Supporting Information

for

The Stabilization of Gallane and Indane by a Ring Expanded Carbene

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Synthetic Procedures

All synthetic manipulations were performed using standard Schlenk and glove box techniques under an atmosphere of high purity argon. All organic solvents were dried, degassed and stored for use under argon in J. Young valved ampoules. Diethyl ether, tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl.

The free RENHC 7Dipp was prepared by the literature method of Cavell, Fallis and Dervisi[S1] followed by extraction and recrystallization from toluene. Lithium tetrahydridogallate ($LiGaH_4$) and tetrahydridoindanate were prepared *in situ* via the reaction of freshly sublimed $GaCl_3$ or $InBr_3$ with 30 equivalents of LiH in diethyl ether at -30 °C (ca. 6 hours) followed by filtration at low temperature (-50 °C).[S2] $[InH_3(PCy_3)]$ was prepared by a literature procedure.[S3] All other reagents and gases were purchased from Alfa-Aesar, Ajax Fine chemicals, Sigma-Aldrich or Strem and used as received.

Unless otherwise specified, ^1H and ^{13}C NMR spectra were recorded in C_6D_6 at 298 K on a Bruker Avance III 400 spectrometer (^1H: 400.13 MHz and ^{13}C: 100.62 MHz) (compound **3**, 7Dipp·HH and ambient temperature decomposition study of **4**), a Bruker Avance III 500 spectrometer (^1H: 500.13 MHz and ^{13}C: 125.76 MHz) (compound **4** at 248 K in toluene-d_8) or a Bruker Avance III 300 spectrometer (^1H: 300.13 MHz and ^{13}C: 75.47 MHz) (compound **6**). Spectra were referenced to the resonances of residual non-deuterated solvent as per the report of Fulmer.[S4] Deuterated solvents were stored over sodium and freeze-pump-thaw degassed prior to use. Multiplicities are denoted as singlet (s), doublet (d), septet (sept) or multiplet (m) and prefixed broad (br) where applicable. Infrared spectra were collected as Nujol mulls (NaCl crystal windows) on a Nicolet Avatar 320 FTIR spectrophotometer (4000 to 400 cm^{-1}) and are denoted broad (*br*) and strong (*s*). Decomposition points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were conducted at the Microanalytical unit of the Australian National University, Canberra, Australia.

[GaH$_3$(7Dipp)] (3)

A solution of 7Dipp (0.41 g, 0.98 mmol) in diethyl ether (40 mL) at -20 °C was added to a stirred solution of LiGaH$_4$ (0.95 mmol) at -20 °C and gradually warmed to ambient temperature overnight. Filtration and removal of volatiles *in vacuo* afforded a white powder that was extracted into toluene (30 mL), concentrated to incipient crystallisation and cooled to -20 °C, which afforded [GaH$_3$(7Dipp)] as colorless octahedra (0.35 g, 0.71 mmol, 75%), dec. 152 °C. ^{1}H NMR (400.13 MHz, C_6D_6, 298 K) δ 1.21 (d, $^3J_{HH}$ = 6.7 Hz, 12H, C*H*$_3$), 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 12H, C*H*$_3$), 1.68 (br m, 4H, NCH$_2$C*H*$_2$), 3.27 (br m, 7H, Ga*H*$_3$ and C*H*(CH$_3$)$_2$), 3.51 (br m, 4H NC*H*$_2$CH$_2$), 7.10 (m, 4H, *m*-Ar*H*), 7.21 (m, 2H, *p*-Ar*H*). ^{13}C NMR (100.62 MHz, C_6D_6, 298 K) δ 24.29 (*C*H$_3$), 24.78 (NCH$_2$*C*H$_2$), 25.90 (*C*H$_3$), 29.13 (*C*H(CH$_3$)$_2$), 56.20 (N*C*H$_2$CH$_2$), 124.79, 127.93, 128.18, 129.14 (Ar*C*), 145.03 (N*C*N). IR (Nujol) *v*/cm^{-1} 1798 (*br s,* Ga-H). Anal. Cal. for $C_{29}H_{45}GaN_2$: C, 70.88; H, 9.23; N, 5.70. Found: C, 70.48; H, 8.87; N, 5.67%.

[InH$_3$(7Dipp)] (4)

