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# Application of Density Functional Theory in Coordination Chemistry: A Case Study of Group 13 Monohalide as a Ligand

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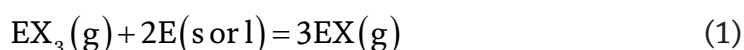
## Abstract

The chemistry of Group 13 Monohalide is of great interest due to its isoelectronic relationship with carbon monoxide and dinitrogen. In recent years, theoretical and experimental studies have been evolved on the group-13 atom-based diatomic molecules as a ligand. The synthetic, characterisation and reactivity of various metal complexes have been well discussed in recent reviews. The nature of the metal bonding of these ligands of various types has been explained in addition by the variety of theoretical studies (using DFT methods) such as FMO and EDA. This chapter has a comprehensive experimental and theoretical study of group 13 monohalides as a ligand in coordination chemistry.

**Keywords:** Group 13 Monohalides, Coordination Chemistry, DFT, FMO, BDE

## 1. Introduction

The monohalides of group 13 elements (EX) are an isoelectronic relationship with molecules like CO and N<sub>2</sub>. The separation of metal complexes containing monohalides of group 13 elements as ligands is made possible by the recent developments in synthetic chemistry and with the investigations on electronic structural analysis and the reactivity of the coordinated diatomic group 13 monohalides. In general, the +3 oxidation states of group 13 elements have dominated the chemistry of their compounds. The applications of these compounds like catalysis, sensing, etc., are due to their inherent Lewis acidic behaviour [1–3]. Research in group 13 elements having lower oxidation states have been normally influenced by clusters of boranes. The availability of sub-valent systems reflects on the development of the ground-breaking synthetic approach in organic synthesis and the applications of some reagents specifically sub-valent indium compounds. For example, the study of Schnoekel et al. approved to access metastable monohalides of aluminium and gallium, by utilising the entropic factor at a high temperature can be driven the equilibrium to the right and defined by Eq. (1) (E = B, Al, Ga, In and Tl) [4–14].



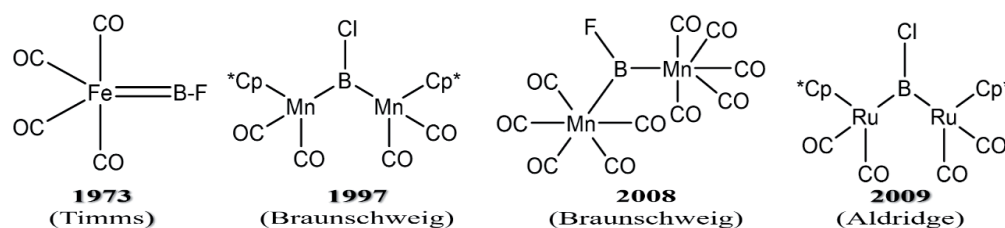
Sub-valent aluminium and gallium compounds can be accessed by consequential entrapping and derivatization. The formation of sub-valent group 13 compounds is proposed by the theory to mimic the accession of a similar state of the elements [8–21]. For separating the discrete molecular systems, chemistry in solution has taken advantage of sterically bulkier groups (amino, guanidinate,  $\beta$ -diketiminato, pentamethyl cyclopentadienyl, terphenyl groups) as an approach [15–17]. Also, the competency of monovalent systems E(I) having such molecules to behave as ligands in complexes for transition metal atoms has been recognised extensively for B, Al and Ga. In organometallic chemistry, group 13 elements have been an unexplored area, even it has an isoelectronic relationship with well-known CO and N<sub>2</sub> molecules. Even though the thorough comparative theoretical investigations on group 13 monohalides, there is no sufficient experimental data [15–17]. Such paucities naturally mimic the coordinated group 13 monohalide fragment's high polarity and low steric loading (as projected theoretically). This book chapter explores both synthetic and theoretical advances in the topic of group 13 monohalides in great depth.

