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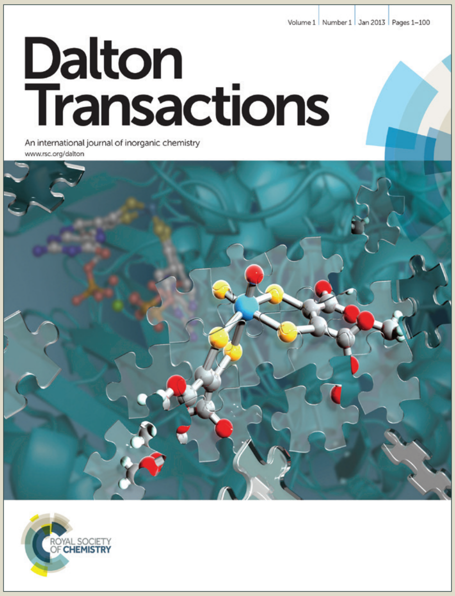

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The Stabilisation of Gallane and Indane by a Ring Expanded Carbene

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7Dipp Complexes of the group 13 binary hydrides GaH_3 and InH_3 have been prepared. Both adducts possess excellent thermal stability in the solid state but decompose readily in solution at ambient temperature. The presence of short M-H····H-C_{Alkyl} distances in the structures of both [MH_3(7Dipp)] complexes is discussed.

The principal binary hydrides of gallium and indium; gallane (GaH_3) and indane (InH_3), are of markedly lower stability than their lighter group 13 counterparts.[1] Gallane decomposes above -30 °C[2] and indane above -90 °C.[3] Somewhat more stable are Lewis base adducts of gallane and indane such as the *N*-heterocyclic carbene (NHC) stabilized [GaH_3(IMes)] (**1**) and [InH_3(IMes)] (**2**)[4] (IMes = 1,3-dimesitylimidazol-2-ylidene) (Figure 1) which are stable at ambient temperature in the solid state and decompose at 214 °C and 115 °C respectively. This makes **1** and **2** the most stable gallane and indane reported.

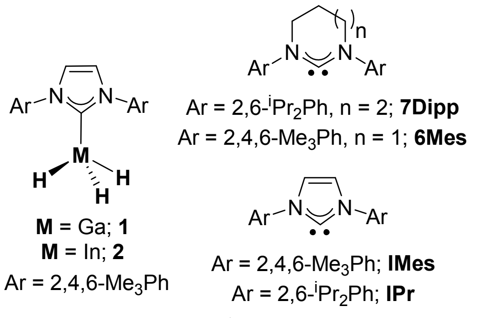
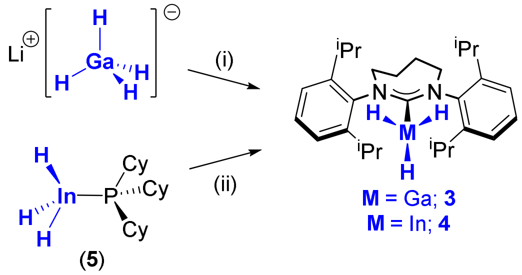


Figure 1. The stable gallane **1** and indane **2**[4] and some candidate NHCs for this work.

The supreme stability of **1** and **2** is borne out of (i) electronic stabilization of the metallane (MH_3) by the NHC donor, and (ii) kinetic stabilization of the metal hydride by the bulky *N*-mesityl substituents.[4] The latter serve to hinder M-H-M interactions, which have been cited as a potential gateway to the decomposition of the heavier group 13 metallanes (MH_3), particularly indane, by reductive dehydrogenation.[5]