A cold (-30 °C) slurry of 7Dipp (0.20 g, 0.48 mmol) in diethyl ether (40 mL) was added to a cold (-30 °C) suspension of [InH$_3$(PCy$_3$)] (0.18 g, 0.45 mmol) in diethyl ether (15 mL) with continuous stirring. After 2 hours at -30 °C the colorless solid was isolated by filtration and washed with cold (-20 °C) diethyl ether (2 x 5 mL) to afford analytically pure [InH$_3$(7Dipp)] (0.17 g, 0.32 mmol, 71%), dec. 92 °C. ^{1}H NMR (500.13 MHz, $C_6D_5CD_3$, 248 K) δ 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 12H, C*H*$_3$), 1.57-1.70 (br m, 16H, C*H*$_3$ and NCH$_2$C*H*$_2$), 3.22 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 3.41 (br m, 4H, NC*H*$_2$CH$_2$), 4.78 (br s*,* $\Delta v_{½} \approx 40$ Hz, 3H, In*H*$_3$), 7.03 (m, 4H, *m*-Ar*H*), 7.18 (m, 2H, *p*-Ar*H*). ^{13}C NMR (125.76 MHz, $C_6D_5CD_3$, 248 K) δ 24.17 (*C*H$_3$), 25.05 (NCH$_2$*C*H$_2$), 26.06 (*C*H$_3$), 28.93 (*C*H(CH$_3$)$_2$), 55.08 (N*C*H$_2$CH$_2$), 124.51, 127.41, 144.78, 145.32 (Ar*C*), 148.69 (N*C*N). IR (Nujol) *v*/cm^{-1} 1650 (*br s*, In-H). Anal. Cal. for $C_{29}H_{45}InN_2$: C, 64.92; H, 8.45; N, 5.22. Found: C, 64.58; H, 8.48; N, 5.19%.

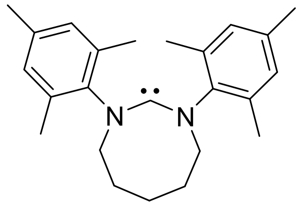
[$InBr_3$(7Dipp)] (6)

A solution of 7Dipp (0.20 g, 0.48 mmol) in THF (30 mL) was added to a stirred solution of $InBr_3$ (0.18 g, 0.51 mmol), also in THF (20 mL), at room temperature. The solution was stirred for 15 minutes, concentrated to the point of incipient crystallisation and stored at 4 °C overnight. This afforded colorless rods of **6** as its THF solvate (0.27 g, 0.32 mmol, 67%), m.p. 230 °C (dec. point beyond range of instrument, >300 °C). ^{1}H NMR (300.13 MHz, C_6D_6) δ 1.07 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.54 (br m, 4H, NCH_2CH_2), 1.64 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3), 3.32 (sept, 4H, $^3J_{HH}$ 6.7 Hz, CH(CH_3)$_2$), 3.49 (br m, 4H, NCH_2CH_2), 7.13 (m, 4H, *m*-Ar*H*), 7.23 (br dd, 2H, *p*-Ar*H*). ^{13}C NMR (75.47 MHz, C_6D_6) δ 24.8 (CH_3). 25.4 (NCH_2CH_2), 26.5 (CH_3), 28.7 ($CH(CH_3)_2$), 56.2 (NCH_2CH_2), 124.2, 128.6, 129.0, 141.8 (Ar*C*), 145.5 (N*C*N). IR (Nujol) *v*/cm^{-1} 665 (*w*), 698 (*w*) 760 (*m*), 803 (*m*), 944 (*br w*), 1064 (*m*), 1172 (*w*), 1260 (*m*), 1304 (*m*), 1365 (*m*), 1388 (*m*), 1465 (*br s*), 1589 (*w*), 1649 (*w*).

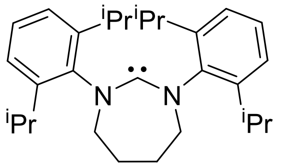
An evaluation of the steric parameters for [AgX(NHC)] complexes[S5]

Table S1

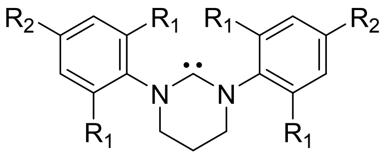
NHC	Halide X	G_{Ag}(NHC) (%)[1]	Ω(NHC)[2]
IPr*[S6]	Cl	59.53	201.98
7Dipp[S7]	**Br**	**53.50**	**188.04**
IDitop[S8]	Cl	52.47	185.66
6Dipp[S7]	Br	51.20	182.76
8Mes[S9]	Br	46.61	172.22
IPr[S10]	Cl	46.53	172.04
6Mes[S11]	Cl	43.46	164.97
IMes[S12]	Cl	39.28	155.23
IPrMe[S13]	Cl	34.94	144.95



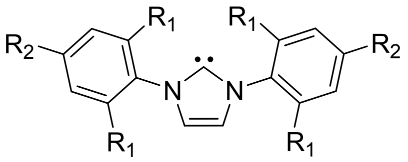
8Mes



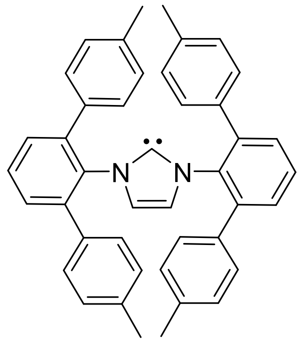
7Dipp



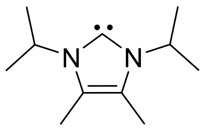
R$_1$, R$_2$ = Me: **6Mes**
R$_1$ = ^{i}Pr, R$_2$ = H: **6Dipp**