## 2. Free molecules of boron (I) halides

In 1935, the properties of gaseous boron monofluoride synthesised from elemental boron and CaF using techniques such as high-temperature in situ method were reported. Since then, it has been studied using several spectral and thermal analyses [22–36]. BF was first synthesised on a preparative scale in 1967, based on Peter Timms' pioneering work to develop a proportionation pathway from BF<sub>3</sub> and elemental boron [37–39]. The boron trifluoride gas is passed through elemental boron at very high temperature (2000°C) and very low pressure (1 mmHg) and in a specially designed reactor [37]. In addition, while BF molecule in the vapour phase maintains its diatomic nature. A variety of BF-containing molecules (such as B<sub>8</sub>F<sub>12</sub>, B<sub>3</sub>F<sub>5</sub> and B<sub>2</sub>F<sub>4</sub>) [37, 40, 41] are then formed with the proportion based on the amount of BF<sub>3</sub> co-condensate. BF insertion into BF<sub>3</sub> produces B<sub>2</sub>F<sub>4</sub>, and BF insertion into B<sub>2</sub>F<sub>4</sub> produces B<sub>3</sub>F<sub>5</sub> [37]. Then, Timms reported how metastable boron monochloride can be prepared by cracking B<sub>2</sub>Cl<sub>4</sub> (which produces BCl<sub>3</sub> and BCl) or by reacting elemental boron with BCl<sub>3</sub> at a very high temperature [39, 42]. A laser-ablated boron atom reacts with its respective X<sub>2</sub> molecule, resulting in combinations of BX<sub>3</sub>, BX<sub>2</sub>, and BX. Matrix isolation offers a feasible way to capturing and interrogating diatomics. Microwave spectroscopy [35] produced a bond length of 1.26267 Å, as well as values for Do 757 kJ mol<sup>-1</sup> [36],  $\omega_e$  (1765 cm<sup>-1</sup>) [33], and the first ionisation energy 11.115 eV [29]. A similar approach was used to determine bond lengths for the BF, BCl and BI 1.715, 1.888, 2.131 Å respectively [1, 2]. Infrared spectroscopy reveals vibrational frequencies of 564 cm<sup>-1</sup> (<sup>11</sup>BI), 667/666 (<sup>11</sup>B<sup>79</sup>Br/<sup>11</sup>B<sup>81</sup>Br), 815/810 (<sup>11</sup>B<sup>35</sup>Cl/<sup>11</sup>B<sup>37</sup>Cl), and 1374 (<sup>11</sup>BF) for BX molecules separated in solid argon atmosphere [43]. Research with C<sub>2</sub>F<sub>4</sub> and SiF<sub>4</sub> has shown that even though the BF insertion is simple for B-F bonds, similar procedures have yielded traces of products with other E-F couplings. When BF is combined with soft donors (such as CO, AsH<sub>3</sub>, SMe<sub>2</sub>, PH<sub>3</sub>, PF<sub>3</sub> and PCl<sub>3</sub>) leads to the formation of (F<sub>2</sub>B)<sub>3</sub>B-L (general formula). Based on the crystallographic description of BCl is very similar to carbonyl complexes [42, 44]. In the presence of acetylene or propene, BF produced acyclic or cyclic products containing BF or BF<sub>2</sub> moieties [38], whereas when BF was combined with gaseous BCl, only cyclic compounds were produced.

