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Dimethylindium hydrazides [Me$_2$In-NH-NHR]$_2$ (R = CMe$_3$, C$_6$H$_5$)

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Abstract

Trimethylindium reacted with phenyl- and *tert*-butylhydrazine by the release of methane and the formation of the corresponding dimethylindium hydrazides (**1** and **2**, respectively). Both products form dimers and possess four-membered In$_2$N$_2$ heterocycles with two exocyclic N–N bonds in their molecular cores. Interestingly, one compound (**1**) crystallizes with centrosymmetric molecules in which the N–N bonds are located on different sides of the In$_2$N$_2$ ring (C$_{2h}$), while both N–N bonds are on the same side in **2** (C$_{2v}$). In contrast, the reaction of tri(*tert*-butyl)indium with *tert*-butylhydrazine yielded a quite unexpected product. Partial decomposition occurred, and in a low yield the adduct of tribenzylindium with the unchanged *tert*-butylhydrazine was isolated. In a remarkable reaction, the trialkylindium derivative did not react with the relatively acidic hydrazine, but by the release of the corresponding alkane with the solvent toluene.
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1. Introduction

The hydrazides of the heavier elements of third main-group found considerable interest in recent research, which essentially is caused by two important subjects. These compounds may be suitable to act as starting materials for the generation of the corresponding element nitrides (e.g., AlN or GaN) under relatively mild conditions and are, thus, of interest with some respect for an application in material science [1]. Indeed, thermal decomposition accompanied by the formation of the nitrides was observed in some recent investigations. However, more systematic experiments are required to get a concise impression of the principal applicability of these precursors. Secondly, these hydrazides showed a nice coordination behaviour owing to their bidentate character with lone electron pairs at two neighbouring nitrogen atoms [2], and many different structural motifs were detected with the formation of adducts [3–6], of monomers containing "side-on" coordi-

nated hydrazide groups [7–9], of dimers possessing heterocycles [5,8,10–16], and of oligomeric compounds with a cage-like arrangement of metal and nitrogen atoms [5,13,14,17–20]. In the past, most work has been done with respect to the synthesis and structural characterization of dialkylelementhydrazides of the elements aluminum and gallium. Usually, these compounds form dimers possessing four- (Al$_2$N$_2$, two exocyclic N–N bonds), five- (Al$_2$N$_3$, one endocyclic N–N bond) or six-membered heterocycles (Al$_2$N$_4$, two endocyclic N–N bonds) in their molecular centers. The respective molecular structure seems to be determined by steric reasons and by the transannular electrostatic repulsion between the positively charged aluminum and gallium atoms or the negatively charged nitrogen atoms [16]. Their synthesis succeeds on different routes: (i) alkane or hydrogen elimination by the reaction of trialkylelement derivatives or dialkylelement hydrides with hydrazines possessing at least one N–H group; (ii) treatment of dialkylelement halides with lithium hydrazides by salt elimination; (iii) formation of adducts R$_2$ECl-NH$_2$NHR and their reaction with alkyllithium reagents by the release of alkane and the precipitation of lithium

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halide; (iv) hydroalumination, and (v) amide replacement reactions. In contrast to the well-known chemistry of aluminum and gallium hydrazides, only very few reports on indium hydrazides can be found in the literature. One salt-like compound was reported by the group of Nöth [21], some adducts were published by our group [22], and only one neutral indium hydrazide was obtained by Gladfelter with the compound In{N(SiMe_3)-NMe_2}_3 [23]. More systematic investigations into the applicability of indium hydrazides for the formation of indium nitride require the availability of a broader spectrum of corresponding compounds possessing different properties such as solubility, volatility or thermal stability. Here, we report on some attempts on the generation of dimethyl- and di(tert-butyl)indium hydrazine derivatives.

