Hydrazine Adducts of Tri(*tert*-butyl)aluminum, -gallium and -indium – a Systematic Approach

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Treatment of the monomeric trialkylelement compounds $Al(CMe_3)_3$, $Ga(CMe_3)_3$, and $In(CMe_3)_3$ with different hydrazines $H_2N–N(H)R$ (R = Me, CMe_3, C_6H_5) yielded the corresponding adducts $(Me_3C)_3E \leftarrow NH_2–N(H)R$, **1** to **9**, in almost quantitative yields. All products were characterized by crystal structure determinations and shown to have the NH_2 group of the hydrazine ligands attached to the central Group 13 atom. These adducts are excellent starting compounds for the generation of hydrazides by thermolysis with release of butane.

Key words: Aluminum, Gallium, Indium, Hydrazines, Adducts

Introduction

Alkylaluminum, -gallium or -indium hydrazides are suitable starting compounds for the generation of the corresponding element nitrides by thermolysis [1]. Furthermore, they found increased interest in recent literature owing to the fascinating coordination behavior of the bifunctional hydrazido ligands, which resulted in the formation of a broad variety of heterocyclic or cage-like compounds. Their synthesis was accomplished *via* several efficient routes, which essentially comprise hydrogen or alkane elimination, salt elimination and hydroalumination reactions [2 – 25]. The formation of adducts was postulated as a reasonable initiating step in particular for the first two types of elimination reactions. However, these adducts were isolated and thoroughly characterized in few cases only [5, 9, 16 – 19, 22, 23, 25]. Steric interactions determine the coordination mode, and usually the less shielded NH_2 nitrogen atom of the hydrazine ligands is attached to the central aluminum or gallium atoms. A single exception was recently observed with the compound $Me_3Ga \leftarrow N(H)(Me)–NH_2$ in which the more basic alkylated nitrogen atom is coordinated to the gallium atom [25]. The formation of this particular compound may be favored by the low steric shielding of acceptor and donor atoms. Systematic investigations into the coordination of tri(*tert*-butyl)element compounds (E = Al, Ga, In) by different hydrazines $H_2N–N(H)R$ (R = Me, CMe_3, C_6H_5) should allow for a concise understanding of steric or electronic influences on the structures and properties of these adducts. A different reactivity pattern may appear owing to the strongly differing polarities of the E–C bonds. For instance, $AlMe_3$ or $InMe_3$ did not yield stable adducts with methylhydrazine at all. Instead spontaneous release of methane occurred below r. t. [25]. $GaMe_3$ and methylhydrazine gave an adduct as described above, and heating was required to initiate a secondary reaction. These compounds are potentially useful precursors for the generation of hydrazides or the corresponding nitrides by thermolysis, because only volatile by-products may be formed. Furthermore, *tert*-butyl substituents are particularly suitable leaving groups for these purposes, because butane may be eliminated by direct deprotonation of the hydrazido ligands or β-elimination may occur followed by release of elemental hydrogen.

Results and Discussion

Synthesis of the adducts $(Me_3C)_3E \leftarrow NH_2–N(H)R$ ***1*** *to* ***9***

A standard procedure was applied for the synthesis of all adducts. The tri(*tert*-butyl) element compounds were dissolved in *n*-pentane or *n*-hexane and treated with equimolar quantities of the respective hydrazine at r. t. (Eq. 1). After stirring for 1 h the solvents were removed in a vacuum to obtain the products in high purity and in almost quantitative yield. Two alkylaluminum (**1** and **2**) and alkylgallium adducts (**4** and **5**)

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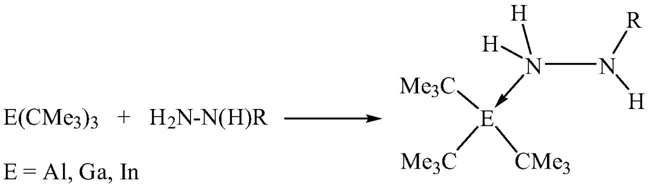

$E(CMe_3)_3 + H_2N\text{-}N(H)R \longrightarrow$ (1)