### 3. Coordination chemistry of boron (I) halides

The boron monohalides used as ligands in organometallic complexes were examined in the context of theoretical approaches were reported since 1998 [15–17] (**Figure 1**). The bonding properties of isoelectronic species of CO, N<sub>2</sub> and BX (X = F – I) molecules were studied in particular. Based on the various proportion of the FMOs and energies of these molecules, BX will be a better sigma donor than CO or N<sub>2</sub>, as well as a similar  $\pi$ -acceptor, although the unbound molecule should have a smaller HOMO–LUMO gap due to stronger localization in the donor atom. In line with the broader focus of the synthetic endeavour, the related ligands BO and BNH<sub>2</sub> have undergone comparable computational research. It also has a set of non-degenerate p-type orbitals, which are similar to those found in the vinylidene (CCR<sub>2</sub>) ligand family. The exceptionally high energy of BO<sup>−</sup> means that it possesses no  $\pi$  acceptor characteristics, but it retains outstanding donor characteristics. It has been determined that BF and related metal complexes have very strong thermodynamic stability, despite heavily polar BF bonds and positive charge build-up at boron. Both methods have already been synthesised, and could be used to shield reactive boron centres: either by shielding with (NH<sub>2</sub> groups) BNR<sub>2</sub> or by incorporating haloborylene as a bridge between two metal sites [8–17]. In 2010, it was predicted that BF would adopt bridging modes of coordination ( $\mu_2$  or  $\mu_3$ ) in ruthenium bimetallic systems [45, 46]. Timms et al. synthesised and characterised a thermally unstable volatile complex [(F<sub>3</sub>P)<sub>4</sub>Fe(BF)] using IR and <sup>19</sup>F NMR spectroscopy [39]. Aldridge and his co-workers successfully synthesised the first fluoroborylene ruthenium complex [Cp<sub>2</sub>Ru<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -BF)] and characterised it by the X-ray diffraction method [47]. The earlier complex was synthesised using a stable source for the BF ligand (Et<sub>2</sub>O-BF<sub>3</sub>) and CpRu(CO)<sub>2</sub><sup>−</sup> (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>). The reaction with BX<sub>3</sub> and [NaMn(CO)<sub>5</sub>] was yielded the haloborylene complexes ( $\mu$ -BX)Mn<sub>2</sub>(CO)<sub>10</sub> [48]. It is very similar to the ruthenium complexes ( $\mu$ -BX)Mn<sub>2</sub>(CO)<sub>10</sub>. Several alkylborylene complexes were synthesised and characterised but studies on the haloborylene complexes were limited [49–51]. Several complexes synthesised with BX fragments attached with metal centres with additional Lewis base support structures [Cp<sup>\*</sup>Fe(CO)<sub>2</sub>{(4-pic)<sub>2</sub>BBr}]<sup>+</sup>Br<sup>−</sup> [52]. Hildendrand et al. synthesised bimetallic complex with manganese [{( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>}<sub>2</sub>( $\eta$ : $\eta$ : $\mu$ -B<sub>2</sub>Cl<sub>2</sub>)] [28]. The geometrical and bonding analysis of halo and alkylborylene complexes [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(BX)(CO)<sub>2</sub>] (M = Mn and Re; R = Et, iPr, Me and tBu; X = F – I) were studied theoretically in 2011 by K. K. Pandey et al., [53]. The steric stability of terminal haloborylene complexes, as well as the pi-electron contribution of the haloborylene ligands, play a significant role in their separation. A variety of alternative synthetic techniques have been developed in response to the shortage of group 13 monohalides, such as halide abstraction/ejection [54–56], metal–metal borylene transfer [57], borane dehydrogenation [58], and salt elimination [49, 50]. The strength of metal complexes depending on the



**Figure 1.**  
Development of boron monohalides based complexes.



coordination of the metal with highly reactive ligands. The difficult separation of metal complexes with highly reactive ligands such as BF drives a strong interest in synthetic approaches to these complexes [59–64]. According to recent studies, polar diatomic BF ligands bind to transition metal centres more effectively than CO ligands, with greater  $\sigma$ -donor and  $\pi$ -acceptor properties [17, 46, 65]. Due to the electron-withdrawing halogen atoms, the haloborylene ligands of metal complexes are particularly significant because they have potential  $\pi$ -acceptor characteristics [66]. The theoretical analysis will be the most appropriate way for understanding the bonding character of the metal borylene complexes [67–73]. The  $C_{3v}$  point group of  $[(CO)_3M-BX]$  complexes have been studied using DFT, as well as the interaction between CO and BX ligands, the covalent character of M-B bonds, and bonding donation to M-B bonds [18–21].