2. Results and discussion

2.1. Synthesis of dimethylindium phenylhydrazide and dimethylindium tert-butylhydrazide

Owing to the instability and non-existence of dialkylindium hydrides one very effective route for the synthesis of aluminum and gallium hydrazides could not be applied for the generation of indium hydrazides at all. A second principal method involved the treatment of adducts formed by hydrazines and dialkylaluminum or -gallium halides with n- or tert-butyllithium. However, only substitution reactions by the replacement of the chlorine atoms were observed for those compounds bearing small alkyl groups attached to their aluminum or gallium atoms, and successful deprotonation of the hydrazine ligands and the formation of hydrazides were achieved with bulky tert-butyl groups only [6]. Owing to the larger radius of indium atoms all attempts for the generation of indium hydrazides on such a route failed even in the case of adducts derived from di(tert-butyl)indium chloride. Instead, the hydrazine adducts of the corresponding trialkylindium derivatives were formed and detected by NMR spectroscopy. Thus, we decided to continue our efforts to synthesize indium hydrazides by employing the direct reaction between hydrazines and trialkylindium compounds.

A solution of trimethylindium in cyclopentane or n-hexane was treated with an equimolar quantity of phenylhydrazine at room temperature. Two phases are formed owing to the low solubility of phenylhydrazine in hydrocarbons. After few minutes the second phase disappeared, and a colorless solid precipitated accompanied by gas evolution. The solid was filtered off and cautiously dried in vacuum over a short period only to yield a colorless powder of product 1 in 59% yield. Longer evacuation caused some significant alterations, which subsequently resulted in the insolubility of the product in organic solvents. The product (1) is relatively unstable in aromatic solvents such as benzene or toluene, so that the characterization by ^{13}C NMR spectroscopy succeeded with some difficulties only. The ^{1}H NMR spectroscopic data including the integration ratio are in clear

agreement with the molecular structure schematically shown in Eq. (1). The expected three signals were observed for the different protons of the phenyl groups. The chemically different N–H protons gave two doublets by a coupling across the N–N bond with chemical shifts of $\delta = 4.75$ and 2.85 and a coupling constant of 3.0 Hz. The resonance of the methyl groups attached to indium occurred at a relatively high field ($\delta = -0.18$). Compound 1 did not melt until 200 °C, however, the color of the powder changed significantly from colorless over yellow to brown at temperatures above 80 °C. Attempts for enhancing the yield by changing the solvent and the reaction conditions (e.g., boiling toluene) failed. Precipitation of elemental indium occurred in many cases, and compound 1 was isolated in moderate yields only. 1 is rather sensitive towards traces of oxygen, and the product adopted an intensive yellow color on contact with air. Single crystals for a crystal structure determination (see below) were obtained by recrystallization from 1,2-difluorobenzene. However, in accordance with the observations reported before this procedure was accompanied by considerable decomposition.

$$2\ InMe_3\ +\ 2\ H_2N\text{-}N(H)R\ \longrightarrow\ \left\{2\ Me_3In\leftarrow NH_2\text{-}N(H)R\right\}$$

1 (R = C_6H_5); 2 (R = CMe_3)
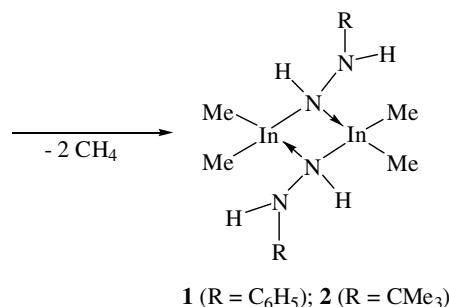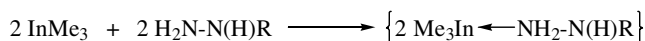
(1)

