Coordination Chemistry

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GaI as Ligand in Transition-Metal Complexes—An Alternative to CO or N_2?

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CO analogues · coordination chemistry ·
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The diatomic molecules N_2 and CO have been extensively used as ligands in transition-metal complexes. The question about whether Group 13–17 diatomics (referred to here as EX) such as BF can likewise function as ligands has intrigued researchers for a long time. A method for the synthesis of (short-lived) BF on a preparative scale was already introduced in 1967; it involved the comproportionation reaction between BF_3 gas and boron at high temperatures.[1] However, only a few reports on reactions with BF (e.g. with C_2H_2) have appeared since then.[1] To date no transition-metal complex with a BF ligand has been described, although, according to quantum-chemical calculations a metal–BF bond should generally be stronger than the corresponding metal–CO bond.[2] The HOMO of BF lies at higher energy than that of the isolobal CO, and consequently a strong σ bond results. This, together with the low energy LUMO, is one of the reasons for the high reactivity towards nucleophilic attack at the positively polarized Group 13 element, which reduces the stability of the complex. Earlier this year, the synthesis of the first complex featuring an EX ligand, $[Cp^*Fe(dppe)(GaI)]^+[BAr^F_4]^-$ ($Cp^*=C_5Me_5$, dppe = 1,2-bis(diphenylphosphanyl)ethane, $Ar^F_4=3,5\text{-}(CF_3)_2C_6H_3$), was achieved.[3]

The preceding years saw considerable activity aimed at the development of synthetic routes to monovalent Group 13 element compounds and the exploration of their chemistry. Much of this work focussed on alkyl and silyl derivatives ER (E = B, Al, or Ga; R = alkyl, silyl), the stabilization of which was generally achieved by using sterically encumbered substituents R. Left alone these ER compounds tend to aggregate to clusters.[4] Thus, for example, with R = *t*Bu the tetrahedral borane cluster $B_4t\text{Bu}_4$[5] and a threefold capped trigonal-prismatic nonagallane cluster $Ga_9t\text{Bu}_9$[6] were obtained. Two general synthetic routes to ER transition-metal complexes were established:[7] the substitution of weakly bound ligands by compounds with monovalent aluminum, gallium, and indium, as well as the salt elimination between carbonyl metalates and halogen derivatives of Group 13 elements. ECp* can occur as a terminal or bridging ligand, as exemplified in the compounds $[Cp^*E{-}Fe(CO)_4]$ (E = B,[8] Al,[9] Ga[10]), $[Cp^*ECr(CO)_5]$ (E = Al,[11] Ga,[12] In,[13]), and $[(CO)_3Co(\mu^2\text{-}ECp^*)_2Co(CO)_3]$ (E = Al,[13] Ga[10]). As a consequence of the interaction with the η^5-coordinated Cp* ring the p orbitals at the atom E are, however, not empty, and are therefore not ideally suited for a possible π-backdonation from the transition-metal atom. Of course, the situation changes for σ-ccordinated alkyl, aryl, or silyl substituents. Among the various known complexes with terminal or bridging ER groups, the homoleptic $[Ni\{EC(SiMe_3)_3\}_4]$ (E = Ga, In) complexes are especially noteworthy.[14] Recently, the monomeric unit of the $B_4t\text{Bu}_4$ tetramer was stabilized in the form of the complex $[Cp(CO)_2Mn{-}Bt\text{Bu}]$ with a terminal bonding mode (see Figure 1).[15] A bridging B*t*Bu group is present in the diamagnetic dinuclear complex $[\{Cp(CO)_2Mn\}_2(\mu\text{-}Bt\text{Bu})]$ (Figure 1).[16] Recently, the experimental determination of the electron density distribution within this complex was achieved.[17] It was suggested that the compound is better described as a dimetallaborane rather than as a borylene complex. These results highlight the differences between BR and CO.

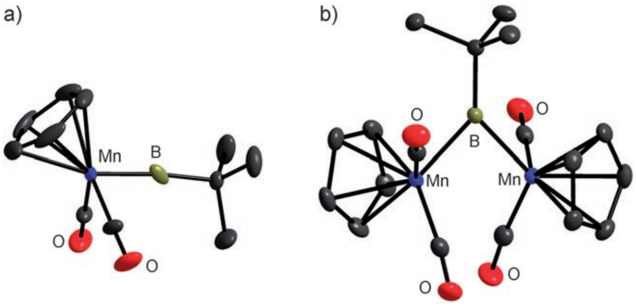

Figure 1. Molecular structures of the two compounds a) $[Cp(CO)_2Mn{-}Bt\text{Bu}]$ and b) $[\{Cp(CO)_2Mn\}_2(\mu\text{-}Bt\text{Bu})]$ with terminal and bridging B*t*Bu groups, respectively.

The synthesis of $[(CO)_4Fe{-}GaAryl]$ (Aryl = $2,6\text{-}(2,4,6\text{-}i\text{Pr}_3C_6H_2)_2C_6H_3$)[18]) initiated a controversial debate about the bonding in ER complexes. Whereas the free EAryl′ (Aryl′ = $2,6\text{-}(2,6\text{-}i\text{Pr}_2C_6H_3)_2C_6H_3$) forms a dimer with only one weak Ga–Ga bond,[19] the Ga–Fe bond in the $[(CO)_4Fe{-}GaAryl]$ complex is extremely short ($d_{Ga-Fe}=222.5$ pm). For compar-