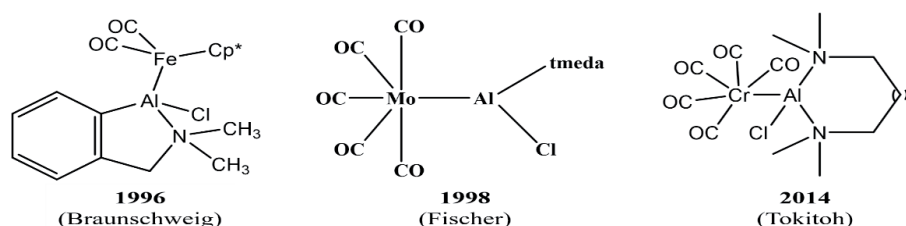
#### 4. Free molecules of the heavier group 13 metal monohalides

Aluminium and gallium monohalides belong to two groups: indium and thallium monohalides (excluding InF), which can be disproportionated into metal and metal trihalide under ordinary conditions, and indium and thallium trihalides, which are stable and commercially available [1, 2]. High temperature/low pressure give rise to entropically favoured Al (I) halides in the gas phase, which could be captured by inert gas matrices. In the gas phase, spectroscopic analysis of the AlX ( $X = F-I$ ) molecule show bond distances of 2.537, 2.295, 2.130 and 1.654 Å for Al-F to Al-I respectively [1, 2, 74–76], whereas in low-temperature matrices, symmetrical bridging halides,  $Al(\mu-Cl)_2Al$  and  $Al(\mu-F)_2Al$  predominate [77, 78]. The bond lengths of the gaseous GaX molecules corresponding to aluminium (1.774, 2.202, 2.352, and 2.575 Å, respectively) varied slightly, which is consistent with Ga(I) having a greater covalent radius [1, 2, 75, 76]. The metastable AlX solutions can be synthesised by using mixtures of AlX molecules and donor solvents like toluene [5–7, 59, 79, 80]. In the solid-state, there are no completely stable Ga (I) halides. GaI was first reported in 1955, and it was synthesised by vacuum heating Ga and I. Green reported a new synthesis of GaI in 1990, employing an ultrasonically activated Ga with iodine in  $C_6H_5CH_3$  [81], but later Raman spectroscopy investigation indicated that it was made up of a mixture of Ga subhalides and its valence salt  $[Ga]_2[Ga_2I_6]$  [82]. This green's reagent acts as an accessible and versatile reagent for the synthesis of various monovalent gallium compounds, as well as a possible source of gallium iodide in addition to procedures involving different chemical bonds [81, 83, 84]. And also acts as an extreme source of the gallium iodide fragment in one newly described compound including GaI diatomic fragments [85–87]. In contrast to AlX and GaX, InX ( $X = Cl-I$ ) and TlX ( $X = F-I$ ) halides are stable to disproportionation in the solid-state at room temperatures, making them a potential candidate for low oxidation state In/Tl compounds and, as a result, their wider use as reagents in organic synthesis [1, 2, 4, 88–90]. Bond distances of 2.754 (I), 2.543 (Br), 2.401 (Cl) and 1.985 Å (F), for the monovalent indium diatomics, have been determined in the vapour phase, with equivalent distances of 2.814, 2.618, 2.485 and 2.084 Å observed for the corresponding Tl molecules [1, 2, 4, 75]. In contrast, in an argon atmosphere, the reactivity of singlets ( $1S$ ) and triplets ( $3P$ ) of monovalent indium chloride towards HX ( $X = H, Cl, \text{ or } OH$ ) has been investigated [91–93]. Tuck previously reported that In(I) halides can be treated with Lewis bases at low temperatures to create insoluble complexes that are disproportionable. So, below 20°C, InBr (16 mM) solutions in toluene/TMEDA mixtures are stable, the crystalline complex InBr(TMEDA) was separated from the same solution, indicating long-range In/In interactions (3.7 Å) [94, 95].

