacts readily with the three-coordinate bridg-

(11) (a) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1996; Vol. 276, p 307. (b) COLLECT: Data Collection Software; Nonius BV, Delft, The Netherlands, 1999. (c) SIR-92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343. (d) Sheldrick, G. M. SHELX97: Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1998. (e) SORTAV: Blessing, R. H. *Acta Crystallogr. Sect. A* **1995**, *51*, 33.

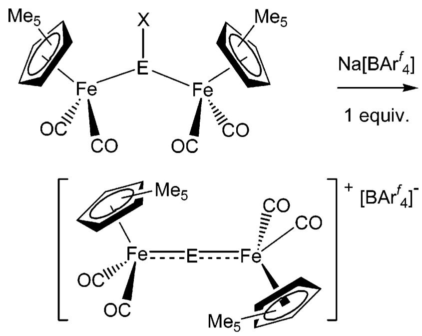
(12) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.

Chart 2 Precursor Systems for Halide Abstraction Chemistry Examined in This Study



1: E = Ga, R_n = H_5, X = Cl
2: E = Ga, R_n = Me_5, X = Cl
3: E = In, R_n = H_5, X = Br
4: E = Ga, X = Cl
5: E = In, X = Br
6: E = In, X = I

Scheme 2. Halide Abstraction Generating Cationic Trimetallic Systems

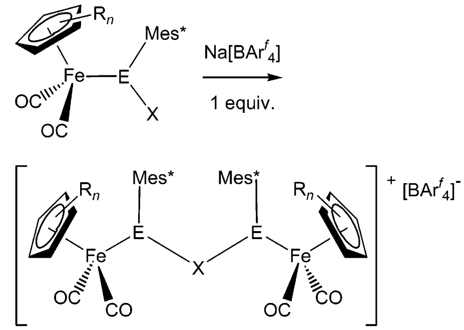


7: E = Ga
8: E = In

ing halogallane- and haloindanediyl complexes [Cp*Fe-$(CO)_2]_2$EX (**4**, E = Ga, X = Cl; **5**, E = In, X = Br; **6**, E = In, X = I). In the cases of **4** and **5** this reaction proceeds in dichloromethane over a period of ca. 2 h to give the expected cationic complexes $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-E})]^+$ (**7**, E = Ga; **8**, E = In) and sodium chloride/iodide (Scheme 2). The composition of the product in each case is implied by ^{1}H NMR and IR monitoring of the reaction, the former being consistent with a 2:1 ratio of Cp* and $[BAr^f_4]^-$ components and the latter revealing the shifts to higher wavenumber expected on formation of a cationic complex (2016, 1994, 1963 vs 1960, 1925, 1910 cm^{-1} for **7** and **4**, respectively; 2005, 1983, 1951 vs 1979, 1946, 1925 cm^{-1} for **8** and **5**, respectively). In both cases, the structures of **7** and **8** have been confirmed crystallographically and are consistent with base-free cationic two-coordinate group 13 systems (vide infra).

In the case of the reaction of the iodo-substituted indanediyl precursor **6**, an entirely different cationic organometallic product is isolated. Whereas abstraction chemistry with bromoindanediyl **5** proceeds as expected (to give **8**), the corresponding reaction with **6** leads to the formation of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-I})]^+[BAr^f_4]^-$ (**9**) in 15% isolated yield. **9** has been characterized by multinuclear NMR, IR, and mass spectrometry (including exact mass determination), and although the precise mechanism for its formation is not clear, indium metal is deposited during the reaction, and IR monitoring reveals that $Cp^*Fe(CO)_2I$ is an intermediate on the overall reaction pathway. In addition to the nature of the halide substituent, the identity of the abstraction agent is also vital to the course of subsequent reaction chemistry. Thus, the reaction of $[Cp^*Fe(CO)_2]_2GaCl$ (**4**) with $Na[BPh_4]$ leads to the formation of $Cp^*Fe(CO)_2Ph$ and BPh_3. Similarly, the course of the reaction of $[Cp^*Fe(CO)_2]_2InI$ (**6**) with $Na[BPh_4]$ is also consistent with the more reactive nature of the $[BPh_4]^-$ anion

Scheme 3. Halide Abstraction from Asymmetric (Supermesityl)halogallyl and -indyl Complexes: Syntheses of Halide-Bridged Dinuclear Species



10: E = Ga, R_n = H_5, X = Cl
11: E = Ga, R_n = Me_5, X = Cl
12: E = In, R_n = H_5, X = Br

