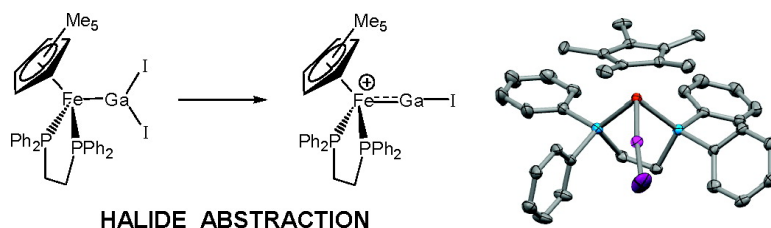## Communication

A Group 13/Group 17 Analogue of CO and N: Coordinative Trapping of the GaI Molecule

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A Group 13/Group 17 Analogue of CO and N₂: Coordinative Trapping of the GaI Molecule

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The fundamental changes in electronic structure which accompany coordination of a diatomic molecule to a transition metal center have been exploited to great effect,[1] both in the activation of inherently inert molecules (such as dinitrogen, N_2)[2] and in the isolation and characterization of otherwise short-lived species (e.g., CS, CSe).[3,4] Relevance to the biological conversion of dinitrogen to ammonia led to the isolation of the first N_2 complexes in 1965;[5] by contrast, the stronger metal–ligand bonds formed by the isoelectronic CO molecule underpin its widespread exploitation in low-oxidation state transition-metal chemistry (ca. 35 000 structurally characterized examples).[6] Extending this isoelectronic analogy one step further, diatomic molecules of the type EX (E = group 13 element, X = group 17 element), although predicted to be inherently less stable in the "free" state (due to small HOMO/LUMO gaps), are thought to offer even more favorable thermodynamics of binding to metal centers.[7–9] However, the complexes so formed, $L_nM(EX)$, are also expected to be extremely reactive, owing to the build-up of positive charge at the group 13 element, E.[7–10] Superficially, this reflects not only the inherent disparity in electronegativities between group 13 and group 17 elements, but also the removal of further electron density from E on coordination to the transition metal. From a practical perspective, a more pertinent (synthetic) obstacle is the lack of readily available sources of diatomic EX molecules. While N_2 and CO are stable diatomic gases, BX (X = F, Cl), AlX (X = F, Cl, Br, I), and GaX (X = Cl, Br, I) are known (as donor-free species) only under conditions of extreme temperature, with problems stemming from disproportionation or aggregation inherent at (or close to) room temperature.[11–14] Thus, to date, coordinative trapping of a simple diatomic molecule EX—and investigation of its electronic structure—has yet to be achieved.[10]

While synthetic methodologies based on coordination of the "free" EX molecule seem likely to flounder, we have sought to exploit an alternative approach, that is abstraction of a halide anion (X⁻) from a pre-exisiting metal complex of the type $L_nM(EX_2)$. Our choice of the metal/ligand fragment, L_nM, targets a sterically hindered, electron-rich metal center (in this case $[(\eta^5\text{-}C_5R_5)M(PR_3)_2]^+$ where M = a group 8 metal), of a type which is known to bind both CO and N_2 molecules,[15,16] and which is likely to offer both steric and electronic protection of the coordinated EX ligand.[17] Herein we report the synthesis

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Scheme 1. Synthesis of Cationic Iodogallylene Complex **2** by Iodide Abstraction
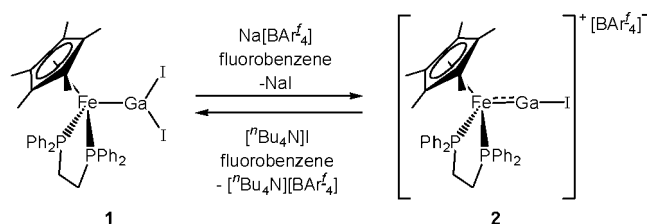
of the compound $[Cp*Fe(dppe)(GaI)]^+[BAr^f_4]^-$ $[Cp* = \eta^5\text{-}C_5Me_5$; dppe = $Ph_2PCH_2CH_2PPh_2$; $Ar^f = C_6H_3(CF_3)_2\text{-}3,5]$, which features a terminally bound GaI ligand and therefore represents the first experimental realization of a valence isoelectronic group 13/group 17 analogue of CO and N_2.