To build on the successful application of IMes to gallane and indane in **1** and **2**, we reasoned that bulkier NHCs with superior donicity to IMes would generate metallanes of greater stability. A number of bulky NHCs have been reported since the preparations of **1** and **2**.[6] To assess the relative merits of these, we surveyed the solid angle steric parameters[7] of a number of silver(I) halide NHC complexes (see Table S1).† This highlighted the substantial steric bulk of the ring expanded NHC (RENHC) 7Dipp (G_{Ag}(NHC) 53.50%),[8] which eclipses those of IMes (39.28%),[9] and its bulkier relatives IPr (46.53%)[10] and 6Mes (43.46%) (Figure 1).[11] Further to greater steric encumbrance, 6- and 7-membered RENHCs like 7Dipp are also attractive as they exhibit markedly superior donor characteristics vis-à-vis imidazol-2-ylidenes like IMes.[12]

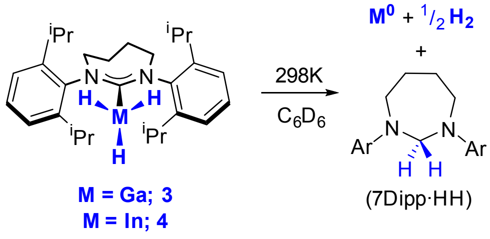


Scheme 1. The preparation of gallane **3** and indane **4**. Reagents and conditions (i) 1.0 eq. 7Dipp, -LiH(s), -20 °C to RT, ≈ 12 hours; (ii) ≈ 1.05 eq. 7Dipp, -PCy_3, -30 °C, 2 hours.

Herein we report the application of 7Dipp (Figure 1) to the stabilization of gallane and indane; [GaH_3(7Dipp)] (**3**) and [InH_3(7Dipp)] (**4**) (Scheme 1). Complex **4** is a rare example of a room temperature stable indane,† in addition **3** and **4** represent the first main group complexes of this RENHC subclass.[13] The solution phase stabilities of **3** and **4** are diminished relative to expectation. This has been rationalized on the basis of short RENHC methyl C-H····H-M distances.

Gallane **3** may be accessed in good yield (75%) by the addition of free 7Dipp to $LiGaH_4$ at low temperature (Scheme 1) followed by recrystallization at room temperature.† Indane **4** may be accessed similarly using $LiInH_4$ instead of $LiGaH_4$, however the low ether solubility of 7Dipp, **4** and the LiH co-product, make isolation of analytically pure **4** troublesome via this method. To address this the PCy_3 adduct of indane; $[InH_3(PCy_3)]$ (**5**),[14] was used as an isolable indane precursor. The reaction of **5** with a small excess of 7Dipp at -20 °C, followed by filtration and washing with cold ether afforded analytically pure **4** in good yield (71%, Scheme 1). †

The aforementioned steric bulk of 7Dipp confers considerable stability to **3** and **4** in the solid state (dec. **3** 152 °C; **4** 92 °C). While these are impressive relative to those of amine and phosphine adducts of gallane and indane, e.g. $[MH_3(Quin)]$ (M = Ga dec. 100 °C,[15] = In dec. -5 °C,[16] Quin = 1-azabicyclo[2.2.2]octane) and $[MH_3(PCy_3)]$ (M = Ga dec. 130 °C,[17] = In dec. 50 °C)[14] they are inferior to those of **1** and **2** *vide supra*.[4] Furthermore, the solution phase instability of **4** necessitates manipulation at temperatures below -30 °C to minimise decomposition *vide infra*.† Most surprising is that **3** also exhibits similar, albeit significantly slower, solution phase decomposition behavior at room temperature. For both metallanes (MH_3) decomposition at 298 K affords the aminal 7Dipp•HH as the major (**4**) or exclusive (**3**) 7Dipp containing product (Scheme 2).†



Scheme 2. The decomposition of **3** and **4**. Example conversions with time: **3**, 40% decomposition at 8 hours (30 mmol/L of **3**); M = In, 95% decomposition at 5 minutes (62 mmol/L of **4**). Note: In the above **4** (M = In) decomposes to 7Dipp•HH (major) and 7Dipp (minor) (3:2 ratio), at 248 K in toluene-d_8 **4** decomposes to solely 7Dipp•HH (21% decomposition, 37 mmol/L of **4**) over a 1 hour period.