R$_1$, R$_2$ = Me: **IMes**
R$_1$ = ^{i}Pr, R$_2$ = H: **IPr**
R$_1$ = C(H)Ph$_2$, R$_2$ = Me: **IPr***



IDitop



IPrMe

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[1] G_M(L) (%) = The percentage of the metal (M) coordination sphere surface shielded by the ligand (L)

[2] Ω(L) = The cone angle that corresponds to the solid angle (Ω) normalized to the actual M-L bond length; it is not the Tolman cone angle θ. These angles are typically smaller than θ as they do not assume rotational freedom about the M-L bond. The values in Table S1 are likely inflated vs Ga/InH_3 due to a 2-coordinate, linear, metal.

Studies of the solution state decomposition of [InH_3(7Dipp)] (4)

Ambient Temperature, C_6D_6

C_6D_6 (600 µL) was added to a 5mm Youngs tapped NMR tube charged with indane **4** (~ 20 mg, ~ 37 µmol, [**4**] ~ 62 mmol/L) at -30 °C. The resulting solution was stored at 0 °C (cf. C_6D_6 m.p. 6.8 °C) for 30 minutes. ^1H NMR spectra were collected upon thawing in the spectrometer at 298 K at t = 5 and t = 60 minutes. An indium mirror was observed upon removal of the sample from the spectrometer. The singlet resonance of dissolved H_2(g) (δ 4.47)[S4] was visible in both ^1H NMR spectra. Decomposition at 298 K is rapid leading to a 10:7 ratio of 7Dipp·HH aminal to free 7Dipp.

Table S2

Time/Minutes	**[InH_3(7Dipp)] (3)**	**7Dipp·HH**	**7Dipp**
5	5	59	36
60	0	59	41

^1H NMR T_1 relaxation studies were carried out on **4**, 7Dipp·HH and 7Dipp to confirm sufficient pulse delays were employed for the measurement of reliable spectrum integrals. The relative quantities of **4**, 7Dipp·HH and 7Dipp have been calculated employing the integrals of the following non-overlapping diagnostic resonances: **4** δ 4.77 (br s, InH_3), 7Dipp·HH δ 3.78 (sept, $CH(CH_3)_2$) and 7Dipp δ 1.82 (m, NCH_2CH_2).

Intentional synthesis of 7Dipp·HH

Diethyl ether (30 mL) was added to a mixture of 7Dipp·HBr (0.20 g, 0.40 mmol) and $LiAlH_4$ (0.02 g, 0.53 mmol) and stirred for 12 hours. The solution was dried *in vacuo* to afford a white solid. Purification by extraction into toluene and cooling to -20 °C overnight yielded 7Dipp·HH as colorless truncated blocks (0.16 g, 0.38 mmol, 95%). ^1H NMR (400.13 MHz, C_6D_6) δ 1.22 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.29 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.68 (br m, 4H, NCH_2CH_2), 3.55 (br m, 4H, NCH_2CH_2), 3.78 (sept, 4H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 4.30 (s, 2H, NCH_2N), 7.14 (m, 4H, *m*-Ar*H*), 7.22 (m, 2H, *p*-Ar*H*). ^{13}C NMR (100.62 MHz, C_6D_6); δ 24.69 (CH_3), 25.10 (CH_3), 28.44 (NCH_2CH_2), 31.73 ($CH(CH_3)_2$), 54.34 (s, NCH_2CH_2), 124.70, 127.19 (Ar*C*), 136.05 (NCH_2N), 145.72, 149.05 (Ar*C*). IR (Nujol) v/cm^{-1} 665 (*w*), 763 (*m*), 805 (*m*), 933 (*w*), 980 (*w*), 1053 (*br*, *m*), 1105 (*br*, *m*), 1152 (*m*), 1264 (*m*), 1326 (*m*), 1379 (*m*), 1407 (*m*), 1465 (*br*, *s*).

Low temperature, 248 K, toluene-d_8

(Conducted during the acquisition of ^{1}H and ^{13}C NMR data for **4**)

Toluene-d_8 (500 µL) was added to a 5mm Youngs tapped NMR tube charged with indane **4** (~ 10 mg, ~ 19 µmol, [**4**] ~ 37 mmol/L). The resulting mixture was shock cooled in an acetone-liquid nitrogen bath (-94 °C, cf. $C_6D_5CD_3$ m.p. -95 °C). ^{1}H NMR spectra were collected upon thawing in the spectrometer at 248 K at t = 0 and t = 60 minutes. No indium mirror was observed upon removal of the sample from the spectrometer. The singlet resonance of dissolved H_2(g) (δ 4.57 at 248 K) was visible in both ^{1}H NMR spectra. Decomposition is substantially slower at 248 K. Further to hydrogen, the sole NMR active product is 7Dipp·HH. This contrasts the ambient temperature formation of a 10:7 mixture of 7Dipp·HH and 7Dipp in C_6D_6. It should be noted that the decomposition of **4** at 248 K was not studied beyond 20% decomposition.