E = Al, Ga, In
R = Me, CMe_3, C_6H_5

1: E = Al; R = Me
2: E = Al; R = CMe_3
3: E = Al; R = C_6H_5
4: E = Ga; R = Me
5: E = Ga; R = CMe_3
6: E = Ga; R = C_6H_5
7: E = In; R = Me
8: E = In; R = CMe_3
9: E = In; R = C_6H_5

remained as amorphous solids, while all other compounds (**3**, **6** to **9**) are colorless liquids at r. t. They could be distilled in vacuum without decomposition. Recrystallization from pentane or hexane afforded colorless crystals, some of which melted below r. t. Nevertheless, we were able to mount crystals of all compounds on the diffractometer and determine their structures (see below). The NMR spectroscopic characterization gave the correct integration ratio of peak intensities in all cases. The ^{1}H NMR spectra of the methylhydrazine adducts **1**, **4** and **7** showed doublets of the hydrazine methyl groups caused by coupling to the hydrogen atoms of the neighboring N–H moieties. However, with exception of the aluminum adduct **1**, the quartets expected for these atoms were not clearly resolved owing to the generally broad resonances of hydrogen atoms attached to nitrogen. For the same reason the H-H coupling constants across the N–N bonds were not detected unambiguously in several cases. A splitting of the N–H resonances into doublets and triplets occurred for compounds **2** ($^3J_{H-H}$ = 5.8 Hz), **3** (4.2 Hz), **8** (5.4 Hz) and **9** (4.0 Hz). In the alkylhydrazine adducts the chemical shifts of the NH and NH_2 groups were about δ = 2.7 and 3.4 on average, while in the phenylhydrazine adducts the N–H protons in geminal position to the aromatic rings were considerably shifted to lower field (δ = 3.9 for NH_2 and 5.1 for N–H). The mass spectra showed reasonable fragmentation patterns for most of the aluminum and gallium compounds. An interesting spectrum was obtained for the indium adduct **7** (methylhydrazine). Under relatively mild conditions (25 °C) it showed the characteristic masses of heterocyclic diindium compounds such as $[(Me_3C)_2InN(H)\text{–}N(H)Me]_2$ which are expected to be formed by thermolysis.

Crystal structure determinations

All adducts (**1** to **9**) were characterized by crystal structure determinations. Three representative examples (**1**: E = Al, R = Me; **5**: E = Ga, R = CMe_3; **9**: E = In, R = C_6H_5) are depicted in Figs. 1 to 3. Table 1 contains important bond lengths and angles. In all cases the NH_2 nitrogen atoms of the hydrazine ligands are coordinated to the central atoms. This result does not reflect the stronger basicity of the alkylated nitrogen atoms, but may be due to weaker steric interactions (see Introduction). The bond parameters are essentially unaffected by the different alkyl or aryl groups attached to the hydrazine ligands. The aluminum, gallium or indium atoms possess a distorted tetrahedral surrounding with relatively large angles between the bulky *tert*-butyl groups (about 116°).

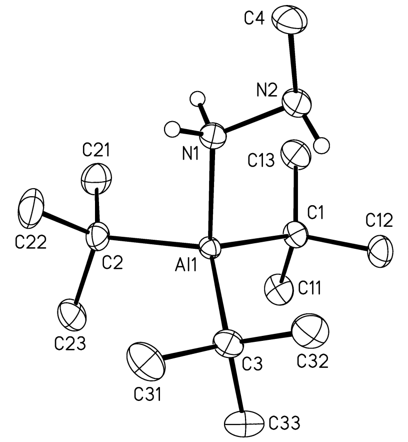

Fig. 1. Molecular structure of the methylhydrazine adduct **1** (E = Al). The displacement ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of N–H are omitted for clarity.

Table 1. Important bond lengths (pm) and angles (deg) of the hydrazine adducts **1** to **9**.