The salt metathesis reaction between $Cp*Fe(dppe)(GaI_2)$ (**1**) (itself prepared from $[Cp*Fe(CO)_2GaI_2]_2$ and dppe under photolytic conditions) and the sodium salt of the weakly coordinating anion $[BAr^f_4]^-$ proceeds quantitatively in fluorobenzene solution (as evidenced by ^{31}P NMR monitoring) to a single phosphorus-containing compound (see Scheme 1).

Similar monitoring of the reaction by ^1H NMR in perdeuteriofluorobenzene is consistent with the formation of a single organometallic product containing the Cp* ligand. Crystallization from a mixture of fluorobenzene and hexanes (ca. 1:10) at −30 °C leads to the isolation of $[Cp*Fe(dppe)(GaI)]^+[BAr^f_4]^-$ (**2**) in 35% isolated yield. The constitution of **2** has been unambiguously established by a combination of multinuclear (^1H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P) NMR, UV–vis and FT-Raman spectroscopies, positive-ion electrospray mass spectrometry (including exact mass measurement, isotopic profiling, and MS–MS fragmentation analysis of the molecular ion peak at $m/z = 785$ (100%)), and by single crystal X-ray diffraction.[18,19]

The structure of **2** determined crystallographically in the solid state is shown in Figure 1. Disorder within the structure was successfully modeled in terms of two cationic species; the major component (79%) features discrete $[Cp*Fe(dppe)(GaI)]^+$ and $[BAr^f_4]^-$ ions, with no short secondary interactions involving the Fe–Ga–I unit (within standard van der Waals contacts). Key structural features are the essentially linear arrangement of the iron, gallium, and iodine atoms $\angle Fe–Ga–I = 171.37(3)°]$ typical of a terminally bound diatomic ligand {cf. $\angle Fe–C–O = 175.8(5)°$ for $[Cp*Fe(dppe)(CO)]^+[PF_6]^-\}$,[15] and the extremely short Fe–Ga [2.2221(6) Å] and Ga–I [2.4436(5) Å] distances. The metal–gallium distance is among the shortest
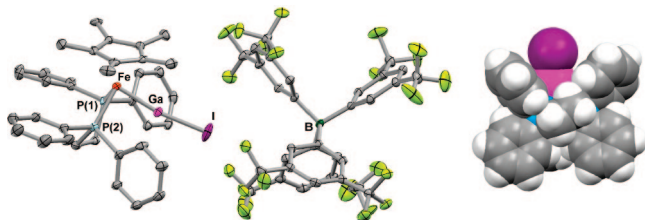
Figure 1. (left) Displacement ellipsoid drawing (50% probability level) of the major (79%) component of [Cp*Fe(dppe)(GaI)]$^+$[BAr$^f_4$]$^-$ (**2**). Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Fe–Ga, 2.2221(6); Ga–I, 2.4436(5); Fe–Ga–I, 171.37(3). (right) Space filling diagram of the cationic component of **2**: (gray) carbon, (white) hydrogen, (blue) phosphorus, (pink) gallium, (purple) iodine.

yet reported involving *any* transition metal (and the shortest involving iron); likewise the Ga–I distance is also the shortest yet reported.[6] Structural evidence also points to a soft bending deformation of the Fe–Ga–I bond, namely, large displacement ellipsoid amplitude for the iodine atom perpendicular to the Fe–Ga–I axis. Secondary off-axis electron density has been modeled as a minor (21%) cationic component featuring a markedly more bent Fe–Ga–I unit [148.92(5)°] and contacts between I′ and C(55)–C(58) of one of the [BAr$^f_4$]$^-$ aromatic rings which fall within the sum of the van der Waals radii of iodine and carbon. Large librational amplitudes at oxygen in related metal–carbonyl complexes are often associated with analogous Fe–C–O bending motions, and the ready deformation of the linear Fe–Ga–I fragment in **2** (and a small calculated

energy difference between the linear and bent geometries) is consistent with the smaller absolute magnitude of directional covalent contributions to the metal–ligand bond (vide infra).