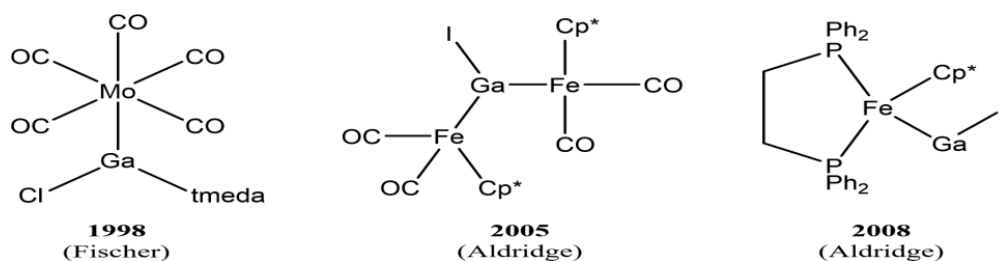
## 5. Coordination chemistry of heavier group 13 metal(I) halides

Aluminium and gallium are the two categories of metal monohalides in Group-13 (**Figure 2**). The organometallic chemistry of these two monohalides of Al and Ga-based molecules is an expeditiously bolster object of research. The complexities in synthesising these compounds and the new situations in which they will be used as synthetic starting materials attracted a great deal of interest. From a theoretical perspective, these molecules that correspond to electronic and molecular structure and bonding have a lot of significance [5]. It has been reported that by co-condensing AlX with combinations of donor solvents and toluene, metastable solutions of aluminium monohalides can be made [6, 7, 59, 79, 80]. The AlX adducts  $[(\text{EEt}_3)\text{AlX}]_4$  ( $\text{X} = \text{Br}, \text{I}$ ;  $\text{E} = \text{N}, \text{P}$ ) were confined and geometrically characterised [74, 96–99]. The symmetrical bridging dimers, which were observable in low-temperature environments [25, 26], contradicted with the spectroscopic investigation of the vapour phase AlX ( $\text{X} = \text{F} - \text{I}$ ) [74, 76]. The reactivity of monovalent Al compounds is high [100–103], and their scope exceeding that of the more reactive transition metal complexes. Fischer et al. described the chemical  $[(\text{CO})_4\text{Fe}-\text{Al}(\eta^5-\text{C}_5\text{Me}_5)]$ , which was synthesised from an  $\text{AlCp}^*$  unit that was bonded to a metal via a terminal non-bridging bond. When compared to dialkyl fragment  $\text{ER}_2$  [43–45], single-source precursors of M-M bonds with ER fragments were significant in attaining the molecular force of the thin film stoichiometry [104–110]. The metal complexes  $(\text{CO})_n\text{ME}[(\text{X})\text{L}_2]$  of Cr, Mo, W, and Fe with the monohalides of aluminium and gallium ligands were explored in depth. The nature of the bonding in the donor-stabilised complexes  $[(\text{NH}_3)_2(\text{CO})_5\text{W}(\text{ECl})]$  for group-13 atoms ( $\text{E} = \text{B-Tl}$ ) was examined [110].

