questions: Which chlorinating enzyme is available in *L. majuscula* and which cofactor is required? Will other amino acids except **1** be suitable substrates for a stereoselective free-radical "biochlorination"? If these assumptions were confirmed, a second enzyme-induced radical process besides coenzyme B_{12} mediated reactions would have been uncovered. The new halogenation reaction could have a significant influence on modern radical chemistry comparable to the role of the alkyl cobalamines,[11] and should stimulate important new research in the field of stereo- and regioselective free radical chemistry.

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Monovalent Group 13 Organometallic Compounds: Weak Association to Monomeric, Versatile Two-Electron Donors**

Ramaswamy Murugavel* and Vadapalli Chandrasekhar*

Dedicated to Professor S. S. Krishnamurthy on the occasion of his 60th birthday

There is currently an immense enthusiasm among chemists to stabilize low-valent, multiply bonded compounds containing low-coordinate elements from Groups 13, 14, and 15. Especially the last few years have been an exciting period in which reports concerning the synthesis of several unusual compounds have appeared in the literature. To name a few, a) a tetrasila-1,3-butadiene,[1a] b) the first silaarene,[1b] c) compounds with unsupported Bi=Bi[2a] and Sb=Sb double bonds,[2b] d) silylium cations,[3a] e) a cyclotrigermenium cation with a 2π-electron system,[3b] f) an Al_{77} cluster ion with concentric spheres of Al atoms,[4] g) compounds containing a discrete metal–chalcogen double bond such as Sn=Se,[5] and h) multiply bonded species involving gallium[6] have been discovered.

During this period another exciting facet of main group chemistry has been unraveled, and there have been important developments in the stabilization of monovalent Group 13 organometallic compounds. These efforts have resulted in the isolation of compounds of the type M^IR (M = Group 13 metal), which, while being monomeric in the gas phase or in solution, show interesting aggregation properties in the solid state. Recently in an important breakthrough Schnöckel and co-workers have shown that although [GaCp*] is hexameric in the solid state, the Ga ⋯ Ga distances are very long and only weakly influence the aggregation.[7] Instead, these clusters are believed to be formed as a result of van der Waals interactions of the organic envelope around the metal. In another development, Power, Niemeyer, and Haubrich have succeeded in preparing examples of unassociated Group 13 monoalkyl compounds that exist as monomers in the solid state.[8] Continuing their studies on the use of In^I compounds as ligands, Uhl et al. have reported an unusual Ni^0 complex bearing only monomeric indium moieties as ligands.[9] Also Jutzi and co-workers have prepared a variety of metal carbonyl clusters containing monomeric [GaCp*] groups as terminal as well as bridging ligands.[10] This article is aimed to highlight these new results and to provide a brief summary of other important results in Group 13 M^I–organometallic chemistry obtained recently.

While subvalency is common among the inorganic and organometallic compounds of heavier Group 13 elements

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such as In and Tl,[11] low-valent compounds of the lighter elements B, Al, and Ga have been synthesized only recently. For example, the common oxidation state for thallium centers in inorganic compounds of thallium is + 1, and several species of the type $[RTl]_n$ are very stable and are often synthesized in aqueous medium. There have also been reports on the stabilization of Tl^I compounds in other situations. Thus the interesting Tl^I amide $[\{(2,6\text{-}i\text{Pr}_2C_6H_3)(SiMe_3)NTl\}_4]$ was synthesized by Roesky and co-workers in 1994.[12] This compound is monomeric in the gas phase. In the solid state, a weak interaction of Tl with the aryl group of a neighboring molecule is seen along with weak Tl···Tl interactions (406.0 pm), leading to a loosely associated tetramer. The $(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)$ group used to stabilize this molecule was also useful later in the development of a new class of kinetically stabilized silanetriols.[13] Even though it has long been believed that + 3 is the most stable oxidation state for B, Al, and Ga, a number of divalent compounds of these elements have been reported; this topic has already been comprehensively reviewed by Uhl.[14] However, the developments in this area have been rather slow, and it was only in the beginning of the 1990s that reports concerning the isolation and unambiguous structural characterization of stable and discrete monovalent M^I organometallic compounds of the lighter Group 13 elements started to appear in the literature.