		N–N	E–N	E–C (av.)	C–E–C (av.)	C–E–N (av.)	E–N–N
$(Me_3C)_3Al\leftarrow NH_2–N(H)Me$	**1**	144.6(2)	205.4(1)	202.6	115.8	97.2/104.4	118.10(9)
$(Me_3C)_3Al\leftarrow NH_2–N(H)CMe_3$	**2**[a]	144.2(3)	206.4(2)	202.8	115.8	96.5/104.7	116.0(2)
$(Me_3C)_3Al\leftarrow NH_2–N(H)C_6H_5$	**3**	142.4(2)	206.5(1)	202.6	116.2	96.7/103.6	117.44(9)
$(Me_3C)_3Ga\leftarrow NH_2–N(H)Me$	**4**	143.2(4)	214.7(2)	205.0	116.3	95.8/103.8	117.8(2)
$(Me_3C)_3Ga\leftarrow NH_2–N(H)CMe_3$	**5**	139.8(4)	216.1(3)	204.2	116.5	97.1/102.8	117.9(2)
$(Me_3C)_3Ga\leftarrow NH_2–N(H)C_6H_5$	**6**	142.6(5)	218.2(4)	203.3	116.7	98.7/104.4[b]	115.1(3)
$(Me_3C)_3In\leftarrow NH_2–N(H)Me$	**7**[c]	141.6	238.6	221.6	117.7	98.7	116.0
$(Me_3C)_3In\leftarrow NH_2–N(H)CMe_3$	**8**	143.7(2)	239.7(2)	221.5	117.4	99.3	114.2(1)
$(Me_3C)_3In\leftarrow NH_2–N(H)C_6H_5$	**9**	142.3(2)	242.0(2)	221.9	118.1	98.0	116.4(1)

[a] Disordered hydrazine ligand; [b] two angles at 99°; [c] four independent molecules.

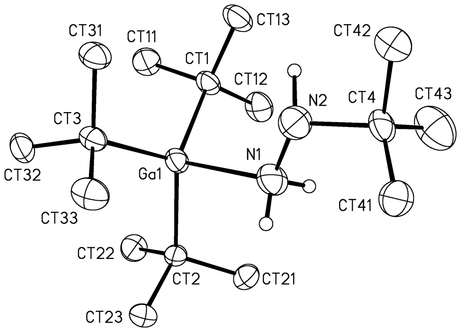

Fig. 2. Molecular structure of the *tert*-butylhydrazine adduct **5** (E = Ga). The displacement ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of N–H are omitted for clarity.

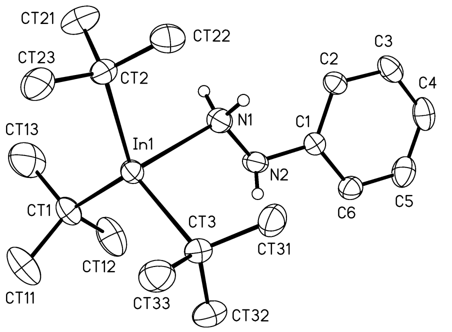

Fig. 3. Molecular structure of the phenylhydrazine adduct **9** (E = In). The displacement ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of NH_2 are omitted for clarity.

The C–E–N angles are between 93 and 105°. In particular with the aluminum and gallium compounds two distinct ranges were observed with two angles at about 97° and one angle at about 104°. The E–C bond lengths are as expected and are almost identical for the Al and Ga compounds (203 and 204 pm, respectively), while they are elongated for indium (222 pm). The E–N distances reflect the different covalent radii, acceptor strengths and electronegativities of these elements, which result in a steady increase of the average values from 206 (Al; **1** to **3**) and 216 (Ga, **4** to **6**) to 240 pm (In, **7** to **9**). The N–N bond lengths (about 143 pm on average) are in the expected range of neutral hydrazine ligands. Longer bonds occur for the monoanionic and dianionic hydrazides [26]. Those nitrogen atoms which are attached to the Group 13 elements adopt a distorted tetrahedral coordination sphere with relatively large E–N–N angles of about 117°, while pyramidal surroundings result for all β-nitrogen atoms.

Outlook

The title compounds will be employed in future investigations for the generation of hydrazides and finally of the corresponding element nitrides. Their volatility may allow for the deposition of the nitrides from the gas phase. Preliminary experiments in particular with the aluminum adducts gave the corresponding hydrazides $[(Me_3C)_2Al–N(H)–N(H)-R]_2$. The decomposition of the trialkylindium methylhydrazine adduct **7** under the conditions of mass spectrometry gave a further hint that thermolysis of these adducts may be successfully applied to produce interesting secondary products by butane elimination.