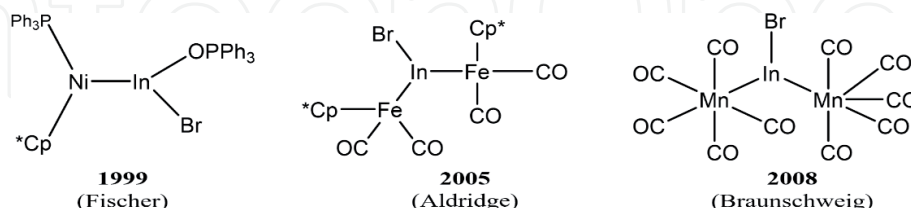
The structural and bonding study of monohalide of group 13 elements as a ligand in metal carbonyls was recently examined (**Figure 3**) [18–21]. Lewis bases such as  $[(\text{tmeda})(\text{CO})_4\text{Fe}(\text{GaCl})]$  assist in the stabilisation of GaX ligands in complexes, however, ligands such as GaR are not supported by Lewis bases [111–114]. The great reactivity of GaX complexes, as well as the scarcity of EX synthons, present difficulties in their synthesis. Aldridge et al. (2008) addressed these obstacles by employing a sterically hindered, rich-electron metalcore as well as a stable  $\text{GaI}_2$  precursor [85, 86]. M-E complexes are more interesting because of their binding properties [115]. Bond dissociation energies for such complexes have been determined thermodynamically, in the same way, that they have been determined for boron monohalide ligands [116]. As a result, BDEs for  $[(\text{CO})_4\text{Fe}(\text{GaX})]$  has been calculated [ $\text{X} = \text{F-I}$  (equatorial/axial): 140.6/141.8; 151.5/151.0; 153.6/152.7; 158.6/157.7  $\text{kJ mol}^{-1}$  respectively] to be 193.7  $\text{kJ mol}^{-1}$  (for CO equatorial/axial) lower than for  $[\text{Fe}(\text{CO})_5]$  but 91.6/88.7  $\text{kJ mol}^{-1}$  (for  $\text{N}_2$  equatorial/axial) less than  $[\text{Fe}(\text{CO})_4(\text{N}_2)]$ . Because various terminal metal gallylene, alumylene, and borylene compounds have been computationally investigated and reported [84, 117–120], very few complexes such as dialkyl, haloaryl, and dihalogallylene complexes have been synthesised and characterised. Moreover, while the covalent to electrostatic



**Figure 2.**  
Development of aluminium monohalides based complexes.



**Figure 3.**  
Development of gallium monohalides based complexes.



**Figure 4.**  
Development of indium monohalides based complexes.

interaction ratios obtained for Fe–GaX bonds are analogous to those calculated for Fe–CO and Fe–N<sub>2</sub>, the impact of sigma donation to the covalent bonding contribution is substantially larger for GaX than for Fe–CO and Fe–N<sub>2</sub> bonds [115]. Although a variety of systems including these lengths EX bridging between two metal centres have previously been characterised, complexes containing the heavier EX as terminal ligands have just previously been reported experimentally [85–87]. Dimeric complexes of the kind [(L<sub>n</sub>M)<sub>2</sub>(μ-X)<sub>2</sub>E(ML<sub>n</sub>)<sub>2</sub>] or polymeric structure with sterically less hindered transition metal fragments [84, 121–125] are examples. The Lewis base coordinated at the group 13 centre can be used to segregate mononuclear systems in such circumstances [121, 126–128]. Pandey et al. (2010) investigated the bonding nature of group 8 and 10 metal complexes with dihalogallyl ligands. As a result, understanding the bonding behaviour of M–Ga in gallyl complexes is significant. The binding behaviour of the M–E bond in charge-neutral compounds coupled with typical metal carbonyls such as chromium hexacarbonyl, iron pentacarbonyl and nickel tetracarbonyl was systematically investigated to gain a greater understanding [69, 72, 73, 129–131].