The reaction of trimethylindium with tert-butylhydrazine was different from that described before. When a solution of the indium compound in n-hexane was treated with an equimolar quantity of the hydrazine derivative, Eq. (1), a colorless solid precipitated after a few minutes, and gas evolution was observed. A small quantity of the product 2 was formed and could be isolated from the solution. The solid could be dissolved in benzene or toluene, but it is stable in these solvents for a short period only. ^{1}H NMR data could be recorded, which verified the formation of an adduct, Me_3In-NH_2-N(H)-CMe_3 [$\delta = -0.02$ (9H, InMe_3), 0.52 (9H, CMe_3), 2.42 (1H, br., NH), 2.53 (2H, br., NH_2)]. We were not able to get further data of characterization owing to the relatively fast decomposition accompanied by the precipitation of elemental indium. The adduct decomposes on evacuation by the release of methane and the formation of the hydrazide 2. However, that reaction is not quantitative and selective enough to offer a reasonable method for the synthesis of 2. The best results were obtained by heating the suspension of the

adduct in toluene under reflux for 3 h, Eq. (1). Elemental indium precipitated, which was removed by filtration. The product (**2**) is highly soluble in non-polar solvents such as cyclopentane or *n*-hexane, thus, all attempts of recrystallization from these solvents failed. It was obtained as a colorless waxy solid from the solvent 1,2-difluorobenzene. Partial decomposition occurred, and the solvent could not be removed completely from the solid without initiating secondary processes. Thus, owing to decomposition and the particular consistence of the product a reasonable figure for the yield could not be detected. The NMR spectroscopic investigations gave similar results as described for compound **1**.

Single crystals of compound **1** were obtained by recrystallization from 1,2-difluorobenzene (20/+8 °C) as described before. It possesses a four-membered In_2N_2 heterocycle in its molecular center with two exocyclic N–N bonds (Fig. 1). With only one exception, similar structures were observed for dimeric organoelement hydrazides of gallium [2,5,6,11,12,14], while a broader variability of structural motifs was determined for the corresponding aluminum derivatives [2,4,10,16]. The only neutral indium hydrazide published so far, In{N(SiMe₃)-NMe₂}₃, formed a monomer in the solid state [23]. Two dimers were detected in the cell of **1**, both reside on crystallographic centers of symmetry and possess ideally planar In_2N_2 rings. The In–N bond lengths (223.2–224.4 pm) are almost indistinguishable and are in the normal range of In–N–In groups with nitrogen bridging two indium atoms [24]. Expectedly, the larger angle in the heterocycles is found at the nitrogen atoms (96.6° vs. 83.4° on average). The N–N distances (143.9 pm on average) are in the usual range observed for aluminum and gallium hydrazides [2]. The inner nitrogen atoms attached to indium possess a distorted tetrahedral coordination sphere, while the *exo* nitrogen atoms have a trigonal pyramidal surrounding (sum of the angles 339.9°).

The growing of single crystals of compound **2** proved to be extremely difficult. In one case only relatively small crystals were obtained, which, however, were twinned. Nevertheless, refinement of the structure to reasonable *R*-values succeeded. **2** forms dimers with an inner In_2N_2 heterocycle and two exocyclic N–N bonds as often observed before for dimeric aluminum and gallium hydrazides. However, for the first time a *cis*-arrangement of the hydrazido ligands was determined (Fig. 2). Schematic drawings of the different structures of both indium hydrazides (approximately C_{2h} for **1** and C_{2v} for **2**) are shown in Scheme 1. Owing to the twin problem the standard deviations of the structural data of **2** are relatively high, thus, the discussion is restricted to a few features only. The In–C distances differ (213.2 vs. 218.2 pm on average) compared to the narrow range observed for the centrosymmetric compound **1**. The shorter ones were detected for those bonds which are on the same side of the In_2C_2 heterocycle as the N–N bonds. The N–N bonds are little lengthened compared to those of **1** (143.9 vs. 149 pm on average), but the In–N bond lengths are in the same range. Owing to the particular molecular symmetry of **2** the central In_2N_2 heterocycle is not planar, but folded across the In···In axis by 18.7°.