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane over $LiAlH_4$). Commercially available methylhydrazine and phenylhydrazine were distilled prior to use and stored under argon. MOCHEM GmbH kindly supported us with *tert*-butylhydrazine and tri-(*tert*-butyl)gallium. Tri-(*tert*-butyl)indium was obtained according to a literature procedure [27]. The synthesis of tri-(*tert*-butyl)aluminum is described in the literature [28]. We applied a slightly modified procedure (see below) which gave the product in a considerably higher yield.

Tri(tert-butyl)aluminum

Aluminum tribromide (25.5 g, 0.0956 mol) was dissolved in 150 mL of *n*-pentane and added dropwise to a cooled solution (−80 °C) of *tert*-butyllithium in *n*-pentane (1.6 M, 179.3 mL, 0.286 mol). The suspension was slowly warmed to r. t. and filtered. The solid was washed with *n*-pentane, and the solvent of the filtrate was removed in a vacuum. The remaining viscous liquid was distilled in a vacuum (10^{-3} Torr) at r. t. into a trap cooled by liquid nitrogen. Yield: 13.65 g (72 %). Characterization: See [28].

*Syntheses of the adducts (Me$_3$C)$_3$E←NH$_2$–N(H)R **1** to **9**; general procedure*

The respective trialkylelement compound (about 0.5 g) was dissolved in 30 mL of *n*-pentane or *n*-hexane and treated with equimolar quantities of the hydrazine derivative without a solvent at r. t. The solution was stirred for 0.5 h. The solvent was removed in a vacuum to yield the products in a high purity and an almost quantitative yield. Crystals were obtained by recrystallization from pentane or hexane or after concentration of the reaction mixtures and cooling of the solutions to −30 °C. The crystals of compounds **3** and **6** to **9** melted upon warming to r. t. In these cases distillation in a vacuum was successful without decomposition (up to 120 °C oil bath temperature/10^{-3} Torr).

*Characterization of (Me$_3$C)$_3$Al←NH$_2$–N(H)CH$_3$ (**1**)*

M. p. (under argon, sealed capillary) 52 °C. – IR (paraffin; CsBr plates): ν = 3348 s, 3285 s, 3198 w, 3150 w ν(NH); 2951 vs, 2922 vs, 2853 vs, 2693 m, 2621 w (paraffin); 1591 s δ(NH); 1462 vs, 1377 vs, 1362 sh (paraffin); 1273 w, 1248 m δ(CH$_3$); 1215 w, 1177 m, 1127 s, 1074 w, 1001 s, 935 s, 810 vs, 789 sh ν_{as}(CC$_3$), ν(CN), ν(NN), ν_s(CC$_3$); 723 w (paraffin); 644 s, 575 m, 527 w, 469 w ν(AlC), ν(AlN), δ(CC$_3$) cm^{-1}. – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 3.30 (s, br., 2 H, NH$_2$), 2.88 (q, br., $^3J_{\mathrm{H-H}}$ = 5.6 Hz, 1 H, NH), 1.66 (d, $^3J_{\mathrm{H-H}}$ = 5.6 Hz, 3 H, NMe), 1.15 (s, 27 H, *t*-Bu). – ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 41.3 (NMe), 32.4 (C*Me*$_3$), 16.5 (br., AlC). – MS (EI, 20 eV, 50 °C): *m*/*z* (%) = 198 (21) [Al(*t*-Bu)$_3$]$^+$, 187 (100) [M–*t*-Bu]$^+$, 141 (28) [Al(*t*-Bu)$_2$]$^+$, 46 (4) [H$_2$NNHMe]$^+$.