One of the key requirements for the stabilization of monovalent Group 13 compounds is a suitable R group on the fragment M^IR. The substituent has to provide steric bulk and also be electronically stabilizing. The types of R groups that have been found to be suitable and have been used so far are a) cyclopentadienyl (Cp) groups (including C_5H_5 (Cp), C_5Me_5 (Cp*), and $C_5(CH_2Ph_5)$ (Cp^B)), b) bulky alkyl or persilylated alkyl groups (including $C(SiMe_3)_3$, *t*Bu, CH_2CMe_3, and $Si(t\text{Bu})_3$), and c) 2,6-disubstituted aryl groups. The first notable breakthrough in this area was achieved by two different synthetic strategies. While Paetzold and co-workers assembled the organo-B^I compound $[\{Bt\text{Bu}\}_4]$ by the reductive dehalogenation of $t\text{BuBF}_2$ with Na/K alloy,[15] Schnöckel et al. reported the synthesis of the first organo-Al^I compound $[\{AlCp^*\}_4]$ by a metathetical exchange of halide in a reaction involving the metastable [AlCl] and $[MgCp^*_2]$.[16] Quite recently Linti and co-workers have shown that the reaction of metastable [GaI] with $LiSi(SiMe_3)$ affords the tetragallane $[R_4Ga_4I_3]^-$ and the polyhedral nonagallane $[R_6Ga_9]^-$ (R = $Si(SiMe_3)$).[17] Roesky and co-workers successfully employed the reductive dehalogenation method to prepare synthetically useful quantities of $[\{AlCp^*\}_4]$ in the reaction of $[Cp^*AlCl_2]$ with potassium in toluene.[18a] These authors have quite recently adopted this synthetic strategy for the reduction of the aluminum diiodide $[(Me_3Si)_3CAlI_2 \cdot THF]$ with Na/K alloy to afford $[\{AlC(SiMe_3)_3\}_4]$.[18b] Jutzi and co-workers have also shown that reductive dehalogenation of $[Cp^*GaI_2]$ with potassium metal and the use of ultrasonic metal activation affords $[\{GaCp^*\}_6]$.[10] Through the use of these two synthetic strategies, many monovalent compounds containing Al, Ga, In, and Tl have been assembled.

The X-ray crystal structures of these monovalent compounds show interesting aggregates in the solid state. $[\{AlCp^*\}_4]$, $[\{Al(Sit\text{Bu}_3)_4\}]$,[19] and $[\{MC(SiMe_3)_3\}_4]$ (M = Al,[18b] Ga,[20] In,[21] Tl[22]) are tetrameric, while [MCp*] (M = Ga[7] and In[23]) are hexameric. In contrast, [InCp], [TlCp], and [InCp*] are polymeric.[24] $[InCp^B]$ and $[TlCp^B]$, obtained with bulky cyclopentadienyl substituents, are dimeric.[25] Accumulated experimental evidence suggests that these compounds are monomeric in solution or in the gas phase.

What holds the clusters together in the solid state? The M···M bond distances observed for the tetrameric derivatives $[\{AlCp^*\}_4]$, $[\{Al\{Sit\text{Bu}_3\}_4]$, and $[\{MC(SiMe_3)_3\}_4]$ (M = Al, Ga, In, Tl) are comparable to that in the native metals, suggesting that this fairly strong interaction is responsible for the formation of the cluster. However, the situation is different for compounds of monovalent Ga, In, or Tl containing Cp-type ligands. The recent X-ray structural investigation of [GaCp*] has thrown new light on the nature of association of these compounds in the solid state.[7] Although [GaCp*] was prepared in 1993, single crystals of this compound were only recently obtained by Schnöckel and co-workers by cooling of a molten solution at + 4 °C. It is found that [GaCp*] is hexameric and made up of two distinct Ga_3 units (Figure 1).

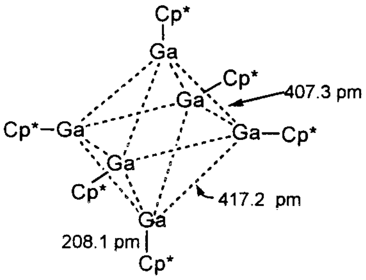

Figure 1. Schematic representation of the weakly associated structure of a [GaCp*] hexamer in the solid state.