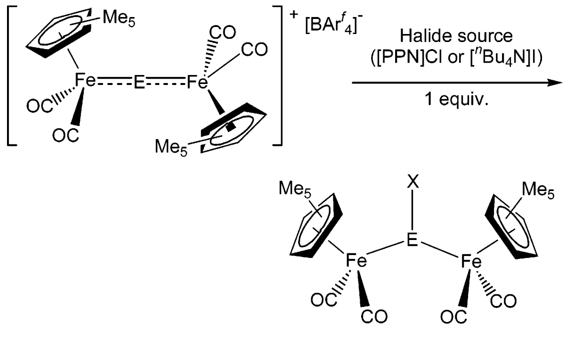
(compared to $[BAr^f_4]^-$). Thus, here too the presence of both BPh_3 and $Cp^*Fe(CO)_2Ph$ among the reaction products is indicative of abstraction of a phenyl group from the tetraphenylborate counterion.[13] Similar reactivity has been observed previously with highly electrophilic group 13 complexes of iron.[5] Consequently, $Na[BAr^f_4]$ has generally been preferred for halide abstraction chemistry, with reactions employing sources of the similarly weakly coordinating $[CB_{11}H_6Br_6]^-$ anion typically proceding at a significantly slower rate.

Similar abstraction methodology can be applied to the (aryl)halogallyl and -indyl precursors **1**−**3**. Given the success of this approach in the synthesis of a cationic aryl-substituted boranediyl complex featuring an isolated Fe═B double bond,[5] we were encouraged to examine the corresponding reactivity of analogous gallium and indium precursors. Complexes **1**−**3**, containing the extremely bulky supermesityl substituent, are readily accessible either by direct reaction of $[(\eta^5\text{-}C_5R_5)\text{-}Fe(CO)_2]^-$ with Mes^*EX_2 or (in the case of gallium) via a two-step process involving insertion of "GaI" into a M−X bond, followed by gallium-centered substitution (e.g. by Li[Mes*]) in the intermediate dihalogallyl $[L_nMGa(I)X]_2$.[7,8]

The reactions of Cp-substituted complexes **1** and **3** with $Na[BAr^f]_4$ proceed in a very similar fashion. Irrespective of reaction stoichiometry, time scale, or order of reagent addition, reaction of **1** with $Na[BAr^f_4]$ in dichloromethane yields the chloride-bridged dinuclear species $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-Cl})]^+[BAr^f_4]^-$ (**10**; Scheme 3). **10** presumably results from trapping of the highly electrophilic first-formed intermediate species $[CpFe(CO)_2Ga(Mes^*)]^+$ by a second equivalent of the chlorogallyl starting material **1**. The formulation of **10** is implied by ^{1}H NMR monitoring of the reaction in dichloromethane-d_2, which reveals a 2:1 ratio of Cp* and $[BAr^f_4]^-$ moieties. In addition, IR data shows the expected shifts to higher wavenumber in the carbonyl stretching bands (2016, 2002, 1972, 1954 vs 1999, 1952 cm^{-1} for **10** and **1**, respectively), and the structure of **10** was subsequently confirmed crystallographically. In a similar fashion, the reaction of the analogous bromoindyl complex $CpFe(CO)_2In(Mes^*)Br$ (**3**) with $Na[BAr^f_4]$ generates $[\{CpFe(CO)_2In(Mes^*)\}_2(\mu\text{-Br})]^+[BAr^f_4]^-$

(13) Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P. *Organometallics* **1995**, *14*, 4471.

Scheme 4. Reaction of Cationic Trimetallic Systems 7 and 8 with Sources of Halide Ions



4: E = Ga, X = Cl
6: E = In, X = I

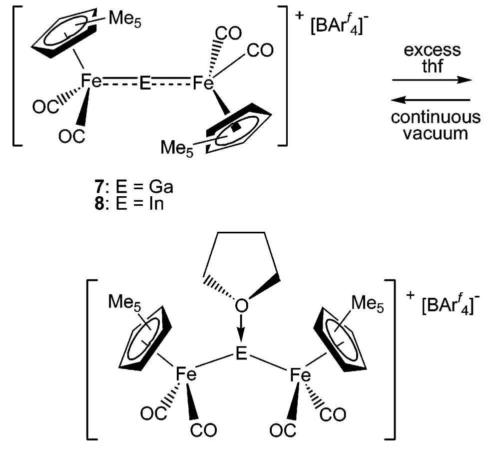
(**12**), which has been characterized by multinuclear NMR, IR, and mass spectrometry and which, by analogy with **10**, would be expected to have an In−Br−In bridged structure formed by trapping of the putative $[CpFe(CO)_2In(Mes^*)]^+$ by a further 1 equiv of **3**.