Table S3

Time/Minutes	[InH$_3$(7Dipp)] (4)	7Dipp·HH	7Dipp
5	95	5	0
60	79	21	0

The relative quantities of **4** and 7Dipp·HH have been calculated employing the integrals of diagnostic non-overlapping resonances at δ 4.78 (br s, **3**, InH_3) and δ 3.79 (sept, 7Dipp·HH, CH(CH$_3$)$_2$).

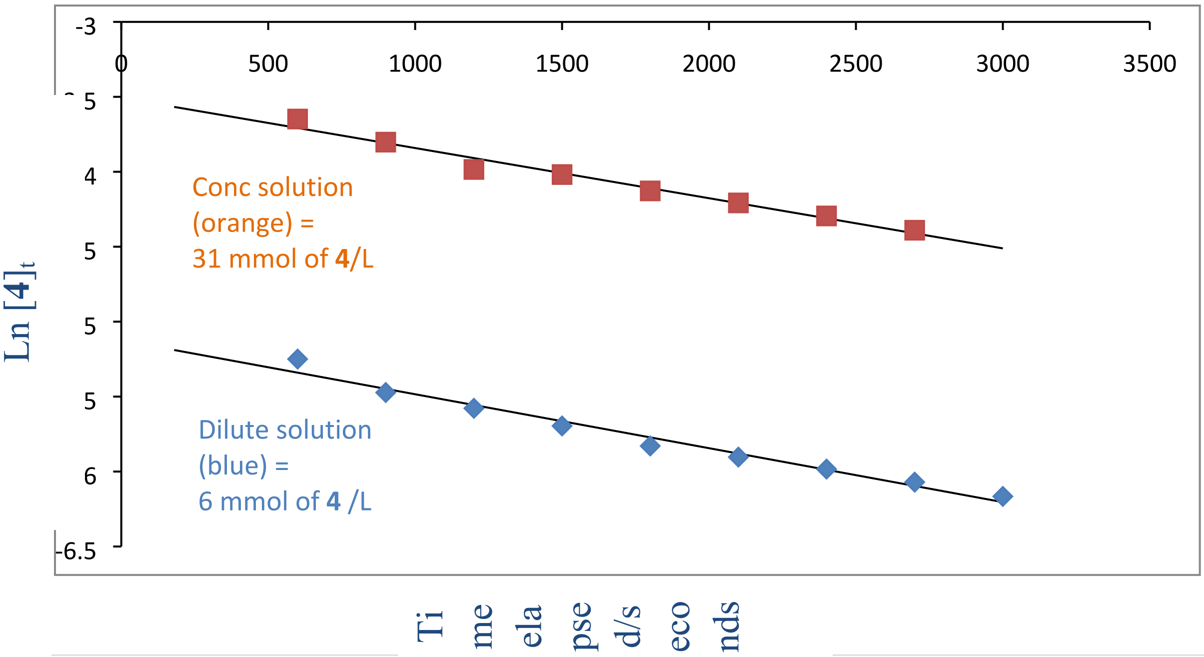
Salient ^{1}H NMR data for 7Dipp·HH in $C_6D_5CD_3$ (253 K): ^{1}H NMR (500.13 MHz) δ 1.23 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.30 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.63 (br m, 4H, NCH$_2$CH_2), 3.57 (br m, 4H, NCH_2CH$_2$), 3.79 (sept, 4H, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$), 4.24 (s, 2H, NCH_2N), 7.01-7.04 (m, 4H, *m*-ArH), 7.21 (m, 2H, *p*-ArH).

Preliminary kinetic studies, 253 K, toluene-d_8

Toluene-d_8 (600 µL) was added to two 5mm Youngs tapped NMR tubes charged with indane **4** (~ 2 mg and ~ 10 mg, ~ 4 µmol and 19 µmol, [**4**] ~ 6 mmol/L and ~ 31 mmol/L). The resulting mixtures were shock cooled in an acetone-liquid nitrogen bath (-94 °C, cf. $C_6D_5CD_3$ m.p. -95 °C). ^{1}H NMR spectra were collected upon thawing of the solutions in the spectrometer at 253 K at t = 10, 15, 20, 25, 30, 35, 40, 45 and 50 minutes. Further to hydrogen, the sole NMR active product is 7Dipp·HH (as per the low temperature decomposition study above). T_1 data from earlier studies were used to ensure valid integrals.