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ison, in the corresponding {GaCp*} complex the Ga–Fe distance is 227.7 pm, and complexes with bridging GaR ligands usually display Ga–Fe distances of around 240 pm. DFT calculations[20] carried out for [(CO)$_4$Fe–Ga(η^5-Cp)] (Cp = cyclopentadienyl) and [(CO)$_4$FeGa(η^1-Ph)] are consistent with an increased Fe→Ga π-backbonding in the latter compound. The crucial factors for the short bond length, however, are the high polarity of the Ga–Fe bond and the low coordination number at the Ga atom. Thus complexes with terminal ER ligands can be stabilized if sterically encumbered substituents are used. But what happens if smaller groups are used? Already some time ago[21] the synthesis of a formal dimer of a gallium(I) organyl complex was reported, namely [{(CO)$_4$Fe–Ga(η^1-C$_2$H$_3$)(thf)}$_2$]. Also, motivated by their interesting functionalities, several GaCl complexes were synthesized by salt elimination starting from Na$_2$[M(CO)$_n$] (M = Fe, Cr) and GaCl$_3$. However, this was only achieved by additional stabilization from donors bound to the Ga atom. One such example is [(CO)$_4$Fe–GaCl(tmeda)] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[22] The polarity of the Ga–Fe bond favors a description that is best expressed by the formula [(CO)$_4$Fe^{2-} GaCl(L)$^{2+}$]. The lack of displacement reactions further supports this description. Because of the blocking of the p orbitals at the Ga atom by the donor, a significant π backdonation from the metal becomes virtually impossible. This also manifests itself in the significant increase of the Ga–Fe bond length ($d_{\text{Ga–Fe}} = 233.8$ pm) and in the lower wavenumbers of the CO stretching modes compared with those for [(CO)$_4$Fe–Ga(η^5-Cp*)] and [(CO)$_4$Fe–Ga(η^1-Aryl)].

It was only this year that a terminal coordination of ER substituents without the stabilizing effect of sterically encumbered substituents R was achieved, namely, the synthesis and characterization of the complex [(Cp*Ga)$_4$Rh(GaCH$_3$)]$^+$ [BAr$^F{}_4$]$^-$ [23] with terminal GaCH$_3$ groups. The necessary kinetic stabilization was ensured by the other complex ligands at the transition-metal center. Reaction of this complex with pyridine (py) gave [(Cp*Ga)$_4$Rh{Ga(CH$_3$)(py)}]$^+$[BAr$^F{}_4$]$^-$, in which the pyridine is bound to the Ga center. This reaction demonstrates the electrophilicity at the Ga atom, and motivates the description as a {Rh^{-I}Ga^{III}} complex. Furthermore, the salt [Cp*Fe(dppe)(GaI)]$^+$[BAr$^F{}_4$]$^-$ (Figure 2) was prepared by abstraction of iodine from [Cp*Fe(dppe)GaI$_2$] with Na[BAr$^F{}_4$] [see Eq. (1)].[6]

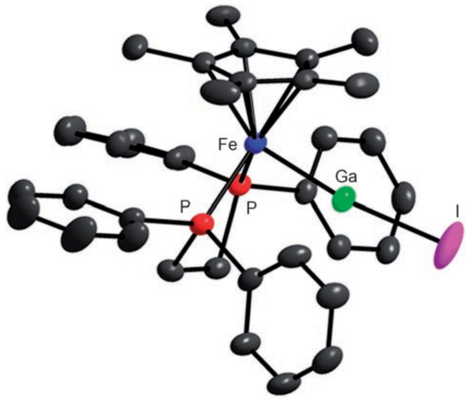
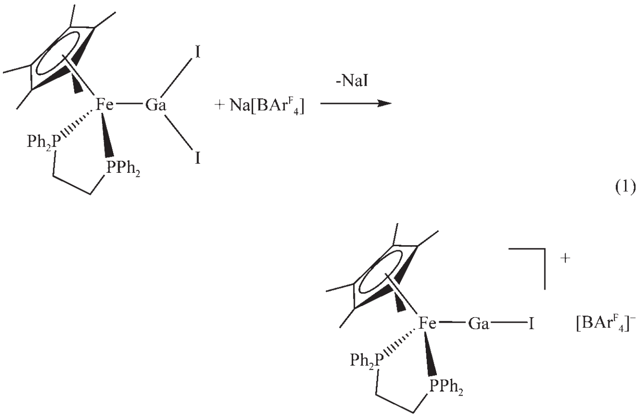


Figure 2. Molecular structure of the complex cation of the salt [Cp*Fe(dppe)(GaI)]$^+$[BAr$^F{}_4$]$^-$ with a terminal GaI group. Only the most abundant of the components in the crystalline phase (79%) is shown. The direction of the ellipsoid at the iodine atom points to a shallow Fe-Ga-I angle potential.



(1)

Quantum-chemical calculations performed for this complex indicate a significant covalent character of the Fe–Ga bond and π-bond contributions. This implies that π-backdonation from filled Fe d orbitals into the degenerate LUMO orbitals of GaI occurs, a situation similar to that for CO complexes. The Fe–Ga bond length is 222.21(6) pm; however, it was emphasized that a short distance does not automatically imply a large multiple bond character. According to quantum-chemical calculations, the Fe–Ga bond energy is significantly smaller than that for the corresponding BF or CO complexes. Although the results of initial calculations are consistent with partial double bond character for the metal–gallium bond, additional experimental as well as quantum-chemical studies are necessary to shed further light on the bonding situation in this and related complexes. Interestingly, the GaI ligand in [Cp*Fe(dppe)(GaI)]$^+$[BAr$^F{}_4$]$^-$ can be displaced by CO. This reaction is of interest not only with respect to the bonding situation, but could probably open up new access to the chemistry of subvalent Group 13 element halides.

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