Given the extremely facile trapping of the putative diyl complexes $[CpFe(CO)_2E(Mes^*)]^+$ implied by the formation of **10** and **12**, a potential route to tractable mononuclear cationic systems involves the use of more sterically bulky and/or more electron releasing substituents at the metal center. The reactivity of Cp*Fe(CO)$_2$Ga(Mes*)Cl (**2**) toward Na[BAr$^f_4$] was therefore investigated. Despite the increased steric requirements of the Cp* ligand, however, the product isolated from this reaction (under a range of different conditions) is the analogous dinuclear compound $[\{Cp^*Fe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**11**). **11** has been characterized by multinuclear NMR, IR, and mass spectrometry, with the similarity in the *pattern* of carbonyl stretches compared to that of **10** (1996, 1986, 1954, 1932 vs 2016, 2002, 1972, 1954 cm^{-1} for **11** and **10**, respectively) and the 2:1 integrated ratio of the Cp* and $[BAr^f_4]^-$ signals in the ^{1}H NMR spectrum providing compelling evidence for a chloride-bridged structure analogous to **10**.

The fundamental reactivity of group 13 diyl and related complexes remains an area which has received relatively little attention,[3f,g] despite obvious parallels with carbenes, silylenes, and their heavier homologues,[14] and the range of interesting and useful reactivity in which these group 14 systems have been implicated. Initial studies of the reactivity of the prototype cationic boranediyl system $[Cp^*Fe(CO)_2B(Mes)]^+$ imply dominant electrophilic character, with anionic and/or neutral nucleophiles displaying a mixture of boron- and iron-centered reactivity.[5] A preliminary survey of the reactivities of two-coordinate metalladiyls **7** and **8** toward neutral and anionic two-electron donors implies that the group 13 center in each is somewhat less electrophilic than that in $[Cp^*Fe(CO)_2B(Mes)]^+$.

Both **7** and **8** react rapidly with sources of halide ions in dichloromethane solution (Scheme 4) to generate the (structurally characterized) bridging halogallane- and haloindanediyl complexes $[Cp^*Fe(CO)_2]_2EX$ (**4**, E = Ga, X = Cl; **6**, E = In, X = I) in a fashion similar to the boron-centered halide addition chemistry observed for $[Cp^*Fe(CO)_2B(Mes)]^+$. However, whereas the latter compound is sufficiently Lewis acidic to abstract fluoride from $[BF_4]^-$ and generate Cp*Fe(CO)$_2$B(Mes)F,[5b] the gallium-centered cation **7**, for example, is unreactive toward sources of $[BF_4]^-$ under similar conditions.

Scheme 5. Reversible Addition of Tetrahydrofuran to the Group 13 Center in 7 or 8



7: E = Ga
8: E = In
13: E = Ga
14: E = In

The reactivity of **7** and **8** toward *neutral* two-electron donors is also reflective of moderate Lewis acid character. Thus, in the presence of tetrahydrofuran, both cationic trimetallic species coordinate a single molecule of thf to generate the 1:1 adducts $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}E(thf)\}]^+[BAr^f]^-$ (**13**, E = Ga; **14**, E = In; Scheme 5), which can be isolated as pale yellow solids. In each case the 1:1 stoichiometry is implied by integration of the ^{1}H NMR signals due to thf and Cp* moieties, and coordination of the oxygen donor at the group 13 center is consistent with the significant shifts to lower wavenumber in the CO stretching bands (1978, 1962, 1927 and 2016, 1994, 1963 cm^{-1} for **13** and **7**, respectively; 1974, 1958, 1922 and 2005, 1983, 1951 cm^{-1} for **14** and **8**, respectively). Furthermore, in the case of **14**, the structure of the adduct has been confirmed crystallographically (vide infra).

The isolation of the Lewis base stabilized derivatives **13** and **14** contrasts markedly with the behavior of the cationic boranediyl complex $[Cp^*Fe(CO)_2B(Mes)]^+$, which reacts rapidly in the presence of neutral two-electron donors with rupture of the metal−group 13 linkage.[5b] Interestingly, the coordination of the thf donor in **13** and **14** appears to be reversible. Thus, upon prolonged exposure to continuous vacuum (10^{-4} Torr), spectroscopic data for both compounds are consistent with loss of coordinated thf. Monitoring of this process by IR and ^{1}H NMR spectroscopy reveals that, in the case of **13**, a mixture of the donor-stabilized complex and the "naked" two-coordinate species **7** is obtained. In the case of **14** complete loss of thf is observed over a period of 6 h, leading to the regeneration of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}In)]^+[BAr^f_4]^-$ (**8**). Such behavior is consistent with a relatively weak Lewis acid/base interaction in each case, with the apparently greater ease of removal of the indium-bound thf ligand being consistent with previous reports of the

(14) See, for example: (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Glaser, P. B.; Wanandi, P. W.; Tilley, T. D. *Organometallics* **2004**, *23*, 693 and references therein. For a review of related germylene and stannylene chemistry, see: (c) Petz, W. *Chem. Rev.* **1986**, *86*, 1019.