Many researchers are still interested in synthesising metal coordination with In ligands, which has been recognised in recent decades [132–134] (**Figure 4**). The cationic derivative [Cp\*Fe(GaCl)(phen)(CO)<sub>2</sub>]<sup>+</sup> was produced as the [BPh<sub>4</sub>]<sup>−</sup> salt by reacting [Cp\*Fe(CO)<sub>2</sub>(GaCl<sub>2</sub>)] with Na[BPh<sub>4</sub>] in the presence of 1,10-phenanthroline [135]. The chemistry of halide abstraction technic was initially utilised to synthesise the trimetallic indium and gallium cations in 2004 and was later extended to synthesise the iodogallylene complex [Cp\*Fe(GaI)(dppe)]<sup>+</sup> [ArBF<sub>4</sub>]<sup>−</sup> by using a more electro-negative and sterically hindered bis(phosphine)iron fragment [85–87, 136, 137]. Gallium has a low coordination number, which is compatible with crystallographic parameters. For the similar bivalent ligand system in [(OC)<sub>4</sub>Fe(Ga–C<sub>6</sub>H<sub>5</sub>)(GaI)], the bond distance of Fe–Ga, Ga–I and Fe–Ga were 2.222, 2.444, 2.225 Å respectively and the bond angle of Fe–Ga–I was 171.4° [85, 115]. The weaker orbital contribution is thought to reflect the more diffuse nature of the 4s/4p orbitals derived from gallium, as well as less effective interactions with the fragment orbitals of [CpFe(dmpe)]<sup>+</sup>, despite the higher energy of the HOMO for GaI (−6.08 eV vs. −9.03 eV for CO) and greater localization of the LUMO at the donor atom. The total metal–ligand bond strengths [ΔE<sub>int</sub> = −103 (GaI), −285 (BF), −213 (CO), and −120 kJmol<sup>−1</sup> (N<sub>2</sub>)] after adding CO to form [Cp\*Fe(dppe)(CO)]<sup>+</sup> [ArBF<sub>4</sub>]<sup>−</sup> reveal very poor binding of the



GaI ligand [52]. The Rh–Ga distance [2.471 Å] becomes noticeably shorter [2.334 Å] when pyridine is coordinated at the gallium atom, this is in marked contradiction to analogous borylene systems, and it appears to indicate that the gallylene ligand is a stronger  $\sigma$ -donor, as well as the system's relative lack of  $\pi$ -back bonding representation. The availability of low valent and highly reactive  $[\text{In}^{\text{I}}\text{R}]$  molecules allowed for the synthesis of many complexes.  $[\text{In}^{\text{I}}\text{R}]$  molecules often operate as two-electron donors for metal fragments in both terminal and bridging modes of coordination [138–140]. The reason that identical complexes are coupled via numerous bonds ( $\text{L}_n\text{M-EX}$ ) reflects not only the significant structural and bonding challenges brought by such complexes but also the insufficiency of strong experimental verification of possible bonding models [115, 141]. Mays *et al.* established the synthesis of the  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2(\text{InCl})]$  complex via the addition of InCl into the Fe–Fe bond of  $[\text{Fe}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2]$  [142]. In most common organic solvents, commercially available monovalent indium compounds disintegrate or become insoluble [4, 71]. In this context, many studies have proposed a protonolytic approach to monovalent indium sources to improve performance and stability. The synthesis of stable metal complexes, particularly with group-13 diyl ligands ER, involved a detailed study of the bonds between the compounds. It's unusual to find a perfect computational analysis that accurately describes the bonding of the  $\text{M-ER}_n$  [68]. The ability of tri-coordinate complexes of the type  $[\text{L}_n\text{M}]_2(\mu\text{-EX})$  to oligomerize through E–X–E bridges are modified by larger additional ligands of electrostatic repulsion induced by the net charge of  $[(\text{OC})_5\text{Cr}_2(\mu\text{-EX})]_2$  where E = In; X = F–I [84, 136, 137, 143]. For the  $\text{Cp}^*\text{Fe}(\text{CO})_2$  systems, synthetic pathways initiating in  $\text{E}^{\text{I}}$  or  $\text{E}^{\text{III}}$  precursors are feasible (using addition or salt elimination techniques), with monomeric complexes generated that differ from the oligo/polymeric structures of similar  $[\text{Cp}^*\text{Fe}(\text{CO})_2]$  complexes [84, 123, 144, 145]. Although the reaction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$  and InI have clear mechanistic similarities to classical oxidative insertion reactions, the assignment of oxidation states in the product is rather arbitrary because iron and indium have similar electronegativities (1.83 and 1.78 on the Pauling scale, respectively).

