Supporting Information

An Exceptionally Stable NHC Complex of Indane (InH₃)

Anthony R. Leverett[a], Marcus L. Cole[a] and Alasdair I. McKay*[,a]

[a] School of Chemistry, University of New South Wales, Sydney,

NSW 2052, Australia; E-mail: alasdair.mckay@unimelb.edu.au

Table of Contents

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 and toluene were distilled from sodium benzophenone ketyl. Pentane was collected from an Innovative Technology MD-7 solvent purification system and stored over a potassium mirror.

The free NHCs IPr[S1] and IPr*[S2,S3] were prepared by literature methods. Lithium tetrahydridoindanate (LiInH$_4$), tetradeuteridoindanate (LiInD$_4$) and tetrahydridogallate (LiGaH$_4$) were prepared *in situ* via the reaction of freshly sublimed InBr$_3$ or GaCl$_3$ with 30 equivalents of LiH or LiD in diethyl ether at -30 °C followed by filtration at low temperature (-50 °C).[S4] All other reagents were purchased from Alfa-Aesar, Ajax Fine chemicals, Sigma-Aldrich or Strem and used as received.

All one dimensional ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (^{1}H: 400.13 MHz and ^{13}C: 100.62 MHz) in C$_6$D$_6$. All two dimensional NMR spectra and ^{2}H NMR experiments were conducted on a Bruker Avance III HD 600 spectrometer fitted with a 5 mm TCI cryoprobe (^{1}H: 600.13 MHz, ^{13}C: 150.90 MHz and ^{2}H: 92.12 MHz) in C$_6$D$_6$ or C$_6$H$_6$. Spectra were referenced to the resonances of residual partially non-deuterated benzene (^{1}H and ^{13}C) or the deuterons of an external C$_6$D$_6$ reference (^{2}H) as per the report of Fulmer.[S5] C$_6$D$_6$ and C$_6$H$_6$ were stored over sodium and freeze-pump-thaw degassed before use. Multiplicities are denoted as singlet (s), doublet (d), triplet (t), 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.

[InH$_3$(IPr)] (3)

A cooled (-40 °C) diethyl ether (50 mL) solution of IPr (780 mg, 2.01 mmol) was added to a cooled (-78 °C) diethyl ether (40 mL) solution of LiInH$_4$ (2.00 mmol) and allowed to slowly warm to 0 °C over a period of 4 hours. The resulting colourless solution was dried *in vacuo,* extracted into cold (0 °C) toluene (60 mL) and concentrated under reduced pressure at 0 °C (ca. 30 mL). Gradual cooling to -25 °C afforded colorless prisms of [InH$_3$(IPr)]. A second crop was obtained by further concentration of the supernatant at 0 °C followed by cooling to -25 °C (combined yield 776 mg, 1.53 mmol, 77%), dec. 94 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K) δ 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3), 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3), 2.68 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 5.05 (br s, Δv½ ≈ 60 Hz, 3H, InH_3), 6.52 (s, 2H, NCH), 7.12 (d, $^{AX2}J_{HH}$ = 7.8 Hz, 4H, *m*-ArH), 7.26 (t, $^{AX2}J_{HH}$ = 7.8 Hz, 2H, *p*-ArH). ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K) δ 23.61, 25.01 (CH_3), 29.01 (CH(CH$_3$)$_2$), 123.81 (NCH), 124.24 (*m*-ArC), 130.60 (*p*-ArC), 135.70 (*ipso*-ArC), 145.72 (*o*-ArC), 150.01 (NCN). IR (Nujol) v/cm^{-1} 1651 (br s, In-H). Anal. Cal. for C$_{27}$H$_{39}$InN$_2$: C, 64.03; H, 7.76; N, 5.53. Found: C, 64.55; H, 7.80; N, 5.69%. C, H, N elemental analysis sample stored under argon at 22 °C for 12 months without decomposition.

Note: The reaction of LiInH$_4$ and IPr·HCl in diethyl ether afforded the dihydroaminal IPrH$_2$.

[InD$_3$(IPr)] (3^D)

Following the procedure outlined for **3** (50% scale) and substituting LiInD$_4$ for LiInH$_4$, [InD$_3$(IPr)] was isolated as a colourless powder upon extraction into cold (0 °C) toluene and removal of volatiles *in vacuo.* [InD$_3$(IPr)] characterises as per [InH$_3$(IPr)] excepting the following data: ^{2}H NMR (92.12 MHz, C$_6$H$_6$, 298 K) δ 5.09 (br s, Δv½ ≈ 4 Hz, InD_3). IR (Nujol) v/cm^{-1} 1181 (br s, In-D).

Salient NMR data for the decomposition products of 3^D

IPrHD: ^{1}H NMR data are as per those of IPrH$_2$[S6] from Rivard and co-workers excepting the following: ^{1}H NMR (600.13 MHz, C$_6$D$_6$, 298 K) δ 5.28 (s, 1H, IPr·HD). ^{2}H NMR (92.12 MHz, C$_6$H$_6$, 298 K) δ 1.28 (br s, Δv½ ≈ 3 Hz, IPr·HD isopropyl CH$_{3-n}$D$_n$), 5.27 (br s, Δv½ ≈ 18 Hz, IPr·HD). ^{13}C NMR (150.90 MHz, C$_6$D$_6$, 298 K) δ 78.32 (1:1:1 t, $^1J_{CD}$ = 23.1 Hz).