Table S4

Time/s	Dilute Solution (~ 6 mmol/L)	Natural log of [4]	Concentrated solution (~ 31 mmol/L)	Natural log of [4]
0	0.0060	-5.250	0.0310	-0.3474
600	0.0053	-5.473	0.0260	-3.64812
900	0.0042	-5.578	0.0223	-3.80227
1200	0.0038	-5.6956	0.0186	-3.98459
1500	0.0034	-5.829	0.0180	-4.0185
1800	0.0029	-5.903	0.0161	-4.12769
2100	0.0027	-5.983	0.0149	-4.20774
2400	0.0025	-6.071	0.0136	-4.29475
2700	0.0023	-6.166	0.0124	-4.39006
3000	0.0021	-5.250	-	-



Single crystal X-ray diffraction structure determinations

Table S5

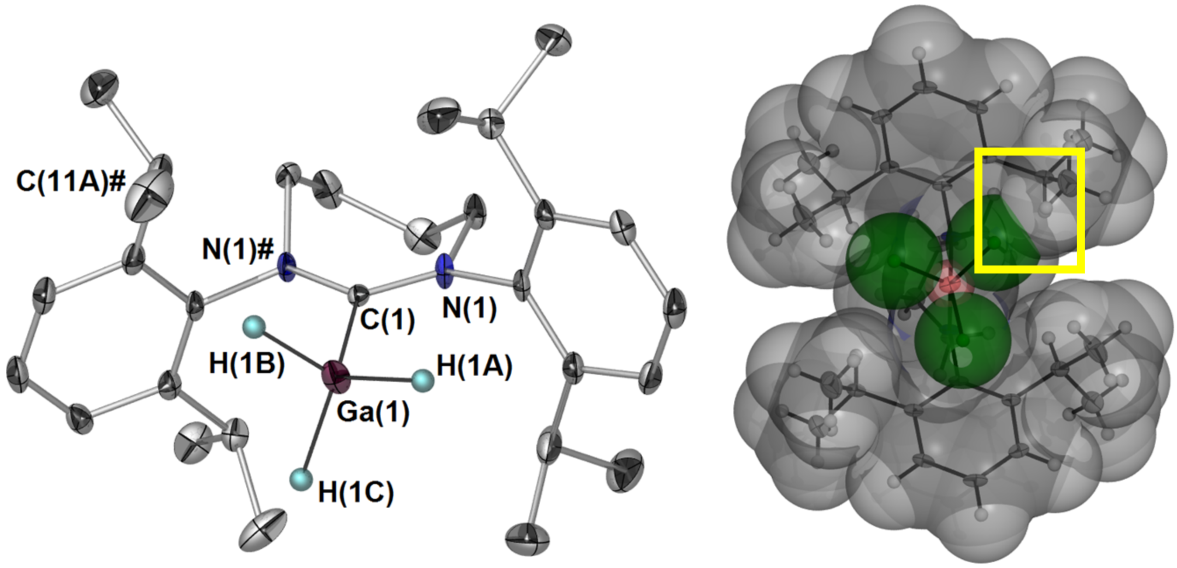
	[GaH$_3$(7Dipp)] (3)	**[InBr$_3$(7Dipp)]·THF (6)**
CCDC Deposition #	1024178	1026033
Mol. Formula	$C_{29}H_{45}GaN_2$	$C_{33}H_{50}Br_3InN_2O$
Mol. Weight	491.39	845.30
Crystal System	monoclinic	orthorhombic
Space Group	*C*2/*c*	*Pbca*
a, Å	17.0085(7)	15.8412(7)
b, Å	9.0804(5)	18.6259(7)
c, Å	17.7985(9)	23.2271(12)
α, deg	90	90
β, deg	92.882(2)	90
γ, deg	90	90
Volume, Å^3	2745.4(2)	6853.3(5)
Z	4	8
Description	octahedron	rod
Color	colorless	colorless
D_c, g cm^{-3}	1.189	1.639
F(000)	1056	3392
μ, mm^{-1}	1.020	4.215
Reflections Collected	15454	110495
R(int)	0.0358	0.0519
R(sigma)	0.0529	0.0713
Unique Reflections	2682	10034
Parameters Varied	209	369
R_1	0.0341	0.0309
wR_2 (all data)	0.0947	0.0526
GooF	1.082	1.004
$\Delta\rho$/e Å^{-3}	0.352/-0.316	0.528/-0.453

General information

Crystalline samples of **3** and **6**·THF were mounted on MiTeGen microloops in type NVH immersion oil at 150(2) K. A summary of crystallographic data can be found in Table S5. Data were collected using a Bruker Quazar Multilayer Optics $Mo_{K\alpha}$ X-ray micro source (λ = 0.71073 Å) on a Bruker Apex II CCD diffractometer, and were corrected for absorption using SADABS.[S14] Unit cell parameters were determined for collection employing software defaults and optimized upon completion of data collection using all collected frames. Structure solution and refinement was carried out using the SHELX suite of programs[S15] with the GUI X-Seed.[S16] For **3**, all non-hydride and non-methine hydrogen atoms were refined in calculated positions (riding model). The hydride ligands and methine hydrogens were located in difference maps and refined isotropically. For **6**, all hydrogens were refined in calculated positions (riding model).