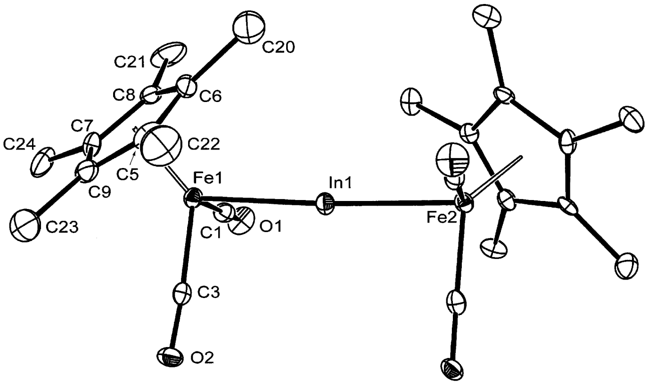


Figure 1. Structure of the cationic component of [{Cp*Fe-$(CO)_2$}$_2$(μ-In)]$^+$[BAr$^f_4$]$^-$ (**8**). Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)−In(1) = 2.460(2), Fe(2)−In(1) = 2.469(2), Fe(1)−Cp* centroid = 1.725(10), Fe(1)−C(1) = 1.757(13); Fe(1)−In(1)−Fe(2) = 175.32(6), Cp* centroid−Fe(1)−Fe(2)−Cp* centroid = 86.8(3).

thermodynamics of oxygen donor coordination to gallium- and indium-based Lewis acids.[15]

(ii) Spectroscopic, Structural and Computational Studies. Single-crystal X-ray diffraction studies were undertaken on compounds **7**, **8**, **10**, and **14**. With the exception of compound **7**, the structure of which has been communicated previously,[7] details of the data collection, structure solution, and refinement parameters for each compound 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.

Compounds **7** and **8** (Figure 1 and Table 1) represent extremely rare examples of structurally characterized species containing two-coordinate cationic gallium or indium centers. Previously reported examples typically feature extremely bulky hydrocarbyl substituents (e.g. [Ar_2Ga]$^+$),[16] and **7** and **8** represent the first examples containing metal−group 13 element bonds. In each case the geometry of the cationic component features a linear trimetallic unit (e.g. ∠Fe(1)−Ga(1)−Fe(2) = 178.99(2)° for **7**) in which the central group 13 atom engages in no significant intra- or intermolecular secondary interactions, for example with the [BAr$^f_4$]$^-$ anion. To our knowledge, the only other example of an isolated transition-metal complex featuring a "naked" bridging gallium or indium center is the neutral species [Cp*Fe(dppe)]-(μ-Ga)[Fe$(CO)_4$], reported by Ueno and co-workers in 2003.[17−20] Like **7** and **8**, this complex also features a near-linear coordination geometry at the group 13 center (176.01(4)°),[17] in marked contrast to the bent frameworks typically found for base-stabilized analogues such as [{CpFe$(CO)_2$}$_2${μ-Ga(bipy)}]$^+$ and [Cp*Fe-$(CO)_2$]{μ-Ga(bipy)}[Fe$(CO)_4$] (132.81(5) and 136.68(2)°, respectively).[17,21]