HD: ^{1}H NMR (600.13 MHz, C$_6$D$_6$, 298 K) δ 4.43 (1:1:1 t, $^1J_{HD}$ = 42.5 Hz) cf. H$_2$ δ 4.47 (C$_6$D$_6$).[S5]

[InH₃(IPr*)] (4)

IPr* (630 mg, 0.69 mmol) was added as a solid to a cooled (-78 °C) solution of LiInH$_4$ (0.69 mmol) in diethyl ether (60 mL). Gradual warming to room temperature overnight, filtration, extraction into toluene (20 mL) and layering with pentane afforded colorless prisms of [InH$_3$(IPr*)] after standing for 7 days at room temperature (410 mg, 0.40 mmol, 58%), dec. 182 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K) δ 1.71 (s, 6H, CH_3), 5.30 (s, 2H, NCH), 5.64 (s, 4H, CHPh$_2$), 5.68 (br s, Δv½ ≈ 25 Hz, 3H, InH_3), 6.86-7.04 (m, 24H, ArH), 7.05 (s, 4H, m-ArH), 7.20 (br t, 8H, ArH), 7.66 (br d, 8H, ArH). ^{13}C NMR (100.62 MHz, C$_6$D$_6$, 298 K) δ 21.32 (CH$_3$), 52.06 (CHPh$_2$), 124.11 (NCH), 126.73, 127.17, 128.45, 128.83, 129.90, 130.47, 130.96, 135.06, 140.43, 141.94, 143.38, 144.42 (ArC), 182.64 (NCN). IR (Nujol) v/cm^{-1} 1633 (br s, In-H). Anal. Cal. for C$_{69}$H$_{59}$InN$_2$: C, 80.38; H, 5.77; N, 2.72. Found: C, 80.65; H, 5.87; N, 2.90%. C, H, N elemental analysis sample stored under argon at 22 °C for 3 months without decomposition.

[GaH₃(IPr*)]·C₇H₈ (5)

IPr* (460 mg, 0.50 mmol) was added as a solid to a cooled (-78 °C) solution of LiGaH$_4$ (0.50 mmol) in diethyl ether (50 mL). After gradual warming to room temperature overnight the solvent was removed *in vacuo* and the residue extracted into room temperature toluene (40 mL). Concentration to insipient crystallisation (ca. 20 mL) and placement at -25 °C afforded the mono toluene solvate of [GaH$_3$(IPr*)] as colorless parallelogramic plates suitable for X-ray diffraction structure determination (210 mg, 0.19 mmol, 38%), dec. 226 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K, vacuum dried sample) δ 1.70 (s, 6H, CH_3), 4.44 (br s, Δv½ ≈ 10 Hz, 3H, GaH_3), 5.34 (s, 2H, NCH), 5.68 (s, 4H, CHPh$_2$), 6.84-6.91 (m, 8H, ArH), 6.92-7.03 (m, 16H, ArH), 7.04 (s, 4H, m-ArH), 7.16-7.19 (m, 8H, ArH), 7.65-7.68 (m, 8H, ArH). ^{13}C NMR (100.62 MHz, C$_6$D$_6$, 298 K, vacuum dried sample) δ 21.29 (CH$_3$), 52.00 (CHPh$_2$), 123.93 (NCH), 126.70, 127.12, 128.47, 128.79, 129.91, 130.45, 130.83, 134.76, 140.37, 141.85, 143.66, 144.18 (ArC), 180.03 (NCN). IR (Nujol) v/cm^{-1} 1790 (br s, Ga-H). Anal. Cal. for C$_{69}$H$_{59}$GaN$_2$: C, 84.06; H, 6.03; N, 2.84. Found: C, 83.04; H, 6.22; N, 3.46% (vacuum dried sample).

A correlation of indane $In \cdots C_{Alkyl}$ distance with decomposition temperature

Table S1

Indane Complex	CSD Ref. (v5.35)	Shortest $In \cdots C_{Alkyl}$ (Å)	Identity of alkyl	Dec. T (K)	$G_{In}(L)$ (%) (normalized to In-L bond length)[S11]
$[InH_3(IMes)]$[S7]	BIBWIS	4.137(7)	C(10), CH_3	392	34.92
$[InH_3(PCy_3)]$[S8]	HAZQEE	3.645(2)	C(2), CH_2	323	27.83
$[(InH_3)_2(\mu\text{-}I^tBuEt)]$[S9]	MODQOL	3.545(2)	C(4), CH_2	283	29.01
$[InH_3(I^iPrMe)]$[S10]	SADWID	3.511	C(9), CHMe$_2$	268	24.52
$[InH_3(IPr)]$ (3)	**This communication**	**4.06(1)**	**C(26C), CH(CH_3)Me**	**367**	**41.71**
$[InH_3(IPr^*)]$ (4)	**This communication**	**4.215(2)**	**C(11), CHPh$_2$**	**455**	**52.69**
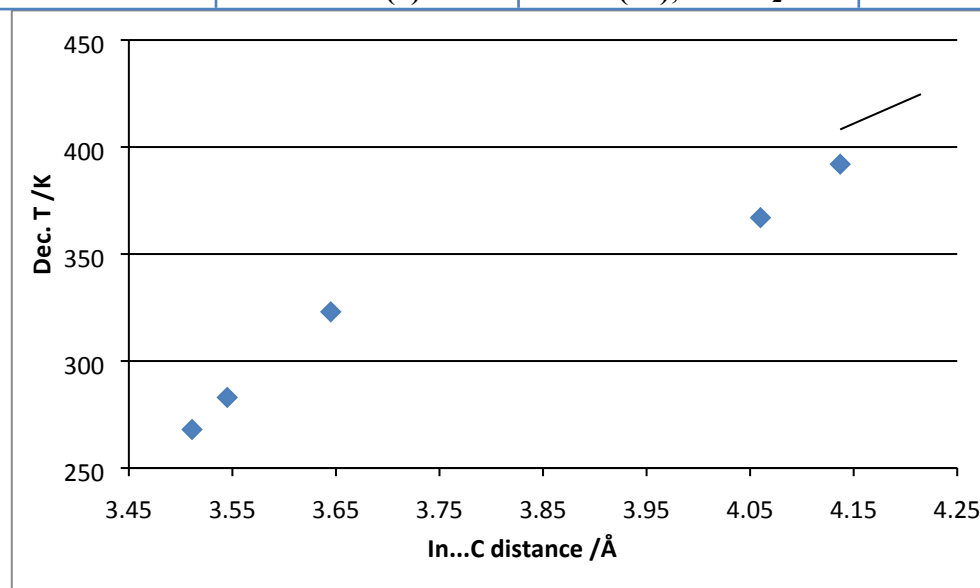
The decomposition of [InH$_3$(IPr)] (3) and [InD$_3$(IPr)] (3^D) in C$_6$D$_6$