*Characterization of (Me$_3$C)$_3$Al←NH$_2$–N(H)CMe$_3$ (**2**)*

M. p. (under argon, sealed capillary) 69 °C. – IR (paraffin; CsBr plates): ν = 3653 w, br., 3346 vw ν(NH); 2924 vs, 2862 vs, 2810 vs (paraffin); 1608 m δ(NH); 1462 vs, 1369 vs (paraffin); 1288 vw, 1249 sh δ(CH$_3$); 1202 s, 1119 w, 1034 w, 995 w, 916 w, 843 m, 812 s ν_{as}(CC$_3$), ν(CN), ν(NN), ν_s(CC$_3$); 638 w, 557 vw ν(AlC), ν(AlN) cm^{-1}. – ^{1}H NMR (400 MHz, C$_6$D$_6$): d = 3.84 (d, br., $^3J_{\mathrm{H-H}}$ = 5.8 Hz, 2 H, NH$_2$), 2.92 (q, br., $^3J_{\mathrm{H-H}}$ = 5.8 Hz, 1 H, NH), 1.24 (s, 27 H, Al-*t*-Bu), 0.56 (s, 9 H, N-*t*-Bu). – ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 53.5 (NC), 32.6 (AlC*Me*$_3$), 25.3 (NC*Me*$_3$); Al–C not detected. – MS (EI, 20 eV, 100 °C): *m*/*z* (%) = 229 (100) [M–*t*-Bu]$^+$, 198 (4) [Al(*t*-Bu)$_3$]$^+$, 141 (9) [Al(*t*-Bu)$_2$]$^+$, 88 (42) [H$_2$NNH-*t*-Bu]$^+$.

*Characterization of (Me$_3$C)$_3$Al←NH$_2$–N(H)C$_6$H$_5$ (**3**)*

Liquid at r. t. – IR (paraffin; CsBr plates): ν = 3644 w, br., 3381 m ν(NH); 2922 vs, 2855 vs, 2825 vs (paraffin); 1601 vs δ(NH); 1497 vs (phenyl); 1464 vs, 1381 m (paraffin); 1360 m, 1308 w, 1260 s δ(CH$_3$); 1200 m, 1177 m, 1155 w, 1103 w, 1076 vw, 1042 w, 1020 vw, 999 m, 934 m, 881 m, 845 w, 810 vs, 754 vs, 692 s ν_{as}(CC$_3$), ν(CN), ν(NN), ν_s(CC$_3$), (phenyl); 664 m, 569 m, 501 m, 417 m ν(AlC), ν(AlN), δ(CC$_3$) cm^{-1}. – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 6.95 (*pseudo*-t, 2 H, *m*-H of phenyl), 6.77 (*pseudo*-t, 1 H, *p*-H of phenyl), 6.12 (d, 2 H, *o*-H of phenyl), 5.24 (t, $^3J_{\mathrm{H-H}}$ = 4.2 Hz, 1 H, NH), 4.28 (d,$^3J_{\mathrm{H-H}}$ = 4.2 Hz, 2 H, NH$_2$), 1.18 (s, 27 H, Al-*t*-Bu). – ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 147.2 (*ipso*-C of phenyl), 130.0, 122.8 and 113.4 (*o*-, *m*-, *p*-C of phenyl), 32.3 (AlC*Me*$_3$); Al–C not detected. – MS (EI, 20 eV, 60 °C): *m*/*z* (%) = 249 (56) [M–*t*-Bu]$^+$, 198 (20) [Al(*t*-Bu)$_3$]$^+$, 141 (50) [Al(*t*-Bu)$_2$]$^+$, 108 (100) [H$_2$NNH-Ph]$^+$.

*Characterization of (Me$_3$C)$_3$Ga←NH$_2$–N(H)CH$_3$ (**4**)*

M. p. (under argon, sealed capillary) 42 °C. – IR (paraffin; CsBr plates): ν = 3352 w, 3312 w ν(NH); 2949 vs, 2922 vs, 2855 vs, 2828 vs (paraffin); 1599 m δ(NH); 1464 vs, 1379 m (paraffin); 1360 m, 1250 w δ(CH$_3$); 1225 w, 1109 m, 1069 w, 1009 w, 937 w, 810 vs, 789 m ν_{as}(CC$_3$), ν(CN), ν(NN), ν_s(CC$_3$); 721 vw (paraffin); 687 vw, 594 w, 528 w, 469 vw δ(CC$_3$), ν(GaC), ν(GaN) cm^{-1}. – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 3.07 (br., 2 H, NH$_2$), 2.70 (br., 1 H, NH), 1.78 (d, $^3J_{\mathrm{H-H}}$ = 4.6 Hz, 3 H, NMe), 1.23 (s, 27 H, *t*-Bu). – ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 42.0 (NMe), 32.8 (C*Me*$_3$); Ga–C not detected. – MS (EI, 20 eV, 25 °C): *m*/*z* (%) = 229 (21), 231 (14) [M–*t*-Bu]$^+$, 183 (100), 185 (89) [Ga(*t*-Bu)$_2$]$^+$, 46 (4) [H$_2$NNHMe]$^+$.