Of significant interest are the Fe−E bond lengths for **7** and **8** (2.266(1), 2.272(1) and 2.460(2), 2.469(2) Å, respectively). These can be compared to the analogous bond lengths found for the bridging halogallane- and haloindanediyl precursors [Cp*Fe$(CO)_2$]$_2$EX (2.352(1) and 2.513(3), 2.509(3) Å for **4** (E = Ga, X = Cl) and **5** (E = In, X = Br), respectively[7,8]) and for three- or four-coordinate base-stabilized cationic systems (e.g. 2.397(2), 2.404(1) and 2.494(2), 2.498(2) Å for [{CpFe$(CO)_2$}$_2${μ-Ga(bipy)}]$^+$ and [{Cp*Fe$(CO)_2$}$_2${μ-In(thf)}]$^+$, respectively (vide infra)).[21] In the case of gallium compound **7**, the shortening with respect to the single bonds found in **4** (ca. 3.5%) places the Fe−Ga distance in the region of values previously reported for two-coordinate gallium-containing systems.[4,17] Thus, the Fe−Ga bond lengths reported for [Cp*Fe(dppe)](μ-Ga)[Fe$(CO)_4$] are 2.248(1) and 2.293(1) Å,[17] with the former distance (for the Cp*Fe(dppe)Ga unit) being described as indicative of "significantly unsaturated character". Clearly the Fe−Ga bond shortening observed on halide abstraction from **4** (to give **7**) is consistent with both steric and electronic factors: i.e., with a reduction in the coordination number at gallium and/or with an increase in the extent of Fe→Ga back-bonding. The extent of bond shortening accompanying the halide abstraction process is significantly less in the case of indium complex **8** (<2% with respect to **6**). This observation is also consistent with both underlying steric and electronic factors: i.e., both the extent of Fe→E back-bonding and the relief of steric strain are likely to be less pronounced in the case of **8**, due to the longer Fe−E linkages. A further point of interest concerning the structures of cations **7** and **8** is the relative alignment of the two [Cp*Fe$(CO)_2$] fragments. In each case the Cp* centroid−Fe(1)−Fe(2)−Cp* centroid torsion angle is close to 90° (e.g. 84.6(1)° for **7**). Given the presence of two formally vacant mutually perpendicular p orbitals at the group 13 center, such an alignment allows in principle for optimal π back-bonding from the HOMO of each of the two [Cp*Fe-$(CO)_2$]$^+$ fragments.[22]

Of significant interest from a comparative viewpoint are the metalloheterocumulene complexes of the type [(η^5-C_5R_5)Mn$(CO)_2$]$_2$(μ-E) (E = Ge, Sn), reported by a number of groups, including those of Hüttner and Herrman.[23] Indeed, the Ge and Sn compounds of this type, which have been described as featuring Mn=E double bonds, are formally isoelectronic with the cationic components of **7** and **8**, respectively. Furthermore, the structural parameters for the crystallographically characterized species [Cp*Mn$(CO)_2$]$_2$(μ-Ge) are remarkably

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(18) For an example of a metal cluster containing near linear M−Ga−M units, see: Scheer, M.; Kaupp, M.; Virovets, A. V.; Konchenko, S. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5083.

(19) For a related boron-containing system, see: Braunschweig, H.; Radacki, K.; Scheschkewitz, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1658.

(20) For cationic compounds containing two-coordinate thallium see, for example: (a) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 4123. (b) Jeffery, J. C.; Jelliss, P. A.; Liao, Y.-H.; Stone, F. G. A. *J. Organomet. Chem.* **1998**, *551*, 27. (c) Catalano, V. J.; Bennett, B. L.; Kar, H. M.; Noll, B. C. *J. Am. Chem. Soc.* **1999**, *121*, 10235. (d) Catalano, V. J.; Bennett, B. L.; Yson, R. L.; Noll, B. C. *J. Am. Chem. Soc.* **2000**, *122*, 10056.

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Table 2. Calculated and Crystallographically Determined Structural Parameters for the Cationic Components of $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+[BAr^f_4]^-$ (7, E = Ga; 8, E = In)

compd	Fe−E dist (Å)	Fe−E−Fe angle (deg)	Ct−Fe−Fe−Ct torsion angle (deg)	σ:π break-down	E_{rel} (kcal mol^{-1})^a
7 (exptl)	2.266(1), 2.272(1)	178.99(2)	84.6(1)		
7 (calcd)	2.338, 2.337	177.93	86.5	61:38	0
8 (exptl)	2.460(2), 2.469(2)	175.32(6)	86.8(3)		
8 (calcd)	2.463,2.463	179.40	161.8	74:26	0
8 (calcd)	2.469, 2.469	179.87	82.8	74:26	+1.78

^{a} Calculated energy relative to minimum energy conformation.

similar to those for **7** (d(Mn−Ge) = 2.18(2) Å; ∠Mn−Ge−Mn = 179(1)°; centroid−Mn−Mn−centroid torsion angle 83(3)°).[23b]

In an attempt to determine whether these structural observations (i.e. the shortening in Fe−E bond lengths on halide abstraction, the orthogonal alignment of $[Cp^*Fe(CO)_2]^+$ fragments, and the close relationship of the structures of $[Cp^*Mn(CO)_2]_2(\mu\text{-Ge})$ and **7**) are related to any Fe−E multiple-bond character, and to relate any trends in bonding to the nature of the group 13 element E, DFT analyses were carried out on compounds **7** and **8** using methods described previously.[6,12]