Sample preparation and data collection for the decomposition of 3 in C$_6$D$_6$

C$_6$D$_6$ (600 µL) was added to a 5 mm Youngs tapped NMR tube charged with **3** (~ 10 mg, ~ 20 µmol, [**3**] ~ 33 mmol/L). The resulting solution was stored at 22°C for 7 days with ^{1}H NMR spectra collected on a 400.13 MHz NMR spectrometer at 24 hour intervals. No change in solution composition was observed after day 4. An indium mirror was noted on day 3. The singlet resonance of dissolved H$_2$(g) (δ = 4.47 ppm)[S5] was visible in all ^{1}H NMR spectra after t = 0. The period of greatest degradation of **3** occurred in the following 24 hours (by day 4) with generation of a 6:1 mixture of free IPr and IPrH$_2$ relative to that documented at day 3.

^{1}H NMR T_1 relaxation studies were carried out on **3**, IPr and IPrH$_2$ to confirm sufficient pulse delays were employed for the measurement of reliable spectrum integrals. The relative quantities of **3**, IPrHD and IPr have been calculated employing the integrals of the "IPr" 4,5-NC*H* singlets at δ = 6.52, 5.62[S6] and 6.57[S1] ppm respectively (Δv_o<0.01 ppm signal breadth).

Table S2

Time/days	[InH$_3$(IPr)] (3)	IPrH$_2$	IPr
0	100	0	0
1	93	7	0
2	86	14	0
3*	84	16	0
4-7	0	28	72

* Indium mirror noted at t = 72 hours.

Sample preparation and data collection for the decomposition of 3^D in C_6D_6

C_6D_6 (500 µL) was added slowly to a 5 mm Youngs tapped NMR tube charged with 3^D (~ 20 mg, ~ 39 µmol, $[3^D]$ ~ 79 mmol/L) in an acetone-liquid nitrogen bath (-78 °C). The resulting solution was stored at 22 °C with ^1H NMR spectra collected on a 400.13 MHz NMR spectrometer at t = 12, 16, 36 and 72 hours (Table S2). A ^2H NMR spectrum (92.12 MHz, referenced to the C_6D_6 solvent) was collected at t = 18 hours on a Bruker Avance III HD 600 spectrometer fitted with a cryoprobe (Δv½ evaluation stymied by the breadth of resonances and variable baseline, the latter due to C_6D_6 signal suppression): δ 1.28 (br s, IPrHD isopropyl $CH_{3-n}D_n$), 5.09 (br s, 3^D InD_3), 5.27 (br s, IPrHD). ^{13}C DEPT 135, ^1H:^{13}C HSQC and ^1H:^{13}C HMBC NMR experiments were carried out on the sample at t = 72 hours.

A grey solid was noted at t = 16 hours. The 1:1:1 triplet resonance of dissolved HD(g) (δ = 4.43 ppm, $^1J_{HD}$ = 42.5 Hz) was visible in all ^1H NMR spectra after t = 0. The period of greatest degradation of 3^D occurred between 16 and 36 hours, wherein the decomposition trended to the generation of IPrHD.

^1H NMR T_1 relaxation studies were carried out on 3^D, IPrHD and the unidentified IPr species to confirm sufficient pulse delays were employed for the measurement of reliable spectrum integrals. The relative quantities of 3^D, IPrHD and the unidentified IPr intermediate were calculated employing the integrals of the "IPr" 4,5-NCH singlets at δ = 6.52, 5.62[S6] and 5.51 ppm respectively.