Interestingly, the Ga···Ga bond distances in these subunits (417.2 and 407.3 pm) are much longer than in Ga metal (245 – 307 pm). A second important finding is that the dimensions of the [GaCp*] units are similar in the solid state and in the gas phase. Thus the distance between Ga and the centroid of the Cp* ligand is 208.1 pm in both the gas phase and the solid state. Indeed, such weak M···M interactions are also found for hexameric [InCp*],[23] dimeric $[MCp^B]$ (M = In, Tl),[25] and polymeric [InCp],[24] [TlCp],[24] [TlCp*],[24] and $[TlCp^B]$.[25] Schnöckel et al. suggest that in these compounds the various monomeric subunits are held together primarily as a result of the van der Waals interactions of the outer organic envelope rather than $M^I \cdots M^I$ interactions.[7] Further evidence for this argument stems from the fact that the unit cell volumes of $[InCp^*]_6$ and $[GaCp^*]_6$ are very similar, although in the former the metal – ring distance is about 11 % longer than in the latter. It is possible that different packing requirements of the ligands enforce the type and structure of the aggregate formed.[7] There is already theoretical evidence for the instability of the aggregates in comparison with the monomers. Theoretical calculations on $[\{AlCp\}_4]$ and $[\{AlCp^*\}_4]$, suggests that the tetramers are unstable with respect to the monomers. This has been primarily attributed to the Cp → Al π backbonding.[26]

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Indirect support for the suggestion by Schnöckel et al. comes from recent studies of Power, Niemeyer, and Haubrich.[8] Using entirely different and sterically encumbered Trip-type ligands (Trip = 2,4,6-iPr$_3$C$_6$H$_2$), these researchers have isolated monocoordinated, monovalent In^I and Tl^I compounds. The packing requirements of these bulky ligands, being different from those of the other Cp-type ligands studied so far, perhaps force monocoordination. For some time, Power et al. and others[6] have been employing several sterically overcrowded Trip ligands to stabilize unusual Group 13 organometallic compounds (Figure 2). This substituent was also used recently by Robinson et al. for the synthesis of multiply bonded gallium compounds,[6] a discovery over which there has been strong disagreement among main group and structural chemists in recent times.[27]

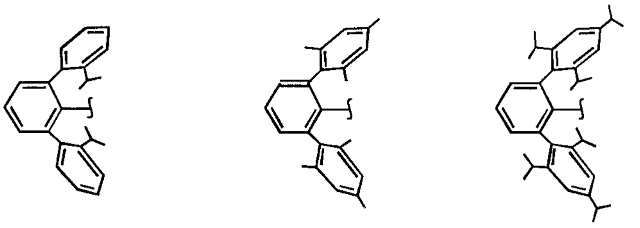
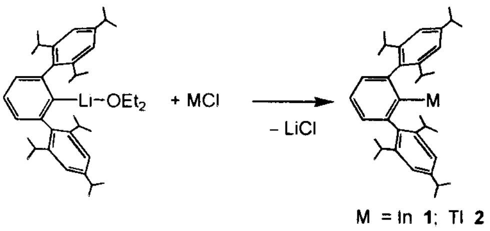


Figure 2. Bulky 2,6-disubstituted aryl ligands.

The bright orange compounds **1** and **2** were obtained in moderate to good yields by a fairly straightforward synthetic route starting from the aryllithium salt and the subvalent metal chlorides [InCl] and [TlCl], respectively (Scheme 1).[8]



Scheme 1. Synthesis of **1** and **2**.