The ^1H NMR spectra of **3** (298 K, C_6D_6) and **4** (248 K, toluene-d_8) exhibit the expected resonances for the coordinated 7Dipp ligand and metal quadrupole broadened ($^{69}Ga/^{71}Ga$; $I = {}^3/_2$, $^{113}In/^{115}In$ $I = {}^9/_2$) hydride resonances at δ 3.27 and 4.78 (**4** $\Delta\nu½ \approx$ 40 Hz, **3** overlaps with methine septet) respectively,† which are at substantially higher field relative to the hydride resonances of gallanes **1** (δ 3.96)[4] and $[GaH_3(PCy_3)]$ (δ 4.32),[17] and indanes **2** (δ 5.20)[4] and **5** (δ 5.61).[14] This is consistent with the superior donation of the RENHC in **3** and **4**,[12] which in turn increases the shielding of the MH_3 ^1H NMR resonance. The M-H infrared stretching absorbances of **3** and **4**, at 1798 and 1650 cm^{-1} respectively, are inconclusive in this regard. For instance, the stretch of **3** is blue shifted relative to **1** (1780 cm^{-1})[4] but more or less identical to that of $[GaH_3(PCy_3)]$ (1800 cm^{-1}).[17] For indane **4**, the In-H stretching frequency is identical to that of **2** (1650 cm^{-1})[4] and red shifted relative to that of **5** (1661 cm^{-1}).[14] It is conceivable that these data are affected by contrasting geometries at the metal centres, e.g. the extent of pyramidalisation of the MH_3 unit, or the contrasting π-acidities of phosphines and imidazol-2-ylidenes.

A ^1H NMR spectroscopic study of the decomposition of **4** in C_6D_6 at ambient temperature displays the rapid formation of the aminal 7Dipp•HH, dissolved H_2 (δ 4.47) and free 7Dipp with the deposition of an indium mirror (Scheme 2).† Similarly, decomposition at a substantially lower temperature (248 K) in toluene-d_8 also affords 7Dipp•HH, H_2 and indium metal, but not free 7Dipp. The rate of decomposition of **3** at ambient temperature occurs at a far slower rate than the decomposition of **4** at 298 K (Scheme 2 caption). This leads us to conclude that H_2 addition at the NCN carbon, i.e. formation of 7Dipp•HH, is dependent on the rate of decomposition. It is noteworthy that deuteration of these products, e.g. HD, is not observed and therefore the evolved H_2 must derive from **3** or **4** (cf. C_6D_6 solvent), and that preliminary investigations of the kinetics of decomposition of **4** at 253 K in toluene-d_8 indicate 1st order dependence in **4** (Table S4).

The greater projection of the *N*-substituents into the metal coordination sphere by RENHCs is typically viewed as a positive feature, however, the decreased stabilities of **3** and **4** relative to **1** and **2** indicate that the greater proximity of the *N*-aryl functions to the metal, in particular the pendant alkyl groups, promotes decomposition. It is probable this occurs by H_2 elimination to form a metallacyclic intermediate that facilitates the addition of H_2 to the NCN carbon of the NHC. Such a unimolecular mechanism is supported by the first order kinetics referred to above (Table S4).