*Characterization of (Me$_3$C)$_3$Ga←NH$_2$–N(H)CMe$_3$ (**5**)*

M. p. (under argon, sealed capillary) 44 °C. – IR (paraffin; CsBr plates): ν = 3339 m ν(NH); 2922 vs, 2855 vs, 2826 vs (paraffin); 1595 m δ(NH); 1464 vs, 1366 vs (paraffin); 1269 vw, 1227 s, 1213 s, 1151 vs, 1070 vw, 1036 s, 1007 s, 935 m, 908 w, 810 vs, 791 s δ(CH$_3$), ν_{as}(CC$_3$), ν(CN), ν(NN), ν_s(CC$_3$); 719 s (paraffin); 689 w, 604 m, 530 m, 446 w ν(GaC), ν(GaN), δ(CC$_3$) cm^{-1}. – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 3.58 (br., 2 H, NH$_2$), 2.77 (br., 1 H, NH), 1.30 (s, 27 H, Ga-*t*-Bu), 0.62 (s, 9 H, N-*t*-Bu). – ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 53.4 (NC), 33.0 (GaC*Me*$_3$), 25.6 (NC*Me*$_3$); Ga–C not detected. – MS (EI, 20 eV, 35 °C): *m*/*z* (%) = 271 (25), 273 (14) [M–*t*-Bu]$^+$, 240

Table 2. Crystal data and numbers pertinent to data collection and structure refinement of **1** to **9**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Crystal data									
Empirical formula	$C_{13}H_{33}AlN_2$	$C_{16}H_{39}AlN_2$	$C_{18}H_{35}AlN_2$	$C_{13}H_{33}GaN_2$	$C_{16}H_{39}GaN_2$	$C_{18}H_{35}GaN_2$	$C_{13}H_{33}InN_2$	$C_{16}H_{39}InN_2$	$C_{18}H_{35}InN_2$
M_r	244.39	286.47	306.46	287.13	329.21	349.2	332.23	374.31	394.3
Crystal system	tetragonal	monoclinic	monoclinic	tetragonal	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group (no.) [30]	$P4_32_12$ (96)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P4_12_12$ (92)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/n$ (14)
a, pm	963.24(2)	847.71(3)	1222.68(3)	969.03(2)	846.61(1)	908.78(8)	1923.4(2)	861.8(2)	1254.2(4)
b, pm	963.24(2)	1222.08(5)	1240.49(3)	969.03(2)	1219.34(2)	1526.2(1)	945.47(7)	1230.0(2)	1238.0(4)
c, pm	3585.3(1)	1914.97(7)	1329.23(3)	3581.8(2)	1928.06(3)	1426.7(1)	3837.0(2)	1955.1(4)	1338.8(5)
β, deg	90	91.643(2)	96.790(1)	90	91.614(1)	91.418(2)	90.355(1)	90.067(4)	94.172(7)
V, $\times 10^{-30}$ m^3	3326.6(2)	1983.0(1)	2001.93(8)	3363.3(2)	1989.56(5)	1978.1(3)	6977.4(8)	2072.3(7)	2073(1)
ρ_{calc}, g cm^{-3}	0.976	0.96	1.017	1.134	1.099	1.173	1.265	1.2	1.263
Z	8	4	4	8	4	4	16	4	4
$F(000)$, e	1104	648	680	1248	720	752	2784	792	824
$\mu(MoK_\alpha)$, mm^{-1}	0.105	0.096	0.099	1.620	1.377	1.389	1.339	1.134	1.138
Data collection									
T, K	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	293(2)	293(2)	153(2)
Unique reflections	3244	3653	3709	3286	3736	1288	21412	6019	6053
Reflections [$I \geq 2\sigma(I)$]	3019	3063	3186	3125	3242	1221	11602	5264	4731
Refinement									
Refined parameters	167	254	211	156	188	202	617	196	211
Final R values									
R [$I \geq 2\sigma(I)$]^a	0.0350	0.0459	0.0415	0.0357	0.0502	0.0315	0.0534	0.0275	0.0265
$wR2^b$ (all data)	0.1018	0.1425	0.1251	0.0984	0.1491	0.087	0.1177	0.0607	0.0512
ρ_{fin} (max/min), e Å^{-3}	0.386/ −0.157	0.461/ −0.237	0.245/ −0.238	0.930/ −0.269	1.678/ −0.310	0.300/ −0.216	1.044/ −1.642	0.901/ −0.355	0.635/ −0.388