A contributory factor to the short bond lengths in **2** is the low coordination number at gallium. Thus, a short Fe–Ga bond is also observed for two-coordinate (OC)$_4$FeGaAr [Ar = C$_6$H$_3$(C$_6$H$_2$^{i}Pr$_3$)$_2$–2,6; 2.2248(7) Å],[20] while longer bonds are measured for the three-coordinate precursor **1** [d(Fe–Ga) = 2.322 Å (mean); d(Ga–I) = 2.630 Å (mean)] and for the four-coordinate system [Cp*Fe(CO)$_2$GaCl(phen)]$^+$ [d(Fe–Ga) = 2.3047(4) Å; phen = 1,10-phenanthroline].[19,21] Potentially, a second factor underlying these short bonds is the presence of off-axis electronic contributions to the bonding, involving gallium-based orbitals of π symmetry. The contraction of the Fe–Ga bond on halide abstraction (ca. 4.3% for **2** compared to **1**) is markedly less than for analogous boron-containing systems (typically 9 – 10%),[22] for which descriptions incorporating Fe=B π bonds have been advanced for the cationic products.

That said, smaller changes in bond length as a function of bond order are typically found for the heavier main group elements,[23] and the Fe–Ga contraction between **1** and **2** mirrors that found between double and single bonds involving the adjacent group 14 element germanium (e.g., 4.7% between Mn–Ge and Mn=Ge bonds).[24] To better understand the bonding in the unprecedented ligand system present in **2** and to provide comparison of group 13/17 EX ligands with group 14/16 and group 15/15 counterparts, an in-depth computational
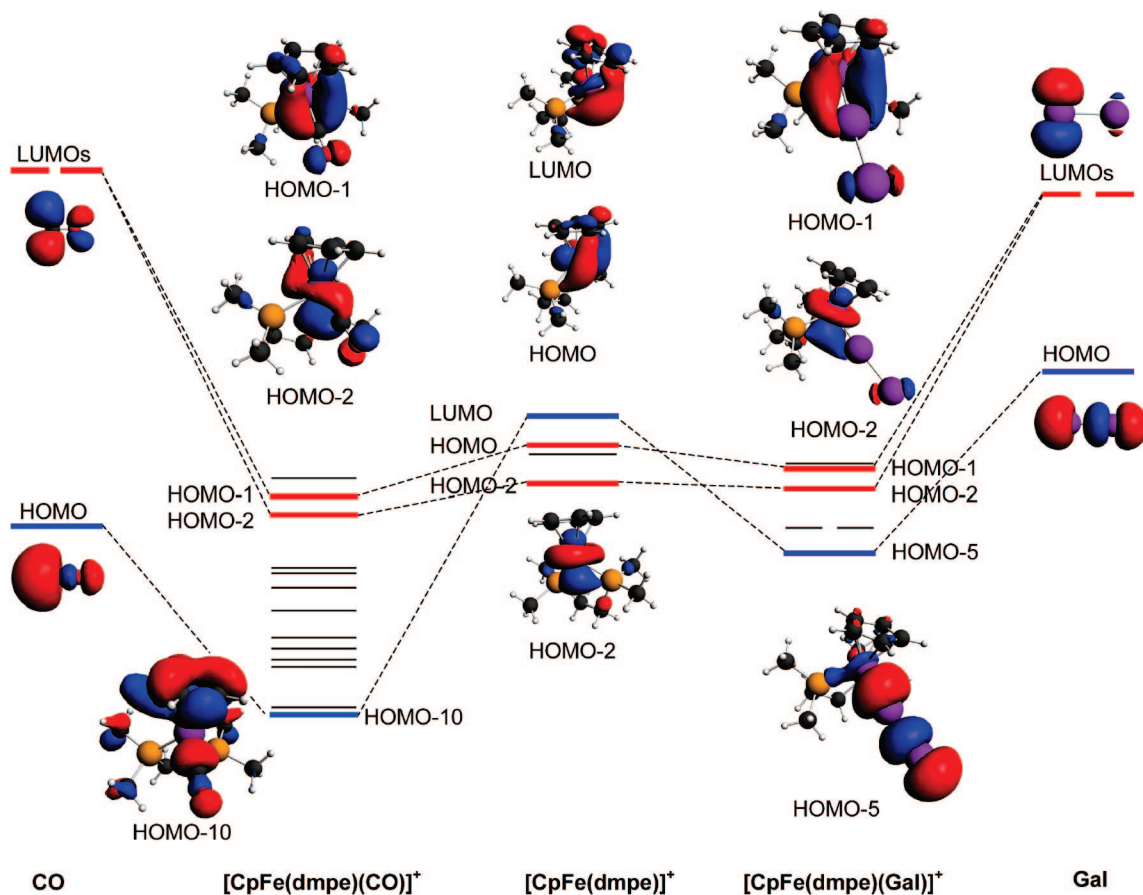