[GaH$_3$(7Dipp)] (**3**) Crystallizes with one half molecule in the ASU. The remaining half is generated by a C_2 rotation about the C(1)-Ga(1) vector. This necessitates disorder of the hydride ligands over two 50:50% occupancies. Similarly, the butyl tether of the 7Dipp ligand, which exhibits disorder over two sites of 50:50 partial occupancy sits across a two-fold rotation axis. The butyl chain NCH_2CH_2 methylene atom locations lead to unrealistic bonding contacts between occupancies afforded the same formal part number. For instance, the atoms C(3A) (= part 1) and C(3B) (= part 2) must contact to provide a sensible mid-butyl C-C bond length (1.527(8) Å *vs* 1.984(7) Å C(3A)-C(3A)# or 1.982(8) Å (C(3B)-C(3B)#). **3** also exhibits disorder of the methyl atoms on one isopropyl group (C(11) and C(12)). These have been modelled over two sites with occupancies of (A:B) 54:46%. Several checkCIF alerts (levels C and G and one level B) are noted due to reflections affected by the beam stop that have either been removed or remain in the .hkl file.

Figure S1



Molecular structure of 3 (50% thermal ellipsoid plot and space fill representation with hydrides in green, NHC in grey and gallium in pink. Unfavorable contacts are boxed in yellow, see solid G analysis below). Symmetry operation used to generate # atoms: 1 - *x*, *y*, ½ - *z*. All hydrogen atoms excepting hydride ligands H(1A)-H(1C), and lower occupancy disordered atoms have been omitted for clarity. Selected bond lengths (Å), angles (º) and steric parameters for **3**: 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), C(1)-N(1) 1.342(2), C(1)-N(1)# 1.342(2), 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). Solid G[S5] calculations using Ga(1)-C(1) as the normalization distance: G_{Ga}(7Dipp) (%) 50.60, normalized cone angle of 7Dipp 181.37°, G_{Ga}(all ligands) (%) 75.79, G_{γ}(ligand overlap) (%) 9.51. Unfavorable close contacts (yellow box above): C(11A)#···H(1B) 2.43(5) Å (sum of C,H radii 2.539 Å), H(11E)#···H(1B) 1.54(5) Å (sum of H,H radii 2.000 Å)

Solid G views normal to 7-Dipp NCN plane (left) and along C(1)-Ga(1) vector (right)[S5]

8Å red sphere, blue 7Dipp

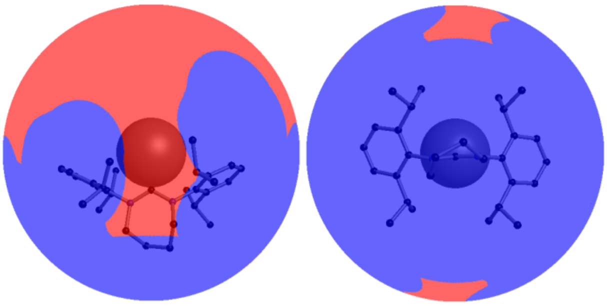
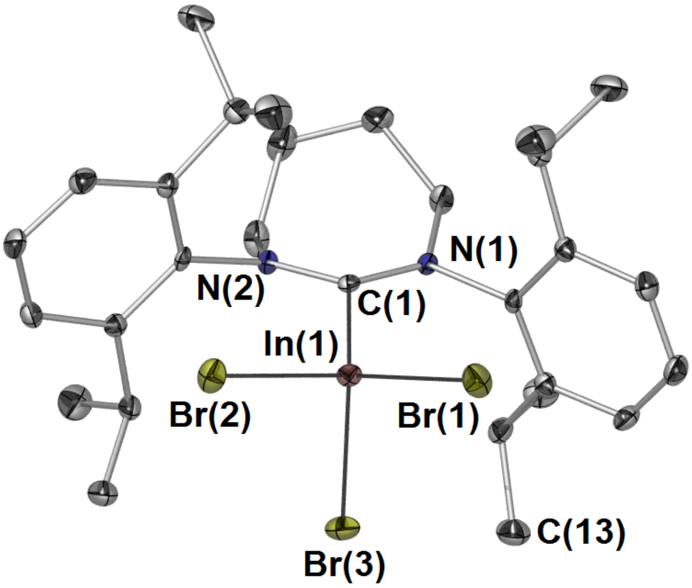
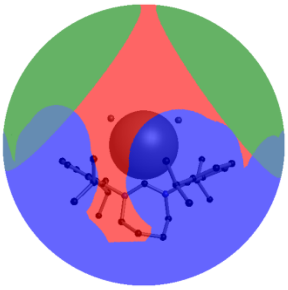