DFT calculations were carried out at the BLYP/TZP level, and salient parameters relating to the fully optimized geometries of $[\{Cp^*Fe(CO)_2\}_2E]^+$ (E = Ga, In) are detailed in Table 2. In the case of $[\{Cp^*Fe(CO)_2\}_2Ga]^+$, the agreement between calculated and experimentally derived geometric parameters is very good, with the near-linear Fe−Ga−Fe trimetallic framework and near-orthogonal alignment of the $[Cp^*Fe(CO)_2]$ fragments being accurately reproduced computationally. The 2−3% overestimate in the calculated Fe−Ga bond lengths mirrors that found for related diyl systems and has been ascribed to solid-state effects, leading to the shortening of donor/acceptor bonds accompanied by a general overestimate in bond lengths by generalized gradient approximation (GGA) methods.[6,12,24] In the case of $[\{Cp^*Fe(CO)_2\}_2In]^+$, the minimum energy conformation calculated by DFT corresponds to a centroid−Fe−Fe−centroid torsion angle of 161.8°, in contrast to the experimentally determined value of 86.3(3)°. Closer inspection, however, reveals that there is a very shallow potential energy surface for rotation about this axis (see the Supporting Information for a complete rotational profile) and that the energy difference between the minimum energy conformer and that corresponding to the approximately orthogonal alignment found in the solid state is very small (e.g. ΔE = 1.78 kcal mol^{-1} between rotamers, corresponding to torsion angles of 161.8 and 82.4°). σ and π contributions to the overall Fe−In bonding density have therefore been calculated for both of these conformations.

A bond population analysis for $[\{Cp^*Fe(CO)_2\}_2Ga]^+$ carried out using a widely precedented method reveals a 61:38 σ:π breakdown of the covalent Fe−Ga interaction,[6,12] which can be put in context by comparison with a ratio of 86:14 for the formal Fe−Ga single bond in the model compound $CpFe(CO)_2GaCl_2$.[6,25] Using the same approach, corresponding values of 62:38 have been calculated for the iron to boron linkage in $[Cp^*Fe(CO)_2(BMes)]^+$. Further evidence for a significant Fe−Ga π component in $[\{Cp^*Fe(CO)_2\}_2Ga]^+$ is provided by the orbitals HOMO-3 to HOMO-6, each of which features in-phase contributions from gallium- and iron-centered π symmetry orbitals (Ga 4p_x and 4p_y; Fe 3d_{xz} and 3d_{yz}). Similar analyses for the indium-centered cation $[\{Cp^*Fe(CO)_2\}_2In]^+$ are consistent with a significantly smaller π contribution to the metal−group 13 element bond. Thus, the σ:π breakdown in this case is 74:26 (for both conformations corresponding to torsion angles of 82.4 and 161.8°); these values can be compared to an 11% calculated π contribution for the formal Fe−In single bond in the model compound $CpFe(CO)_2InCl_2$.[25] The significantly smaller π contribution for E = In than for E = Ga is as expected on the well-precedented basis of diminished π orbital overlap for the heavier main-group elements.[26] In addition, although the barrier to rotation about the Fe−In−Fe axis is not a direct measure of π bond strength (rather the difference in π contributions between 0 and 90° orientations), the relatively flat potential function for rotation about his bond is consistent with the similar (and relatively low) π contributions calculated for both conformations.

An X-ray diffraction study has also been carried out on the thf-stabilized complex $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-In(thf)}\}]^+[BAr^f_4]^-$ (**14**), with the results being displayed in Figure 2 and Table 1. This is consistent with the 1:1 stoichiometry and indium-coordinated thf donor implied by spectroscopic data. The indium center is trigonal planar (sum of angles at indium 360.0(3)°), and the approximately orthogonal alignment of Fe_2In and OC_2 planes (torsion Fe(1)−In(1)−O(5)−C(57) = 80.0(4)°) is presumably enforced on steric grounds. As expected, given the relatively small π component determined for the Fe−In bonds in base-free **8**, there is only a relatively minor lengthening of these linkages on coordination of the thf molecule (2.498(2), 2.494(2) vs 2.460(2), 2.469(2) Å for **14** and **8**, respectively). **14** represents only the second structurally characterized cationic three-coordinate indium species and the first containing bonds to a transition metal,[27] although related N-donor-stabilized gallium complexes of the type $[(L_nM)_2GaD_2]^+$ have previously been reported.[21,28] The Fe−In−Fe angle (156.72(6)°) is somewhat wider than that found in $[\{CpFe(CO)_2\}_2\{\mu\text{-Ga(bipy)}\}]^+$, presumably reflecting not only the longer Fe-E bonds for E = In but also the lower coordination number at the group 13 center in **14** (i.e.