Figure 2. Molecular orbital energy level diagram for the model complexes [CpFe(dmpe)(CO)]$^+$ and [CpFe(dmpe)(GaI)]$^+$ showing correlation with the [CpFe(dmpe)]$^+$ and CO/GaI fragments. Local σ-symmetry interactions involving the LUMO of [CpFe(dmpe)]$^+$ and the HOMO of the CO/GaI ligand are shown in blue; π-symmetry interactions originating in the HOMO and HOMO-2 of [CpFe(dmpe)]$^+$ and the degenerate pair of LUMOs of CO/GaI are shown in red.

investigation of the bonding in **2** and related complexes was undertaken.

Density functional theory (DFT) analyses of electronic structure were carried out using the computationally efficient model systems $[CpFe(dmpe)(EX)]^+$ (EX = GaI, BF, CO, and N_2; Cp = η^5-C_5H_5; dmpe = $Me_2PCH_2CH_2PMe_2$), revealing for EX = GaI an essentially linear minimum-energy geometry ($\angle$Fe–Ga–I = 174.4 °) consistent with crystallographic studies. Moreover, a very shallow potential energy surface is found to be associated with the Fe–Ga–I bending deformation ($\Delta E < +3.5$ kJ mol^{-1} for $159 < \vartheta < 179°$, and $\Delta E = +11$ kJ mol^{-1} for $\vartheta = 149°$).[19]

From a bonding perspective, a breakdown of the covalent (orbital) components of the metal–ligand bonds of each of the four model compounds reveals notable similarities. In each case, orbital interactions of π symmetry are significant (representing 33 (GaI), 42 (BF), 39 (CO), and 38% (N_2) of the total covalent bonding density).[9] Moreover, the fragment correlation diagram for $[CpFe(dmpe)(GaI)]^+$ (Figure 2) reveals HOMO-5 ($E = -9.55$ eV) and HOMO-2/HOMO-1 ($E = -8.34, -7.95$ eV) orbitals consistent with Ga→Fe σ donor and Fe→Ga π back-bonding interactions, respectively. Despite this, the magnitude of the covalent (orbital) bonding component for the GaI complex (-236 kJ mol^{-1}) can be put into context by values of $-469, -397$, and -262 kJ mol^{-1} for the corresponding BF, CO, and N_2 complexes and by a value of -234 kJ mol^{-1} for the *electrostatic* contribution to the (highly polar) Fe–GaI bond. Presumably, despite the higher energy of the HOMO for GaI (-6.08 eV cf. -9.03 eV for CO; see Figure 2) and the greater localization of the LUMO at the donor atom, the weaker orbital contribution for GaI reflects (at least in part) the more diffuse nature of the 4s/4p derived orbitals at gallium and less effective interaction with the fragment orbitals of $[CpFe(dmpe)]^+$.[25]

Overall metal–ligand interaction energies [$\Delta E_{int} = -103$ (GaI), -285 (BF), -213 (CO), and -120 kJ mol^{-1} (N_2)][26] reveal significantly weaker binding of the GaI ligand than BF or CO,[7–9] which can consequently be displaced quantitatively from **2** by the addition of CO (at 1 atm pressure) to give $[Cp^*Fe(dppe)(CO)]^+[BAr^f_4]^-$. In the absence of such reagents, **2** is stable for weeks in fluorobenzene solution, presumably reflecting (i) effective steric shielding of the gallium center by the ancillary phosphine and Cp* ligands (Figure 1); (ii) a net cationic charge which retards the tendency toward dimerization found in putative charge-neutral systems;[27] and (iii) population of the LUMOs of the GaI molecule through π overlap with the HOMO and HOMO-2 of the $[Cp^*Fe(dppe)]^+$ fragment.