Table S3

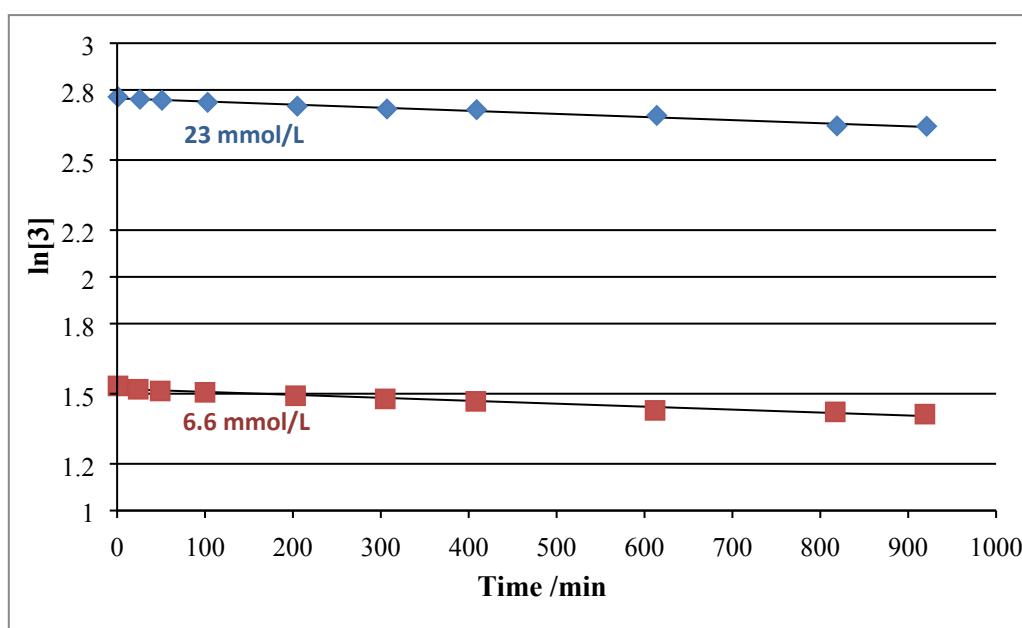| Time/hours	[InD$_3$(IPr)] (3^D)	IPrHD	Unidentified IPr Species
0	100	0	0
12	62	38	0
16*	45	39	16
36	5	92	3
72	0	100	0

*   Grey deposit noted at t = 16 hours. No indium mirror deposition.

The first order decomposition of [InH₃(IPr)] (3) in C₆D₆ at room temperature

C₆D₆ (600 µL) was added to two 5 mm Youngs tapped NMR tubes charged with indane **3** (2 mg, 3.9 mmol and 7 mg, 13.8 mmol respectively). The resultant mixtures were frozen in an acetone-liquid nitrogen bath (-50 °C *cf.* C₆D₆ m.p. 5.5 °C) and ^{1}H NMR spectra taken upon thawing at t = 1, 26, 51, 103, 205, 307, 409, 614, 819 and 912 minutes. Further to dihydrogen, the sole NMR active decomposition product during this time interval was IPrH₂.

Table S4

Time/min	[3] Dilute solution ($\approx$ 6.6 mmol/L)	Dilute solution In[3]	[3] Conc. solution ($\approx$ 23 mmol/L)	Conc. Solution In[3]
1	4.634	1.533	15.964	2.770
26	4.568	1.519	15.803	2.760
51	4.535	1.512	15.734	2.756
103	4.509	1.506	15.596	2.747
205	4.443	1.491	15.342	2.731
307	4.384	1.478	15.158	2.719
409	4.337	1.467	15.112	2.715
614	4.173	1.429	14.743	2.691
819	4.147	1.422	14.098	2.646
921	4.107	1.413	14.075	2.644

The decomposition of [InH$_3$(IPr*)] (4) in the solid state and in C$_6$D$_6$

Sample preparation and data collection for the decomposition of 4 in air

A 50 mL round bottom flask charged with 45 mg of **4** (89 μmol) under argon was placed under air and fitted with a silica drying tube. After standing for 14 days a representative sample was removed and a ^{1}H NMR spectrum collected using freshly freeze-pump-thaw degassed C$_6$D$_6$. An infrared spectrum (nujol mull) was collected on the same solid.

The remaining solid was left open to air in the absence of a drying tube for five days with spectra collected at t = 3 and 5 days.

^{1}H NMR T_1 relaxation studies were carried out on **4**, IPr*H$_2$ and the unidentified IPr* species to confirm sufficient pulse delays were employed for the measurement of reliable spectrum integrals. The relative quantities of **4**, IPr*H$_2$ and the unidentified IPr* species have been calculated employing the integrals of the "IPr*" 4,5-NC*H* singlets at δ = 5.30, 5.71 and 5.13 ppm respectively.

Table S5

Time/days	[InH$_3$(IPr*)] (4)	IPr*H$_2$	Unidentified IPr* Species
0	100	0	0
14 (drying tube)	97	3	0
+3 no silica	93	> 6	< 1
+5 no silica	90	7	3

IPr*H$_2$ characterizes as follows: ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): δ 1.82 (s, 6H, C*H$_3$*), 5.02 (s, 2H, NC*H$_2$*N), 5.71 (s, 2H, NC*H*), 6.52 (s, 4H, C*H*Ph$_2$), remaining resonances obscured by resonances for **4**.

The unidentified IPr* species characterizes as follows: ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): δ 1.81 (s, 6H, C*H$_3$*), 5.13 (s, 2H, NC*H*), 6.03 (s, 4H, C*H*Ph$_2$), remaining resonances obscured by resonances for **4**. IR (Nujol) v/cm^{-1} 1705 (br s, In-H, cf. **4** 1633 cm^{-1}), no absorbance above 3000 cm^{-1}.

Sample preparation and data collection for the decomposition of 4 in C$_6$D$_6$

C$_6$D$_6$ (600 µL) was added to a 5 mm Youngs tapped NMR tube charged with **4** ($\sim$ 10 mg, $\sim$ 9.7 µmol, [**4**] $\sim$ 16 mmol/L). The resulting solution was stored at 22°C for 6 days with ^{1}H NMR spectra collected at 24 hour intervals on a 400.13 MHz NMR spectrometer. An indium mirror was noted on day 3. The singlet resonance of dissolved H$_2$(g) (δ = 4.47 ppm)[S5] was visible in all ^{1}H NMR spectra after t = 0. Decomposition is gradual in terms of free IPr* and IPr*H$_2$ formation. Unlike **3**, the indium mirror does not initiate the rapid formation of free NHC.