[a] $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; [b] $wR2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

(5), 242 (3) $[Ga(t\text{-}Bu)_3]^+$, 183 (100), 185 (67) $[Ga(t\text{-}Bu)_2]^+$, 88 (5) $[H_2NNH\text{-}t\text{-}Bu]^+$.

*Characterization of $(Me_3C)_3Ga \leftarrow NH_2–N(H)C_6H_5$ (**6**)*

Liquid at r. t. – IR (paraffin; CsBr plates): ν = 3389 vs, 3312 m, 3279 w, 3233 w, 3167 w ν(NH); 2953 vs, 2922 vs, 2852 vs (paraffin); 1979 vw, 1925 w, 1830 w, 1765 w, 1693 m (phenyl); 1599 vs δ(NH); 1497 m (phenyl); 1454 vs, 1379 vs (paraffin); 1312 m, 1258 s $\delta(CH_3)$; 1186 vs, 1157 vs, 1103 w, 1076 s, 1045 m, 1013 vs, 934 s, 880 m, 847 m, 808 w, 752 vs $\nu_{as}(CC_3)$ ν(CN), ν(NN), $\nu_s(CC_3)$; 691 s, 669 m, 652 w, 592 w, 528 w, 492 w, 433 w ν(GaC), ν(GaN), $\delta(CC_3)$ cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.02 (*pseudo*-t, 2 H, *m*-H of phenyl), 6.76 (*pseudo*-t, 1 H, *p*-H of phenyl), 6.26 (d, 2 H, *o*-H of phenyl), 4.89 (br., 1 H, NH), 3.67 (br., 2 H, NH_2), 1.24 (s, 27 H, Ga-*t*-Bu). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 149.3 (*ipso*-C of phenyl), 129.6, 121.3 and 112.9 (*o*-, *m*- and *p*-C of phenyl), 32.7 (GaC*Me*$_3$). – MS (EI, 20 eV, 25 °C): *m*/*z* (%) = 183 (43), 185 (29) $[Ga(t\text{-}Bu)_2]^+$, 108 (100) $[H_2NNH\text{-}Ph]^+$.

*Characterization of $(Me_3C)_3In \leftarrow NH_2–N(H)CH_3$ (**7**)*

Liquid at r. t. – IR (paraffin; CsBr plates): ν = 3347 vw ν(NH); 2922 vs, 2853 vs, 2835 vs (paraffin); 1603 w δ(NH); 1460 vs, 1381 m (paraffin); 1360 s, 1255 w, 1240 m $\delta(CH_3)$; 1190 m, 1160 m, 1103 w, 1056 w, 1013 m, 937 w, 880 vw, 831 m, 808 m, 746 w $\nu_{as}(CC_3)$, ν(CN), ν(NN), $\nu_s(CC_3)$; 646 vw, 542 m, 474 vw ν(InC), ν(InN), $\delta(CC_3)$ cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 2.62 (br., 3 H, NH_2), 2.5 (very br., 1 H, NH), 1.77 (d, $^3J_{H-H}$ = 6.2 Hz, 3 H, NMe), 1.38 (s, 27 H, *t*-Bu). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 42.8 (NMe), 34.0 (C*Me*$_3$); In–C not detected. – MS (EI, 20 eV, 25 °C): *m*/*z* (%) = 547 (8) $[In_2(CMe_3)_4(NH–NHMe)_2 –H]^+$, 491 (95) $[In_2(CMe_3)_4(NH_2)_2]^+$, 229 (100) $[In(t\text{-}Bu)_2]^+$, 46 (2) $[H_2NNHMe]^+$.