Supporting Information Available: Complete synthetic, spectroscopic, and structural data for compounds **1** and **2** (including mass spectra); details of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Synthetic procedure for **2**: To a suspension of $Na[BAr^f_4]$ (0.053 g, 0.060 mmol) in fluorobenzene (1 cm^3) at-30 °C was added an orange-red solution of **1** (0.049 g, 0.054 mmol) also in fluorobenzene (2 cm^3) and the reaction mixture warmed to room temperature over a period of 20 min. Monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed quantitative conversion of **1** (δ_P 103.9) to a single phosphorus containing species giving rise to a broad resonance at δ_P 87.0. The resulting deep violet solution was filtered and concentrated in vacuo and purple crystals suitable for X-ray diffraction were obtained by layering with hexanes and storage at-30 °C. Isolated yield, 0.031 g, 35%. Although NMR monitoring of the reaction is consistent with quantitative conversion of **1** to **2**, the lower isolated yield reflects mechanical losses associated with the recrystallization of the extremely air- and moisture-sensitive compound **2**. Spectroscopic data for **2**: ^1H NMR (C_6D_5F, 300 MHz): δ_H 1.18 (s, 15H, CH_3 of Cp*), 1.88 (m, 2H, CH_2 of dppe), 2.04 (m, 2H, CH_2 of dppe), 7.14–7.37 (overlapping m, 20H, aromatic CH of dppe), 7.54 (s, 4H, *para*-CH of anion), 8.27 (s, 8H, *ortho*-CH of anion). ^{13}C NMR (C_6D_5F, 76 MHz). (i) Signals due to cation: δ_C 9.2 (CH_3 of Cp*), 31.5 (m, CH_2 of dppe), 86.5 (quaternary carbon of Cp*), 128.0 (pseudo t, $J = 4.6$ Hz, *meta*-CH of dppe), 130.0 (pseudo t, $J = 4.6$ Hz, *meta*-CH of dppe), 129.1 (pseudo t, $J = 5.1$ Hz, *ortho*-CH of dppe), 131.8 (pseudo t, $J = 5.1$ Hz, *ortho*-CH of dppe), 130.4 (*para*-CH of dppe), 130.8 (*para*-CH of dppe), *ipso*-carbons of dppe not observed. (ii) Signals due to anion: 117.0 (sept, $J = 4.1$ Hz, *para*-CH of anion), 124.3 (1:3:3:1 q, $J = 272.1$ Hz, CF_3 of anion), 128.5 (1:3:3:1 q, $J = 29.8$ Hz, *meta*-carbon of anion), 134.4 (*ortho*-CH of anion), 161.9 (1:1:1:1 q, $J = 49.8$ Hz, *ipso*-carbon of anion). ^{11}B NMR (C_6D_5F, 96 MHz): δ_B 1.9. ^{19}F NMR (C_6D_5F, 282 MHz): δ_F -62.7. ^{31}P NMR (C_6D_5F, 122 MHz): δ_P 87.0. ES-MS (positive ion mode), *m/z*: 785.0 {100%, $[Cp^*Fe(dppe)(GaI)]^+$}, correct isotope pattern for $C_{36}H_{39}FeGaIP_2$. Exact mass: calcd for $[(\eta^5-C_5Me_5)Fe(dppe)(GaI)]^+$ (i.e., M$^+$) 785.0173; measured, 785.0204. FT-Raman (C_6D_5F solution): 186 cm^{-1}, ν(Ga-I) 100%. UV–vis (C_6H_5F solution): $\lambda_{max} = 549$ nm; $\epsilon = 754$ cm^{-1} mol^{-1} dm^3. Crystallographic data for **2**: $C_{68}H_{51}BF_{24}FeGaIP_2$, $M_r = 1649.3$, triclinic, $P\bar{1}$, $a = 12.582(1)$, $b = 14.204(2)$, $c = 19.828(2)$ Å, $\alpha = 83.458(1)$, $\beta = 73.203(1)$, $\gamma = 86.731(1)°$, $V = 3369.2(6)$ Å^3, $Z = 2$, $\rho_c = 1.626$ Mg m^{-3}, $T = 120(2)$ K, $\lambda = 0.6710$ Å (synchrotron); 37981 reflections collected, 19961 independent [R(int) = 0.0401], which were used in all calculations. $R_1 = 0.0575$, $wR_2 = 0.1388$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0931$, $wR_2 = 0.1571$ for all unique reflections. Maximum and minimum residual electron densities: 1.31 and-1.04 e Å^{-3}. CSD ref: 673697.
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