^{1}H NMR T_1 relaxation studies were carried out on **4**, IPr*H$_2$ and IPr* to confirm sufficient pulse delays were employed for the measurement of reliable spectrum integrals. The relative quantities of **4**, IPr*H$_2$ and IPr* have been calculated employing the integrals of the "IPr*" 4,5-NC*H* singlets at δ = 5.30, 5.71 and 5.78[S3] ppm respectively (Δv_o<0.01 ppm signal breadth).

Table S6

Time/days	[InH$_3$(IPr*)] (4)	IPr*H$_2$	IPr*
0	100	0	0
1	94	5	1
2	88	10	2
3*	80	14	6
4	67	16	17
5	55	18	27
6	46	21	33

* Indium mirror noted at t = 72 hours

The decomposition of [InH$_3$(IPr)] (3) and [InH$_3$(IPr*)] (4) at 75 °C in C$_6$D$_6$

Sample preparation and data collection

C$_6$D$_6$ (500 µL × 2) was added to two 5 mm Youngs tapped NMR tubes, one charged with **3** (~ 10 mg, ~ 20 µmol, [**3**] ~ 40 mmol/L) and the other with **4** (~ 15 mg, ~ 15 µmol, [**4**] ~ 30 mmol/L). Both tubes were sealed and suspended in a 75 °C oil bath. ^{1}H NMR spectra were collected 1 hour after the samples exhibited an indium mirror (**3** In^0 at ca. 1 hour, **4** In^0 ca. 2 hours), at which point resonances attributable to the precursor indanes were absent. A singlet for dissolved H$_2$(g) at δ 4.47 ppm[S5] was observed for both samples.

The final resting composition of each solution was as follows based on the magnitudes of the integrals of signals assigned to the 4,5-heterocyclic protons of "IPr" or "IPr*":

Table S7

Compound	NHCH$_2$	NHC
[InH$_3$(IPr)] (**3**)	19	81
[InH$_3$(IPr*)] (**4**)	14	86

X-ray structure determinations, collection parameters, data and figures

Table S8

	[InH$_3$(IPr)]	[InH$_3$(IPr*)]	[GaH$_3$(IPr*)]·C$_7$H$_8$
CCDC Deposition #	1852179	1852180	1852178
Mol. Formula	C$_{27}$H$_{39}$InN$_2$	C$_{69}$H$_{59}$InN$_2$	C$_{69}$H$_{59}$GaN$_2$·C$_7$H$_8$
Mol. Weight	506.42	1031.00	1078.03
Crystal System	triclinic	monoclinic	triclinic
Space Group	*P*-1	*P*2$_1$/*n*	*P*-1
a, Å	12.591(4)	14.9001(3)	11.1383(16)
b, Å	15.893(5)	18.1641(4)	13.614(2)
c, Å	15.980(6)	19.6086(4)	21.511(3)
α, deg	119.048(13)	90	71.868(7)
β, deg	90.951(17)	90.2040(10)	80.282(8)
γ, deg	92.806(17)	90	70.514(8)
Volume, Å^3	2789.1(17)	5306.97(19)	2914.6(8)
Z	4	4	2
Description	prism	prism	plate
Color	colorless	colorless	colorless
D$_c$, g cm^{-3}	1.206	1.290	1.228
F(000)	1056	2144	1136
μ, mm^{-1}	0.861	0.490	0.518
Reflections Collected	42774	83942	35199
R(int)	0.0550	0.0290	0.1709
R(sigma)	0.0534	0.0515	0.1210
Unique Reflections	10924	10500	11091
Parameters Varied	645	679	727
R$_1$	0.0420	0.0354	0.0682
wR$_2$ (all data)	0.1073	0.1020	0.1795
GooF	1.012	1.056	0.984
Δ*ρ*/e Å^{-3}	1.173/-1.235	0.483/-0.687	0.674/-0.544

General details

Crystalline samples of **3-5** were mounted on MiTeGen micromounts in type NVH immersion oil at 150(2) K. A summary of crystallographic data can be found in Table S8. Data were collected using a Bruker Quazar Multilayer Optics Mo$_{K\alpha}$ X-ray micro source ($\lambda = 0.71073$ Å) on a Bruker Apex II CCD diffractometer, and were corrected for absorption using SADABS.[S12] 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[S13] with the interface OLEX2.[S14] All non-hydride hydrogen atoms were refined in calculated positions (riding model). The hydride ligands of all complexes were located in the Fourier difference map and refined isotropically.

Variata

Several carbon atoms of a single diphenylmethyl arene of **[InH₃(IPr*)]** (C(34)-C(36)) exhibit significant thermal motion in one dimension. Attempts to model the disorder of these atoms and the remainder of the arene (C(25)-C(30)) afforded no change in R-factor and unsatisfactory thermal anisotropic parameters. As a result these atoms exhibit a large non-solvent U_{eq}(max)/U_{eq}(min) range (PLAT220 alert level C), as do the bonded H atoms (PLAT222 alert level C) and generate significant disparities in U_{eq} values compared with neighboring atoms (alert level C).

