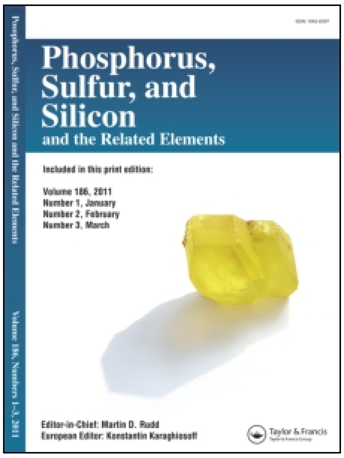

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Novel Heterocyclic Ring Systems Containing Heavier Group 13 Elements

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NOVEL HETEROCYCLIC RING SYSTEMS CONTAINING HEAVIER GROUP 13 ELEMENTS

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Abstract The reactivities of the new dihydrides, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]MH_2$ (M = Al, Ga), and the bis-azide, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$ have been investigated. The indium tetramer, $[InC(SiMe_3)_3]_4$, has been prepared via the metathetical reaction of $LiC(SiMe_3)_3{\cdot}2\,THF$ with InCl. The first neutral galla- and indacyclopentadienes have been synthesized by treatment of the zirconacycle, $(\eta^5\text{-}C_5H_5)_2Zr(C_4Me_4)$ with $Ar'MCl_2$ (Ar' = 2,4,6-t-$Bu_3C_6H_2$; M = Ga, In).

INTRODUCTION

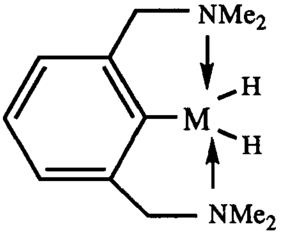
One of the facets of our research program concerns the chemistry of low valent, low coordination number species involving the heavier group 13 elements. For example, base-free fragments of the type RM (R = organic ligand; M = Al, Ga, In) are one-coordinate and the main-group metal is formally in the +1 oxidation state. Several approaches can be taken to developing this area of chemistry including:

(1) Oligomerization reactions
(2) Incorporation of RM fragments into ring systems
(3) Incorporation of RM fragments into the coordination spheres of transition metals
(4) Detection by rapid time scale experiments
(5) Trapping experiments

The present discussion is focused on areas (1) and (2).

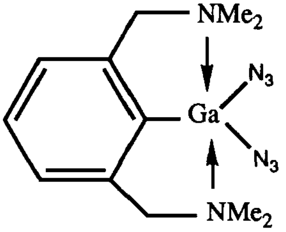
RESULTS AND DISCUSSION

Since RM fragments involve only four valence electrons on the main-group metal, our initial attempts to generate such species involved varying degrees of intramolecular Lewis base stabilization. The target molecules **1** and **2**, for example, were selected in anticipation that facile thermal or photochemical elimination of molecular hydrogen



1 (M = Al)
2 (M = Ga)

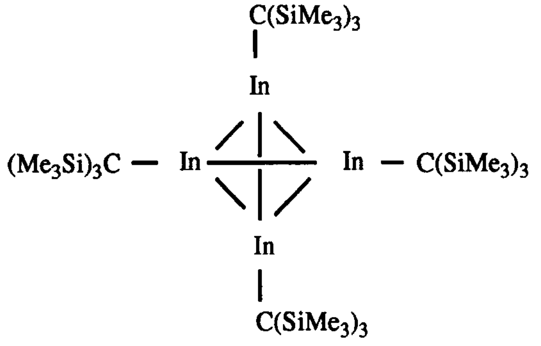
would occur and thus generate the desired metal(I) species. Compound **1** was synthesized[1] by treatment of the corresponding aluminum dichloride, $[2,6\text{-}(Me_2NCH_2)C_6H_3]AlCl_2$ with $LiAlH_4$ or *via* reaction of the lithium aryl, $[2,6\text{-}(Me_2NCH_2)C_6H_3]Li$ [2] with $Me_3N{\cdot}AlClH_2$. Compound **2**, the first stable organogallium dihydride, was isolated[3] from the reaction of the corresponding arylgallium dichloride with $LiGaH_4$. The monomeric nature of **1** and **2** was established by X-ray crystallographic studies.[1,3] Both CH_2NMe_2 "arms" of the ligand are coordinated and the coordination spheres of aluminum and gallium in **1** and **2** comprise trigonal bipyramids in which the axial sites are occupied by two nitrogen atoms and the equatorial sites by the aryl carbon and two hydride ligands. Curiously, however, even though **1** and **2** exhibit diverse and unusual patterns of reactivity, they do not undergo elimination of molecular hydrogen and survive attempted photolysis (254 nm light, Et_2O solution) and vapor-phase heating to 350°C. Accordingly, attention was turned next to the synthesis of azide derivatives in the hope that facile elimination of molecular nitrogen would occur. Compound **3**, the first bis(azide) of gallium, was prepared[4] *via* the metathetical reaction of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaCl_2$ with NaN_3.



3

As in the cases of **1** and **2**, the X-ray crystal structure of **3** involves an axially distorted trigonal bipyramidal geometry at the group 13 element. The two terminal azide groups, which are quasi-linear (average N-N-N angle = 174.9(6)°), are arranged in an open "scissors-like" fashion. Because the percentage by weight of azide nitrogen in 3 is equal to 24.4%, low thermal stability was anticipated. Interestingly, however, 3 is surprisingly robust and survives vapor phase heating to 400°C and UV irradiation at 254 nm.