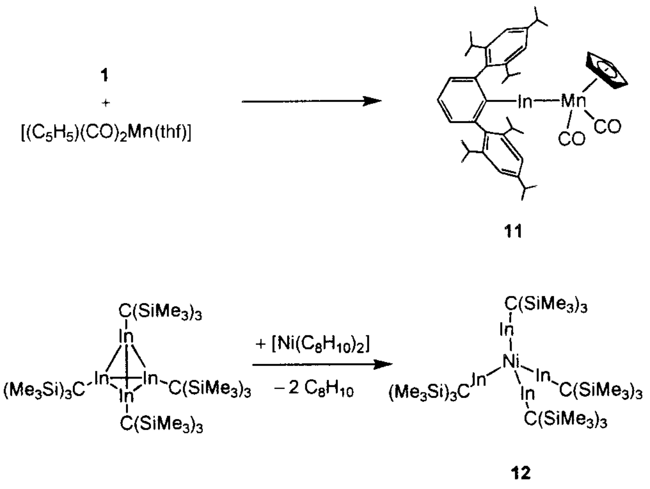
While the In compound **1** is thermally stable and decomposes only above 215 °C, the light-sensitive Tl^I derivative **2** is only stable for extended periods of time in solution below – 40 °C. The isolated solid of **2** slowly decomposed even at low temperatures with deposition of thallium metal. Compounds **1** and **2** show characteristic absorptions at 440 and 487 nm, respectively. The single-crystal X-ray structure analyses reveal that **1** and **2** exist as monomers [RM] with monocoordinated metal centers in the solid state. While the shortest intermolecular In $\cdots$ In contact in **1** is 6.89 Å, the corresponding Tl $\cdots$ Tl distance for **2** is 6.81 Å. It is interesting to compare these values with those of "polymeric" [TlCp] (6.38 Å), [TlCp*] (5.41 Å), and [TlCp^B] (7.37 Å). Thus, the degree of association of the monomeric units in monovalent Group 13 compounds can be adjusted by the ligand used. Clearly, more data in terms of number and variety of structures as well as detailed theoretical calculations are required to obtain a quantitative understanding on this ligand-driven nature of association.

Are these monovalent (associated and monomeric) Group 13 compounds useful to synthetic organometallic chemists in any way? Based on the reactivity studies of [In{C(SiMe$_3$)$_3$}]$_4$ with various transition metal centers reported in a series of recent papers by Uhl et al.[9, 28] and the studies of [GaCp*]$_6$ with a variety of first-row transition metal carbonyl complexes reported by Jutzi and co-workers,[10] the answer to this question seems to be "yes". The ability of monovalent Group 13 compounds to function as Lewis bases[29] makes them useful two-electron donor ligands in transition metal organometallic chemistry.

Studies on the reactivity of [RM] fragments toward soft metal centers are not new. As early as 1994 Schnöckel et al. reported on [(CpNi)$_2$(μ_2-AlCp*)$_2$] (**6**), the first transition metal complex bearing a M^{I}R fragment as a bridging two-electron donor in a μ_2 coordination mode.[16b] The ability of [AlCp*] to act as a two-electron ligand was further substantiated by the synthesis of [(μ_2-AlCp*)$_2$Co$_2$(CO)$_6$] (**7**) through a facile reaction between [AlCp*] and [Co$_2$(CO)$_8$] in toluene at 80 °C.[30] Similarly, the In^I compound [{InC(SiMe$_3$)$_3$}$_4$] acts as a bridging ligand in [Mn$_2$(CO)$_8${μ_2-InC(SiMe$_3$)$_3$}$_2$] (**8**), [Co$_2$(CO)$_7${μ_2-InC(SiMe$_3$)$_3$}] (**9**), and [Mn$_2$(CO)$_6${μ_2-InC(SiMe$_3$)$_3$}$_2$] (**10**).[28] Recently Linti and co-workers have carried out reactions of [{Ga(Cl)[Si(SiMe$_3$)$_3$]$_4$}] with iron carbonylates Na$_2$[Fe(CO)$_4$], Na$_2$[Fe$_2$(CO)$_8$], and Na$_2$[Fe$_3$(CO)$_{11}$] to afford derivatives of [Fe$_2$(CO)$_9$] in which some or all of the bridging carbonyls have been replaced with monomeric Ga[Si(SiMe$_3$)$_3$] fragments.[31]