The IPr ligands of the two distinct molecules of **[InH₃(IPr)]** exhibit substantial thermal motion particularly that of molecule 'A' (all non-H atoms labelled A or C). Attempts to model disorder for the isopropyl methyl groups; C(12B), C(15B), C(15A), C(27A), C(11A), C(23A) and C(25A) and the heterocycle of molecule A (C(1A)-C(3A), N(1A) and N(2A)) were unsuccessful owing to unreasonable geometry or poor anisotropic parameters. As a result they have been retained as single occupancies (multiple level C alerts PLAT213, -220, -222, -234, -241, -242, -245). However, the remaining methyl groups were modelled over two sites with relative occupancies; 0.60:0.40 C(12A/C), 0.35:0.65 C(24A/C), 0.31:0.69 C(11B/D) and 0.65:0.35 C(14B/D). Some of the hydride ligands of **[InH₃(IPr)]** display significant deviation from a sensible In-H bond length or tetrahedral geometry. Furthermore, some were unstable to the least squares refinement. This required the equal bond length restraint (SADI, $\sigma = 0.02$ (A molecule), 0.01 (B molecule)) to be applied between indium and

the hydride ligands. In addition, to obtain sensible geometry, an equal bond length restraint (SADI, σ = 0.04) was also applied between the three hydride ligands (molecule A). For molecule B, to achieve refinement stability a fixed bond length restraint (DANG, σ = 0.04) needed to be applied.

The lattice toluene of **[GaH$_3$(IPr*)]·C$_7$H$_8$** is reasonably well behaved but exhibits significantly higher thermal motion than the metal complex. No attempt was made to model disorder for the lattice toluene. Some of the FCF reflections were below theta minimum due to obstruction from the beam stop (PLAT910 level B and PLAT911 level C) and were subsequently omitted from the final refinement. Multiple checkCIF/PLATON alerts, aside from those associated with a large range of carbon U$_{eq}$ values (level C alert, PLAT220), can be attributed to the lattice solvent (level C and G alerts).

Figure S1
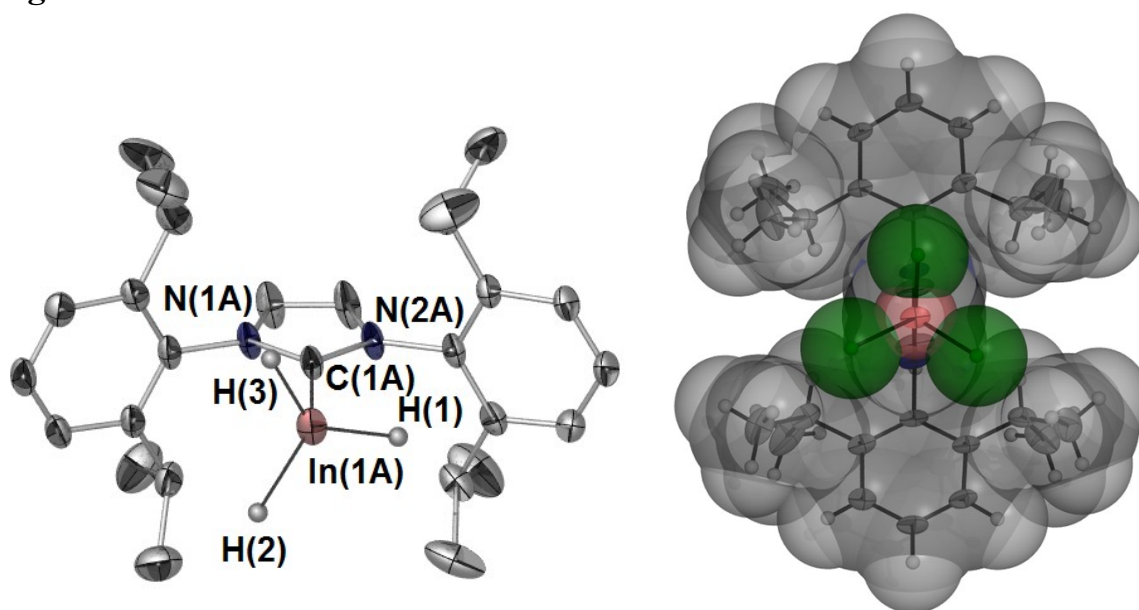
Molecular structure of 3 (50% thermal ellipsoid plot and space fill representation with hydrides in green, NHC in grey and indium in pink). Second unique molecule in the ASU and all hydrogen atoms excepting hydride ligands H(1)-H(3) omitted for clarity. Selected bond lengths (Å), angles (º) and steric parameters for **3** (values in square parentheses refer to 2nd (B) unique molecule in the ASU): In(1A)-H(1) 1.70(4) [1.64(3)], In(1A)-H(2) 1.71(5) [1.64(4)], In(1A)-H(3) 1.71(4) [1.78(3)], In(1A)-C(1A) 2.279(2) [2.259(2)], C(1A)-N(1A) 1.342(4) [1.349(4)], C(1A)-N(2A) 1.345(4) [1.352(5)], H(1)-In(1A)-H(2) 115(2) [114(2)], H(1)-In(1A)-H(3) 113(2) [111(2)], H(2)-In(1A)-H(3) 113(2) [109(2)], H(1)-In(1A)-C(1A) 105(1) [109(1)], H(2)-In(1A)-C(1A) 106(1) [109(1)], H(3)-In(1A)-C(1A) 104(1) [106(1)], N(1A)-C(1A)-N(2A) 104.0(3) [104.3(2)], Solid G[S11] calculations using In(1A)-C(1A) as the normalization distance: G_{In}(IPr) (%) IPr 40.88 [41.04], normalized cone angle of IPr 158.99° [159.35°], G_{In}(all ligands) (%) 65.18 [66.97], G_{γ}(ligand overlap) (%) 6.25 [4.66].
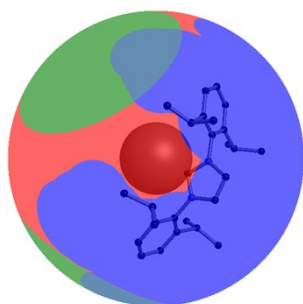
Solid G views of Molecule A (left) and Molecule B (right)[S11]