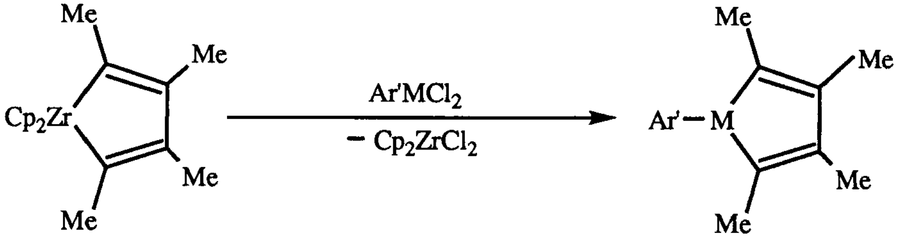
In view of the fact that intramolecular Lewis base coordination resulted in unusual thermal and photochemical stabilities of hydrides and azides of aluminum and gallium, it was decided to attempt the generation of base-free moieties. Since indium(I) halides are stable, we opted initially for a metathetical reaction of InCl with the bulky lithium alkyl, $LiC(SiMe_3)_3 \cdot 2\ THF$.[5] The resulting indium (I) alkyl is a purple colored tetramer, $[InC(SiMe_3)_3]_4$ (4).[6] Unfortunately, the X-ray crystal structure of 4 was complicated by disorder problems. Nevertheless, it was possible to establish that the structure involves a tetrahedral In_4 core. The only previously reported non-polymeric In(I) organometallics are the dimer, $[In\{C_5(CH_2Ph)_5\}]_2$ [7] and the hexamer, $[In(C_5Me_5)]_6$.[8] Presumably, the tetrameric constitution of 4 stems from the distinctive packing requirements of the bulky $C(SiMe_3)_3$ ligand. Interestingly, the average indium-indium distance in the tetramer 4 (3.09(2)Å) is considerably shorter than those in the dimeric (3.631(2)Å) and hexameric (3.952(1)Å) indium (I) compounds. Whether or not there is indium-indium bonding in these indium (I) derivatives remains an open question. It is interesting to note, however, that 4 exhibits an absorption band at 486 Å which might be associated with metal-metal interactions. It should also be pointed out that Uhl et al.[9] have prepared and structurally characterized the analogous gallium tetramer, $[GaC(SiMe_3)_3]_4$.



4

Attention is focused next on the incorporation of heavier group 13 moieties of the general type RM (M = Al, Ga, In) into carbocyclic rings. Unsaturated ring systems are of special concern not only because of intrinsic interest in the bonding descriptions, but also on account of their potential importance as ligands and as thermal and photochemical sources of RM fragments. The boroles (boracyclopentadienes), for example, constitute a well-known class of compound.[10] However, information on the heavier group 13 analogues of these interesting compounds is extremely sparse. The only structurally characterized example of which we are aware is pentaphenylaluminacyclopentadiene[11] which was isolated as an Et_2O adduct and which could be converted into a (COD)Ni complex by treatment with $(COD)_2Ni$.

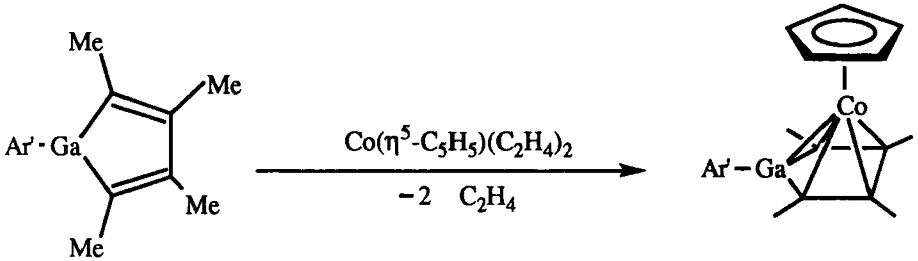
Boracyclopentadienes are known to undergo self-dimerization if the boron and ring substituents are of modest steric bulk.[12] In order to obviate dimerization in the desired gallium and indium analogues, we chose to employ the bulky group strategy. Thus it was discovered[13] that the bulky aryl gallium and indium dichlorides, $Ar'MCl_2$ ($Ar' = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$; M = Ga, In)[14] react readily with the appropriate zirconium metallacycle to afford the first examples of organogalla-and indacyclopentadienes, 5 and 6 respectively. So far, it has only proved possible to produce crystals of 5 that are suitable for X-ray diffraction study. The gallacyclopentadiene crystallizes with two independent molecules in the asymmetric unit; however the bond lengths and angles of these molecules are very similar. The five-membered GaC_4 ring is planar within experimental error and the double bonds within this ring are localized as evidenced by the fact that their distances (average 1.312(37)Å) are significantly shorter than the remaining carbon-carbon bond distance (1.542(37)Å). An interesting feature of the structure is the observation that the Ar' and gallacyclopentadiene rings are very close to orthogonal. This particular conformation undoubtedly contributes to the stability of 4.



($Ar' = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$)

5 (M = Ga)
6 (M = In)

We are particularly interested in the coordination chemistry of the new galla- and indacyclopentadiences because the resulting complexes are potential precursors to intermetallic phases and such as β-CoGa and ε-NiIn.[15] Thus far, we have found that the gallacyclopentadiene, 5, reacts readily with [Co(η^5-C_5H_5)(C_2H_4)$_2$] to produce the corresponding cyclopentadienylcobalt (I) complex, 7. An X-ray crystallographic



5

7

study of 7[13] revealed that upon coordination to the (η^5-C_5H_5)Co moiety, the gallacyclopentadiene ring changes from a planar to an envelope conformation. Moreover, all three C-C bond distances in the GaC_4 ring become equal within experimental error. Interestingly, the Co-Ga distance in 7 (2.706(2)Å) is significantly shorter than the sum of van der Waals radii for cobalt and gallium. Nevertheless, extended Hückel calculations on a model system indicate that these atoms are not bonded and that the mode of attachment of cobalt to the gallacyclopentadiene ring is η^4.

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