(23) For examples of metalloheterocumulene complexes of the type $L_nM{=}E{=}ML_n$ (E = Ge, Sn), see: (a) Gäde, W.; Weiss, E. *J. Organomet. Chem.* **1981**, *213*, 451. (b) Korp, J. D.; Bernai, I.; Horlein, R.; Serrano, R.; Herrmann, W. A. *Chem. Ber.* **1985**, *118*, 340. (c) Herrman, W. A.; Kneuper, H. J.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 437. (d) Ettel, F.; Hüttner, G.; Imhof, W. *J. Organomet. Chem.* **1990**, *397*, 299. (e) Ettel, F.; Hüttner, G.; Zsolnai, L.; Emmerich, C. *J. Organomet. Chem.* **1991**, *414*, 71.

(24) See, for example: (a) McCullough, E. A., Jr.; Aprà, E.; Nichols, J. *J. Phys. Chem. A* **1997**, *101*, 2502. (b) MacDonald, C. A. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12113. (c) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571. (d) Giju, K. T.; Bickelhaupt, M.; Frenking, G. *Inorg. Chem.* **2000**, *39*, 4776. (e) Uddin, J. Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683.

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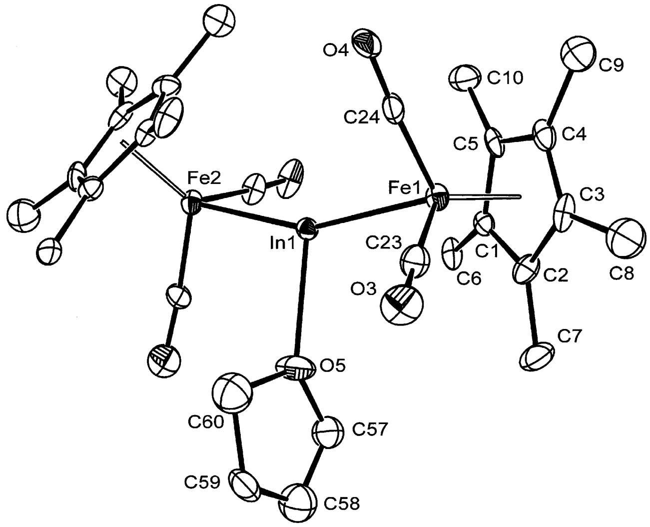

Figure 2. Structure of the cationic component of $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}In(thf)\}]^+[BAr^f_4]^-$ (**14**). Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)−In(1) = 2.498(2), Fe(2)−In(1) = 2.494(2), Fe(1)−Cp* centroid = 1.729(12), Fe(1)−C(23) = 1.748(13); Fe(1)−In(1)−Fe(2) = 156.72(6), Fe(1)−In(1)−O(5) = 100.1(3), Fe(2)−In(1)−O(5) = 103.2(3), Fe(1)−In(1)−O(5)−C(57) = 80.0(4).

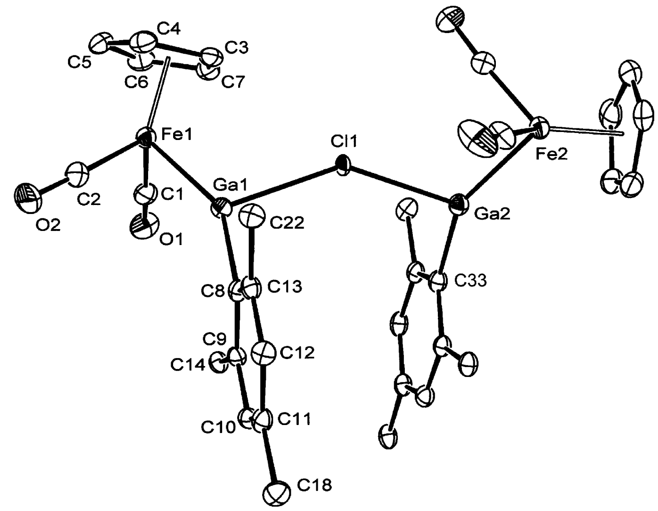

Figure 3. Structure of the cationic component of $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**10**). Hydrogen atoms and ^tBu methyl groups have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (deg): Fe(1)−Ga(1) = 2.333(1), Fe(2)−Ga(2) = 2.328(1), Fe(1)−Cp* centroid = 1.724(4), Fe(1)−C(1) = 1.755(4), Ga(1)−Cl(1) = 2.552(1), Ga(2)−Cl(1) = 2.476(1); Fe(1)−Ga(1)−C(8) = 149.07(8), Fe(2)−Ga(2)−C(33) = 150.50(9), Ga(1)−Cl(1)−Ga(2) = 142.16(3).