Figure S2



Molecular structure of 6 (50% thermal ellipsoid plot). All hydrogen atoms and lattice THF omitted for clarity. Selected bond lengths (Å), angles (º) and steric parameters for **6**: In(1)-Br(1) 2.5054(3), In(1)-Br(2) 2.5163(3), In(1)-Br(3) 2.5209(3), In(1)-C(1) 2.2603(19), C(1)-N(1) 1.333(2), C(1)-N(2) 1.336(3), Br(1)-In(1)-Br(2) 100.205(9), Br(1)-In(1)-Br(3) 106.728(10), Br(2)-In(1)-Br(3) 103.190(10), Br(1)-In(1)-C(1) 123.71(5), Br(2)-In(1)-C(1) 119.08(5), Br(3)-In(1)-C(1) 101.81(5), N(1)-C(1)-N(2) 121.44(17), Solid G[S5] calculations using In(1)-C(1) as the normalization distance: G_{In}(7Dipp) (%) 45.46, normalized equivalent cone angle of 7Dipp 169.58°, G_{In}(all ligands) (%) 86.88, G_{γ}(ligand overlap) (%) 6.67. Unfavorable close contacts: Br(3)···H(13C) 2.826 Å (H(13C) = C(13) methyl hydrogen, sum of Br,H radii 2.845 Å).



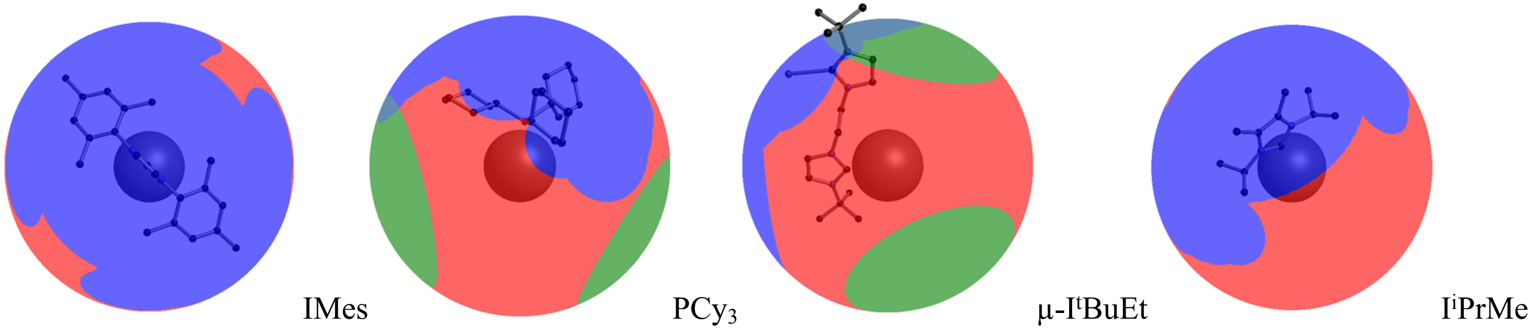
Solid G view[S5]
8Å red sphere, blue 7Dipp,
green Br

Steric parameter calculations for 3, 6 and the reported indane complexes

Table S6[S5]

Complex	CSD Ref. Code	G_{M}(L) (%)[3]	Ω (L)[4]	G_{γ}(L) (%)[5]
[GaH_3(7Dipp)] (3)	**This communication**	**50.60**	**181.38**	**9.51**
[$InBr_3$(7Dipp)] (6)	**This communication**	**45.46**	**169.58**	**6.67**
[InH_3(IMes)][S17]	BIBWIS	34.92	144.89	-
[InH_3(PCy_3)][S3]	HAZQEE	27.83	127.37	0.51
[$(InH_3)_2$(μ-I^{t}BuEt)][S18]	MODQOL	29.01	130.36	3.01
[InH_3(I^{i}PrMe)][S19]	SADWID	24.52	118.73	-

Solid G Viewer Images (Red Sphere 8Å, blue NHC/PCy_3, green hydrides)



IMes

PCy_3

μ-I^{t}BuEt

I^{i}PrMe

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[3] G_M(L) (%) = The percentage of the metal (M) coordination sphere surface shielded by the ligand (L).

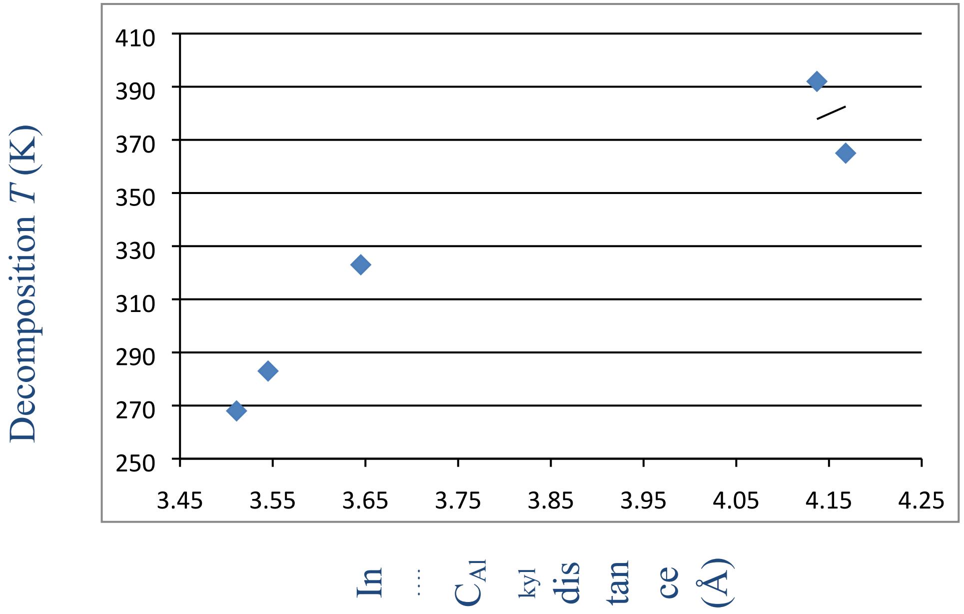
[4] Ω(L) = The cone angle that corresponds to the solid angle (Ω) normalized to the actual M-L bond length; it is not the Tolman cone angle θ. These angles are typically smaller than θ as they do not assume rotational freedom about the M-L bond and, in the current instance, use an M-L distance that is longer than the 2.10 Å convention for θ.