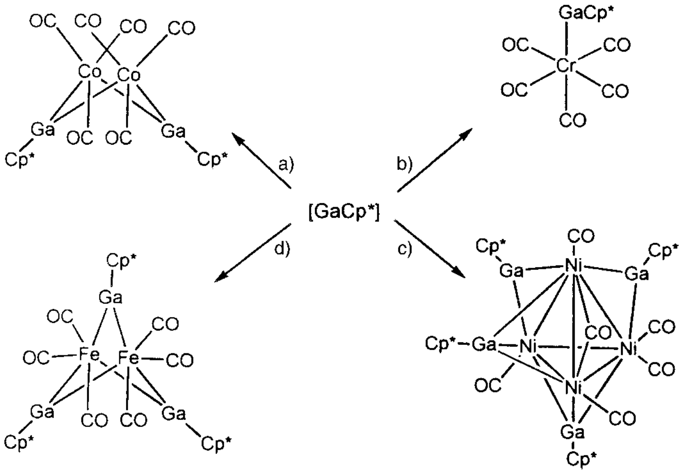
The monomeric M^{I}R compounds formally have two empty p orbitals perpendicular to the M–C bond (or the centroid of the C$_5$ ring in the case of Cp ligands) apart from a lone pair of electrons at the metal. Hence the frontier orbitals of M^{I}R are similar to those of the CO ligand. In fact, the recent studies clearly lend evidence to the ease of substitution of CO groups by M^{I}R groups in compounds **6**–**10**. However, it is interesting to note that until recently there have been no reports on the synthesis of complexes where [M^{I}R] compounds coordinate to the metal in a terminal coordination mode, which is the most commonly observed mode for the CO ligand. Preparation of terminally coordinated M^{I}R ligands would, in fact, allow us to draw an isolobal relationship between CO and MR ligands.

The In^I compound **1** and the tetrameric derivative [In{C(SiMe$_3$)$_3$}$_4$] have been used to synthesize low-valent transition metal complexes with terminal MR ligands. Compound **1** readily combines with [Cp(CO)$_2$Mn(thf)] to afford [Cp(CO)$_2$Mn(InR)] (**11**) in 46 % yield (Scheme 2).[8a] Similarly, the reaction between [Ni(cod)$_2$] (cod = cyclooctadiene) and [In{C(SiMe$_3$)$_3$}$_4$] results in a facile substitution of both the alkene ligands by four [In{C(SiMe$_3$)$_3$}] units to form [Ni{In[CSiMe$_3$)$_3$]}$_4$] (**12**) in 76 % yield.[9] In particular, the synthesis of **12** is very interesting since this compound represents the first transition metal complex in which the metal is coordinated to only M^{I}R groups and no other type of ligand, as in the case of [Ni(CO)$_4$], thereby clearly drawing an isolobal analogy between CO and M^{I}R ligands. The M-M′-C bonds are linear in this molecule; the Ni-In-C bond angle in **12** is 180.0° and the Mn-In-C angle in **11** is 175.4°. Although the short Ni–In bonds



Scheme 2. Synthesis of **11** and **12**.

(2.310 Å) are indicative of π backbonding, the extent of the same is uncertain in the absence of any MO calculations.[9, 32] On the other hand, the observed CO stretching frequencies for **11** lend evidence for a description of the the $M^{I}R$ ligands as σ donors with weak π-acceptor properties.[8a] Similar to the In^{I} derivative, $[\{GaCp^*\}_6]$ also interacts with transition metal carbonyl complexes to afford compounds in which the monomeric GaCp* functions as a terminal and a bridging ligand (Scheme 3).[10] The cone angle of this ligand has been estimated to be 112°, and this ligand has been shown to be predominantly an electron donor with weak π-accepting properties. This observation parallels those for the ferrogallyne complex $[(CO)_4Fe\{Ga(2,4,6\text{-}Trip_3C_6H_2)\}]$ from Robinson et al., where the monomeric GaR unit is also believed to function with almost no π-acceptor properties.[32]



Scheme 3. Reactions of [GaCp*]: a) $[Co_2(CO)_8]$; b) $[Cr(CO)_5(C_8H_{14})]$; c) $[Ni(CO)_4]$; d) $[Fe(CO)_3(cht)]$ (cht = cycloheptatriene).

In conclusion, the recent syntheses and structure determinations of monovalent Group 13 compounds have taken this subject one step ahead of its previous limits. The problem of understanding the ligand-mediated weak association[7] is likely to capture the attention of theoretical and experimental chemists further. Likewise, the demonstration of the use of these compounds as both terminal and bridging ligands in transition metal chemistry is likely to have a huge impact on the way new metal–metal bonds are made in the future. If these results are any indication and if many other cluster chemists are to adopt these results in their research, there is no doubt that we will be witnessing the synthesis of a whole range of new cluster types in the future.

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