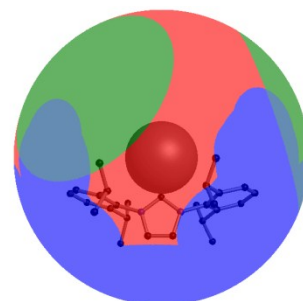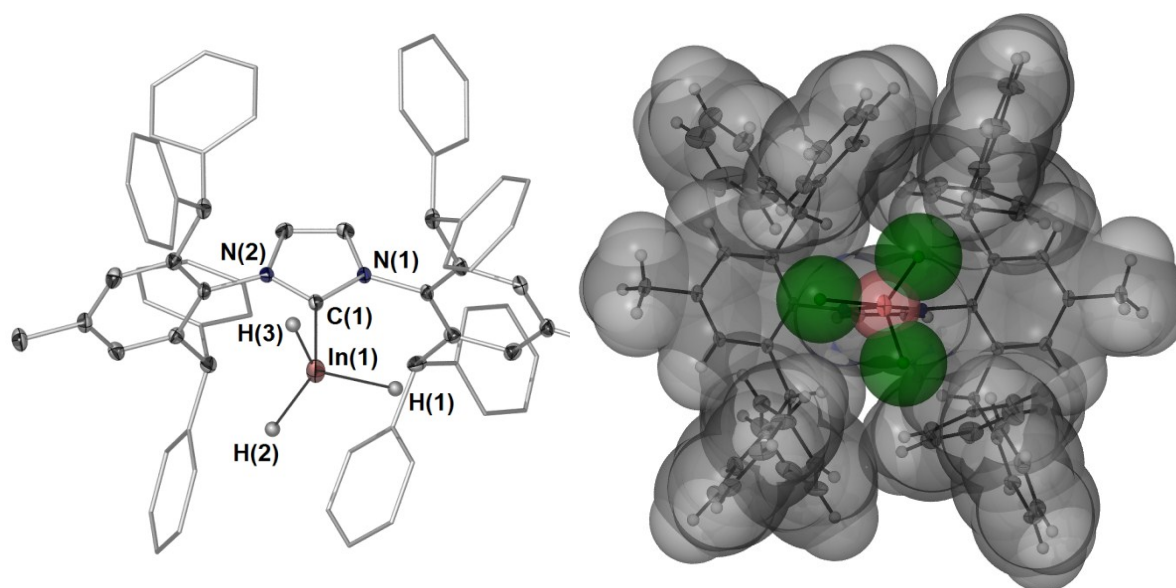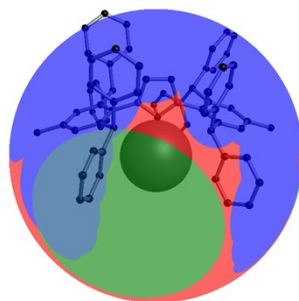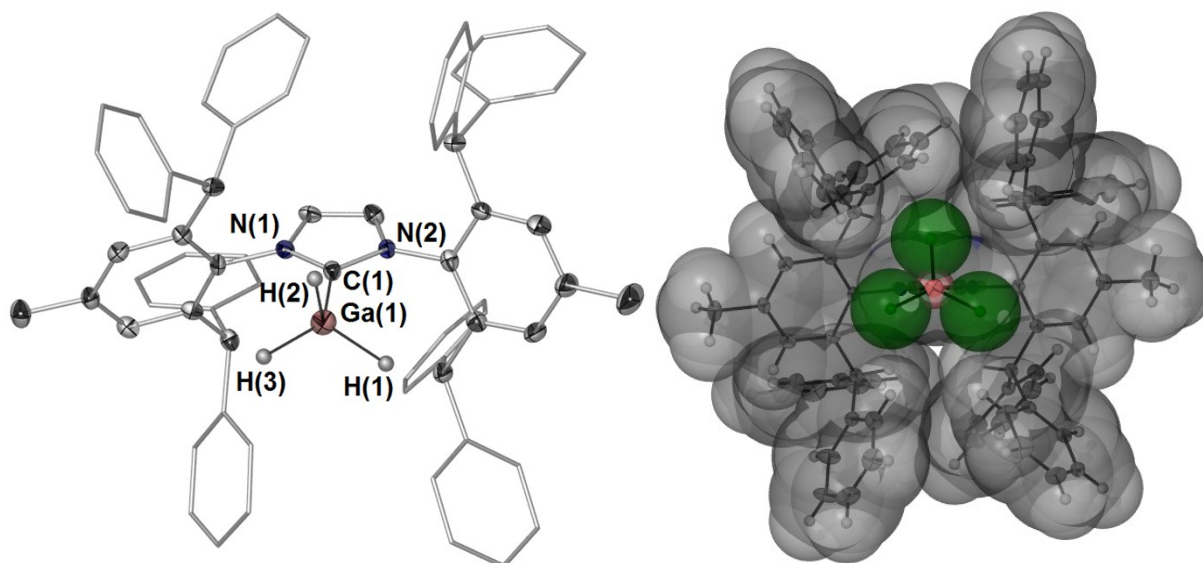**8Å red sphere, blue IPr, green hydrides**