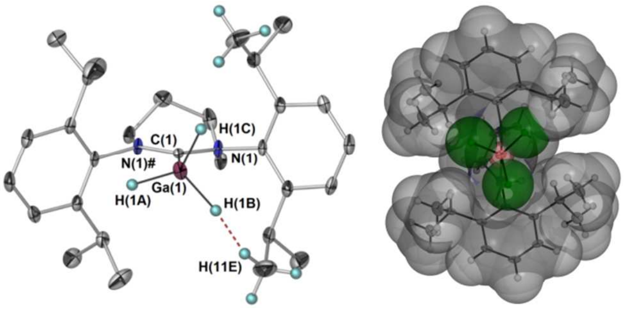


Figure 2. Molecular structure of **3** (50% thermal ellipsoid plot). Symmetry operation used to generate # atoms: *1 - x, y, ½ - z*. All hydrogen atoms excepting hydride ligands H(1A)-H(1C) and those of the methyl groups close to GaH_3 have been omitted for clarity, as have lower occupancy disordered atoms. Selected bond lengths (Å), angles (°) and steric parameters for **3**: H(11E)#····H(1B) 1.54(5) Å (sum of H,H radii 2.000 Å), Ga(1)-H(1A) 1.52(5), Ga(1)-H(1B) 1.55(5), Ga(1)-H(1C) 1.62(7), Ga(1)-C(1) 2.111(3), H(1A)-Ga(1)-H(1B) 112(3), H(1A)-Ga(1)-H(1C) 111(3), H(1B)-Ga(1)-H(1C) 105(3), H(1A)-Ga(1)-C(1) 111(2), H(1B)-Ga(1)-C(1) 104(2), H(1C)-Ga(1)-C(1) 113(3), N(1)-C(1)-N(1)# 118.7(3). G_{Ga}(7Dipp) (%) 50.60.[7]

Attempts were made to crystallise **4** for X-ray structure determination in order to evaluate the relative proximity of its alkyl functions to the InH_3 moiety. Unfortunately all attempts were frustrated by the low solubility of **4** and its rapid decomposition even at sub -30 °C temperatures. To provide a model of the structure of **4**, the indium tribromide congener, [$InBr_3$(7Dipp)] (**6**), was prepared and characterised by XRD methods (see Figure S2), as was gallane **3** (Figure 2). The M-C_{NCN} distances of **3** and **6** (2.111(3) and 2.2603(19) Å) are extended relative to those in [$GaClH_2$(IMes)][18] and **2** respectively (2.005(6), 2.253(5) Å),[4] especially in the case of **3** (>0.1 Å). With respect to the proximity of the alkyl groups to the GaH_3 or $InBr_3$ units of **3** and **6**, it is noteworthy that both structures contain short 7Dipp methyl C-H to X-M distances that are within the combined van der Waals radii of the H and X atoms (**3** X = H, M = Ga Figure 2; **6** X = Br, M = In Figure S2).[7] Although the greater size of the bromides in **6** relative to hydrides in **4** limit the extent to which the 7Dipp in **6** accurately describes that in **4**, the short alkyl to metal distances in **3** and **6** are consistent with hydride alkyl activation as a pathway for the solution state decomposition of **3** and **4**. Further support for this model may be derived from a plot of the solid state decomposition temperatures of the four structurally characterised indane complexes against their shortest $In\cdots C_{alkyl}$ distances. This affords a close to linear trend (R^2 = 0.90) (see Table S7).

Conclusions

In summary, the greater steric bulk and increased ligand donicity of 7Dipp lead to a gain in thermal stability for gallane and indane complexes in the solid state. Solution phase studies of the decomposition of **4** by ^1H NMR spectroscopy, and observations made regarding the diminished stability of **3** in solution, identify 7Dipp·HH as the principle decomposition product as well as H_2 and indium metal. 7Dipp is also formed, but only when the rate of decomposition is more rapid (cf. 248 K versus 298 K, Tables S2 and S3). Preliminary kinetic data indicate that decomposition is first order in **4**. Lastly, the short distances between the hydride or bromide ligands and alkyl functions in **3** and **6** support the viability of a hydride alkyl activation decomposition pathway.

Notes and references

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† Electronic Supplementary Information (ESI) available: Syntheses, ^1H NMR decomposition studies, steric parameter data for [AgX(NHC)] complexes, known indane complexes, and **3** and **6**, X-ray crystal structures and parameters for **3** and **6**. See DOI: 10.1039/c000000x/

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