3 vs 4).[21] Furthermore, this angle is significantly wider than that found in the charge-neutral bridging haloindanediyl complexes $[Cp^*Fe(CO)_2]_2InX$ (141.46(1), 141.98(2)° for **5** (E = Br) and **6** (E = I), respectively), despite the greater steric demands of thf (cf. Br^- or I^-).[7,8] This phenomenon has previously been observed for a range of group 13 adducts. Thus, for example, the Cl−Ga−Cl angles in $GaCl_3$·thf (113.07° (mean)) are significantly wider than those in the corresponding Cl^- adduct (109.5° (mean)).[29]

An X-ray diffraction study has also confirmed the chloride-bridged structure of $[\{CpFe(CO)_2Ga(Mes^*)\}_2(\mu\text{-}Cl)]^+[BAr^f_4]^-$ (**10**; see Figure 3 and Table 1). The synthesis of **10** is viewed as being due to the trapping of the putative cationic gallanediyl $[CpFe(CO)_2Ga(Mes^*)]^+$ by a second equivalent of the precursor $CpFe(CO)_2Ga(Mes^*)Cl$ (**1**). Thus, the structure of **10** can be viewed as a base-stabilized gallanediyl complex, in which the gallium-coordinated donor is the bridging chloride ligand. In common with other base-stabilized diyl complexes, the metal−group 13 distance is more akin to that expected for related single bonds rather than for unsaturated species (e.g. 2.333(1), 2,328(1) and 2.346(1) Å for **10** and **1**, respectively).[7,8] By comparison, an Fe−Ga distance of 2.416(3) Å has been reported by Fischer and co-workers for base-stabilized $(OC)_4FeGaMe(tmpa)$ (tmpa = $Me_2NCH_2CH_2CH_2NMe_2$), compared with 2.225(1) Å for two-coordinate $(OC)_4FeGaAr$ (Ar = 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_3$).[4,30] In contrast, the structural effects of the abstraction and Ga−Cl−Ga bridge formation processes are much more pronounced on the Ga−Cl bonds and on the Fe−Ga−C_{ipso} angles. Thus, the bridging nature of the remaining chloride substituent is reflected in markedly longer Ga−Cl bond lengths (2.476(1), 2.552(1) and 2.272(1) Å for **10** and **1**, respectively), which in turn allows for significant opening out of the Fe−Ga−C_{ipso} angle (149.07(8), 150.50(9) and 139.18(10)° for **10** and **1**, respectively).

Conclusions

Halide abstraction chemistry has been demonstrated to offer a viable synthetic route to cationic two-coordinate complexes featuring the heavier group 13 elements gallium and indium as donor atoms. Thus, the linear trimetallic species $[\{Cp^*Fe(CO)_2\}_2(\mu\text{-}E)]^+$ (**7**, E = Ga; **8**, E = In) featuring naked bridging gallium or indium atoms can be synthesized by the reaction of the corresponding chloro- or bromo-substituted bridging diyl complexes with $Na[BAr^f]_4$. Analogous reactions utilizing the supermesityl-substituted gallyl or indyl precursors of the type $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)X$, on the other hand, lead to the synthesis of halide-bridged species of the type $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)\}_2(\mu\text{-}X)]^+$, presumably by trapping of the highly electrophilic putative cationic diyl complex $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(Mes^*)]^+$. Ongoing further attempts to modify these systems, e.g. by the introduction of bulky, strongly σ-basic phosphine ligands at the group 8 metal center, are aimed at the isolation of such cationic gallane- and indanediyl systems.

Preliminary studies have shown complexes **7** and **8** to be reactive toward both anionic and neutral nucleophiles, although the reversible coordination of thf is indicative of surprisingly weak Lewis acidic behavior. Structural, spectroscopic, and computational studies performed for **7** are consistent with appreciable Fe−Ga π-bonding character, as proposed for the only other previously reported example of a trimetallic system featuring a naked bridging gallium atom. The analogous

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indium-bridged complex **8**, in contrast, is shown both by structural and quantum chemistry methods to feature a much smaller π component to the metal−ligand interaction.

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Supporting Information Available: Complete details of the crystal structures of compounds **7**, **8**, **10**, and **14**, details of the DFT derived (fully optimized) geometries of the cations $[\{Cp^*Fe(CO)_2\}_2E]^+$ (E = Ga, In), and NMR spectra for all compounds (as evidence for bulk purity). This material is available free of charge via the Internet at http://pubs.acs.org. Crystal data for **7**, **8**, **10**, and **14** have also been deposited with the Cambridge Structural Database.

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