Figure S2

Molecular structure of 4 (50% thermal ellipsoid plot and space fill representation with hydrides in green, NHC in grey and indium in pink). All hydrogen atoms excepting hydride ligands H(1)-H(3) omitted for clarity. Phenyl groups depicted as wireframes. Selected bond lengths (Å), angles (º) and steric parameters for **4**: In(1)-H(1) 1.76(4), In(1)-H(2) 1.67(4), In(1)-H(3) 1.68(4), In(1)-C(1) 2.275(2), C(1)-N(1) 1.356(3), C(1)-N(2) 1.363(3), H(1)-In(1)-H(2) 113(2), H(1)-In(1)-H(3) 115(2), H(2)-In(1)-H(3) 120(2), H(1)-In(1)-C(1) 102(1), H(2)-In(1)-C(1) 98(1), H(3)-In(1)-C(1) 104(1), N(1)-C(1)-N(2) 104.2(2), In$\cdots$C$_{alkyl}$ 4.215(2)-4.682(2) Å. Solid G[S11] calculations using In(1)-C(1) as normalization distance: G_{In}(IPr*) (%) 52.69, normalized cone angle of IPr* 186.17°, G_{In}(all ligands) (%) 72.60, G_γ(ligand overlap) (%) 8.39.
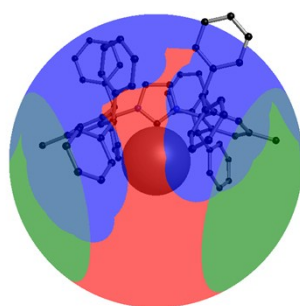

Solid G view, 8Å red sphere, blue IPr*, green hydrides[S11]

Figure S3

Molecular structure of 5 (50% thermal ellipsoid plot and space fill representation with hydrides in green, NHC in grey and gallium in pink). Lattice toluene and all hydrogen atoms excepting hydride ligands H(1)-H(3) omitted for clarity. Phenyl groups depicted as wireframes. Selected bond lengths (Å), angles (º) and steric parameters for **5**: Ga(1)-H(1) 1.57(4), Ga(1)-H(2) 1.61(4), Ga(1)-H(3) 1.48(4), Ga(1)-C(1) 2.073(4), C(1)-N(1) 1.353(6), C(1)-N(2) 1.357(4), H(1)-Ga(1)-H(2) 111(2), H(1)-Ga(1)-H(3) 111(2), H(2)-Ga(1)-H(3) 115(2), H(1)-Ga(1)-C(1) 109(1), H(2)-Ga(1)-C(1) 105(2), H(3)-Ga(1)-C(1) 105(1), N(1)-C(1)-N(2) 104.4(3), Ga$\cdots$C$_{alkyl}$ 3.688(3)-4.888(5) Å. Solid G[S11] calculations using Ga(1)-C(1) as the normalization distance: G_{Ga}(IPr*) (%) 52.89, normalized cone angle of IPr* 186.62°, G_{Ga}(all ligands) (%) 78.30, G_{γ}(ligand overlap) (%) 11.55.

Solid G view, 8Å red sphere, blue IPr*, green hydrides[S11]

References

[S1]   L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49-54.

[S2]   G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Markó, *Dalton Trans.* **2010**, *39*, 1444-1446.

[S3]   A. Gómez-Suárez, R. S. Ramón, O. Songis, A. M. Z. Slawin, C. S. J. Cazin, S. P. Nolan, *Organometallics* **2011**, *30*, 5463-5470.

[S4]   C. Kümmel, A. Meller, M. Noltemeyer, *Z. Naturforsch., Teil B* **1996**, *51*, 209-219.

[S5]   G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

[S6]   S. M. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, E. Rivard, *J. Am. Chem. Soc.* **2011**, *133*, 777-779.

[S7]   C. D. Abernethy, M. L. Cole, C. Jones, *Organometallics* **2000**, *19*, 4852-4857.

[S8]   D. E. Hibbs, C. Jones, N. A. Smithies, *Chem. Commun.* **1999**, 185-186.

[S9]   R. J. Baker, M. L. Cole, C. Jones, M. F. Mahon, *J. Chem. Soc., Dalton Trans.* **2002**, 1992-1996.

[S10]   D. E. Hibbs, M. B. Hursthouse, C. Jones, N. A. Smithies, *Chem. Commun.* **1998**, 869-870.

[S11]   Solid G – A program for the computation of ligand steric effects based on solid angles: I. A. Guzei, M. Wendt, *Dalton Trans.* **2006**, 3991-3999. Normalization distance = In/Ga-C_{NHC} bond length, $G_M(L)$ (%) = the percentage of the metal coordination sphere shielded by the ligand L, G_M(all ligands) (%) = the percentage of the metal coordination sphere shielded by all ligands, G_γ(ligand overlap) (%) = the percentage of the metal coordination sphere shielded by more than one ligand.

[S12]   SADABS, A program for area detector absorption correction, G. M. Sheldrick, Bruker Analytical X-Ray-Division, **2008**, Madison, Wisconsin, USA.

[S13]   (a) G. Sheldrick, *Acta. Cryst.*, **2015**, *C71*, 3-8; (b) G. M. Sheldrick, *Acta. Cryst.*, **2015**, *A71*, 3-8.

[S14]   O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341.
.