*Characterization of $(Me_3C)_3In \leftarrow NH_2–N(H)CMe_3$ (**8**)*

Liquid at r. t. – IR (paraffin; CsBr plates): ν = 3339 m, 3237 w ν(NH); 2920 vs, 2857 vs, 2814 vs (paraffin); 1599 m δ(NH); 1462 vs (paraffin); 1391 m $\delta(CH_3)$; 1375 s (paraffin); 1360 s, 1225 m $\delta(CH_3)$; 1213 m, 1190 w, 1157 m, 1132 s, 1028 s, 1007 s, 935 m, 907 m, 806 vs, 789 m $\nu_{as}(CC_3)$, ν(CN), ν(NN), $\nu_s(CC_3)$; 716 s (paraffin); 555 m, 501 w, 440 vw ν(InC), ν(InN), $\delta(CC_3)$ cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 3.30 (d, $^3J_{H-H}$ = 5.4 Hz, 2 H, NH_2), 2.63 (t, $^3J_{H-H}$ = 5.4 Hz, 1 H, NH), 1.42 (s, 27 H, In-*t*-Bu), 0.59 (s, 9 H, N-*t*-Bu). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 53.6 (NC), 34.1 (InC*Me*$_3$), 25.6 (NC*Me*$_3$); In–C not detected. – MS (EI, 20 eV, 35 °C): *m*/*z* (%) = 286

(4) $[\text{In}(t\text{-Bu})_3]^+$, 229 (100) $[\text{In}(t\text{-Bu})_2]^+$, 88 (5) $[\text{H}_2\text{NNH-}t\text{-Bu}]^+$.

*Characterization of $(Me_3C)_3In{\leftarrow}NH_2{-}N(H)C_6H_5$ (**9**)*

Liquid at r. t. – IR (paraffin; CsBr plates): ν = 3383 w, 3323 w ν(NH); 2922 vs, 2853 vs, 2830 vs (paraffin); 1601 s δ(NH); 1497 s (phenyl); 1462 vs, 1377 m (paraffin); 1360 s, 1308 w, 1260 m $\delta(\text{CH}_3)$; 1190 m, 1180 m, 1157 m, 1074 w, 1011 m, 935 m, 881 w, 831 vw, 808 m, 752 s $\nu_{\text{as}}(\text{CC}_3)$, ν(CN), ν(NN), $\nu_{\text{s}}(\text{CC}_3)$; 692 s, 557 w, 500 w, 482 m ν(InC), ν(InN), $\delta(\text{CC}_3)$ cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.01 (*pseudo*-t, 2 H, *m*-H of phenyl), 6.77 (*pseudo*-t, 1 H, *p*-H of phenyl), 6.21 (d, 2 H, *o*-H of phenyl), 4.87 (t, $^3J_{\text{H-H}}$ = 4.0 Hz, 1 H, NH), 3.49 (d, $^3J_{\text{H-H}}$ = 4.0 Hz, 2 H, NH_2), 1.37 (s, 27 H, In-*t*-Bu). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ = 149.5 (*ipso*-C of phenyl), 130.1, 122.0 and 113.4 (*o*-, *m*- and *p*-C of phenyl), 34.3 (InC*Me*$_3$); In–C not detected. – MS (EI, 20 eV, 25 °C): *m*/*z* (%) = 286 (1) $[\text{In}(t\text{-Bu})_3]^+$, 229 (28) $[\text{In}(t\text{-Bu})_2]^+$, 108 (100) $[\text{H}_2\text{NNH-Ph}]^+$.

Crystal structure determinations

Single crystals were obtained by cooling of saturated solutions in *n*-hexane or *n*-pentane to −30 °C. Data collections were performed on a Bruker Smart Apex diffractometer employing graphite-monochromated MoK_α radiation. The structures were solved by Direct Methods and refined with full-matrix least-squares calculations based on F^2 [29]. The hydrogen atoms of methyl groups were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 2. The hydrazine ligand of compound **2** was disordered. The atoms were refined on split positions. Only very small crystals of **6** were obtained, thus, data collection was restricted to $2\theta_{max}$ = 35°. Compound **7** crystallized with four independent molecules in the asymmetric unit, which possess quite similar structural parameters.

CCDC 663264 (**1**), 663265 (**2**), 663266 (**3**), 663267 (**4**), 663268 (**5**), 663269 (**6**), 663270 (**7**), 663271 (**8**), and 663272 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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