[5] G_{γ}(L) (%) = The percentage of the total metal coordination sphere surface that is shielded by more than one ligand. This parameter requires more than one refined ligand.

A correlation of In-H····H-C_{Alkyl} distance with solid-state decomposition T

Table S7

Indane Complex	CSD Ref. (v5.35)	Shortest In···C_{Alkyl} (Å)	Identity of alkyl	Dec. T (K)	G_{In}(L) (%) (normalized to In-L bond length)[S11]
$[InH_3(IMes)]$[S17]	BIBWIS	4.137(7)	C(10), CH_3	392	34.92
$[InH_3(PCy_3)]$[S3]	HAZQEE	3.645(2)	C(2), CH_2	323	27.83
$[(InH_3)_2(\mu\text{-}I^tBuEt)]$[S18]	MODQOL	3.545(2)	C(4), CH_2	283	29.01
$[InH_3(I^iPrMe)]$[S19]	SADWID	3.511	C(9), C*H*Me_2	268	24.52
$[InH_3(7Dipp)]$ (4)[6]	**This communication**	**4.168(3)**	**C(28), CH_3**	**365**	**45.46**



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[6] NB: The structural data used is that of tribromide **6** as a model for **4**. It is likely that **4** has shorter In-H···H-C_{Alkyl} contacts than **6** due to the expansion of 7Dipp, cf. **3**.

References

S1 M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279-3289.

S2 C. Kümmel, A. Meller and M. Noltemeyer, *Z. Naturforsch., Teil B*, 1996, **51**, 209-219.

S3 (a) D. E. Hibbs, C. Jones and N. A. Smithies, *Chem. Commun.* 1999, 185-186; (b) M. L. Cole, D. E. Hibbs, C. Jones and N. A. Smithies, *Dalton Trans*, 2000, 545-550.

S4 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

S5 Solid G – A program for the computation of ligand steric effects based on solid angles: I. A. Guzei and M. Wendt, *Dalton Trans.* 2006, 3991-3999.

S6 G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek and I. E. Markó, *Dalton Trans*, 2010, **39**, 1444-1446.

S7 E. L. Kolychev, I. A. Portnyagin, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *J. Organomet. Chem.,* 2009, **694**, 2454-2462.

S8 S. G. Alexander, M. L. Cole and J. C. Morris, *New J. Chem.*, 2009, **33**, 720-724.

S9 W. Y. Lu, K. J. Cavell, J. S. Wixey and B. Kariuki, *Organometallics*, 2011, **30**, 5649-5655.

S10 X.-Y. Yu, B. O. Patrick and B. R. James, *Organometallics*, 2006, **25**, 2359-2363.

S11 W. A. Herrmann, S. K. Schneider, K. Öfele, M. Sakamoto and E. Herdtweck, *J. Organomet. Chem.,* 2005, **689**, 2441-2449.

S12 T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay and J. A. C. Clyburne, *Inorg. Chem*., 2003, **42**, 1391-1393.

S13 P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy and S. P. Nolan, *Organometallics,* 2005, **24**, 6301-6309.

S14 SADABS, A program for area detector absorption correction, G. M. Sheldrick, Bruker Analytical X-Ray-Division, 2008, Madison, Wisconsin, USA.

S15 SHELX, G. M. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64***,* 112.

S16 L. J. Barbour, X-SEED: A graphical interface for use with the SHELX suite of programs, University of Missouri, USA, **1999**.

S17 C. D. Abernethy, M. L. Cole and C. Jones, *Organometallics*, 2000, **19**, 4852-4857.

S18 R. J. Baker, M. L. Cole, C. Jones and M. F. Mahon, *J. Chem. Soc., Dalton Trans,* 2002, 1992-1996.

S19 D. E. Hibbs, M. B. Hursthouse, C. Jones and N. A. Smithies, *Chem. Commun.,* 1998, 869-870.