## 6. Conclusions

Although monohalides of group 13 atoms have a rich history, their applications in the synthesis of limited alkyl, aryl, amide groups and related compounds have developed significantly in recent years because of the contribution of Schnöckel, Power, Fischer, Jones and Aldridge. Simple diatom capture EX was just recently completed. Furthermore, at extremely high temperatures, the source of EX (E = B, Al, Ga) is widely thought to be a non-donor species (different from the equivalent electron ligand of CO or  $\text{N}_2$ ), which will appear in (or close to) Ligand: general electron temperature asymmetry or aggregation problem. The complex's most recent structural characteristics, such as terminal BF and GaI bridging fragments (for example,  $[\{\text{CpRu}(\text{CO})_2\}_2(\mu\text{BF})]$  [47] and  $[\text{Cp}^*\text{Fe}(\text{dppe})(\text{GaI})]^+[\text{ArBF}_4]^-$ ). The BF ligand attaches to two metal atoms in the form of a  $\mu_2\text{CO}$  ligand (that is, the ligand is in a singlet form) [146, 147], or the BF fragment is produced from conditional triplets if the boron centre is an effective triangle. Of course, the last case is comparable to the combination of CO units in ketones and is similar to Stalke and Braunschweig's  $[\text{CpMn}(\text{CO})_2(\mu\text{BtBu})]$  system [148].  $[\text{CpRu}(\text{CO})_2(\mu\text{BF})]$  [47]. Because of the triple BF fragment and the interaction between two fragments  $[\text{CpRu}(\text{CO})_2]$ , the final description may have some reality in a better form. The BF singlet-triplet gap (with a singlet ground state) is determined to be around  $86 \text{ kcal mol}^{-1}$  [149], although the M–B bond value in the relevant system is around  $6070 \text{ kcal mol}^{-1}$ . The iron boron bond in  $[\text{CpFe}(\text{CO})_2(\text{BF}_2)]$  complex



is 66 kcal mol<sup>-1</sup> [150], assuming that it is made up of three BF bonds and two [CpRu(CO)<sub>6</sub>]. This corresponds to BF bond length 1.348 Å [47], which is significantly larger than the formal triple bond in BF diatoms (1.263 Å) [35], but slightly shorter than the Valence Radius co-beam (1.46 Å) [151]. The GaI distance in the terminal cationic iodoaromatic compound is 2.444 Å, which is less than the parent diatom's (2.575 Å) distance. Even with gallium's low coordination number, the Fe-Ga bond length is found to be quite short. This is owing to the strong M-Ga  $\pi$ -orbital interaction, rather than the  $s$ -orbital donation of a considerable amount of gallium sorbate to the M-Ga [53] bonding orbital. The orbital interaction between the model [CpFe(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [GaI] fragments is dominated by  $\Delta E$ , indicating that GaI ligands are mostly utilised as donors. Quantum chemistry investigations of comparable neutral charge complexes containing GaI ligands, particularly the [(CO)<sub>4</sub>Fe(GaI)] axis, found significant electronic/geometric similarities to the cationic system, including the gap between Ga and GaI. The modest overall interaction energy, the short distance, and the contribution ratio of all interaction energies with similar electrostatic and covalent interactions (about 1:1). (Approximately 20%). These results suggest that GaI ligands interact similarly in each of these systems [53, 116]. Given the long history of capturing coordination chemistry and subsequent spectroscopic/structural interrogation of species with highly unstable kinetics, as well as the recent isolation of complexes containing terminally bound CF, GaI, BO<sup>-</sup> and even Ga<sup>+</sup> ligands [85–87, 152–158], it appears that more progress in this field will be made soon. Because it offers precise experimental comparisons of electronic structures with CO and N<sub>2</sub> textbook systems, the BF terminal junction complex would be an appealing target. The key to this experiment is to establish a new preparation-scale procedure to make the most of the kinetic depressant chemical, despite quantum chemistry studies showing it to be thermodynamically stable. Comparing experimental results with theory will help to resolve the current controversy over the possible ways of binding in these molecules.

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