Fig. 2. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms of methyl groups are omitted. Important bond lengths (pm) and angles (°): In1–C11 212(2), In1–C12 220(1), In1–N11 223(1), In1–N21 225(1), In2–C21 214(2), In2–C22 217(2), In2–N11 225(1), In2–N21 222(1), N11–N12 149(2), N21–N22 148(2), In1···In2 328.8(1), N11–In1–N21 83.9(5), In1–N11–In2 94.5(4), N11–In2–N21 84.0(4), In1–N21–In2 94.8(4).
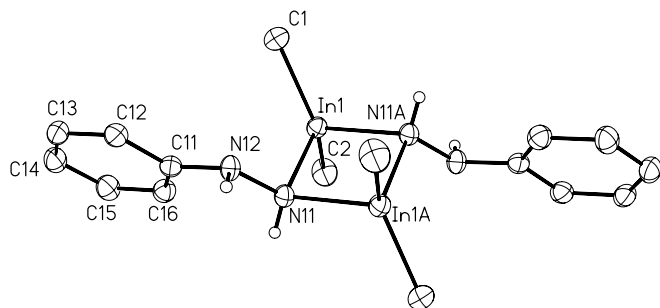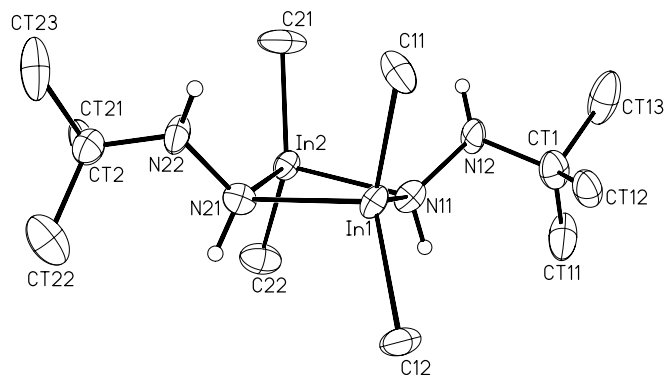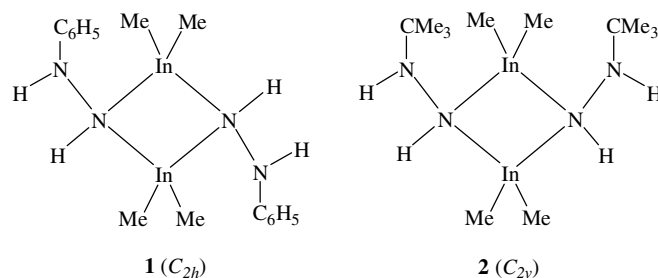

Fig. 1. Molecular structure of **1**. The thermal ellipsoids are drawn at the 40% probability level. Methyl and phenyl hydrogen atoms are omitted. Only one dimer is depicted. Important bond lengths (pm) and angles (°): In1–C1 214.7(3), In1–C2 215.5(3), In1–N11 223.2(2), In1–N11′ 224.4(2), N11–N12 143.9(3), In1·In1′ 335.51(4), C1–In1–C2 130.2(1), N11–In1–N11′ 82.88(8), In1–N11–In1′ 97.13(8) [second molecule: In2–C3 215.6(2), In2–C4 215.2(3), In2–N21 223.4(2), In2–N21″ 223.9(2), N21–N22 143.8(3), In2–In2″ 332.79(5), C3–In2–C4 133.8(1), N21–In2–N21″ 83.86(9), In2–N21–In2″ 96.14(9)]. N11′ and In1′ generated by −x, −y + 2, −z + 1; N21″ and In2″ generated by −x, −y + 1, −z + 2.
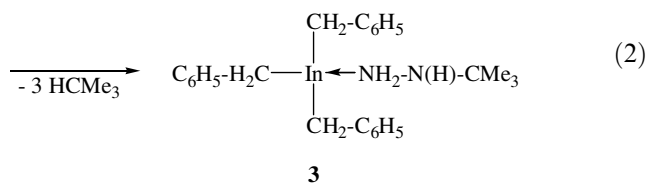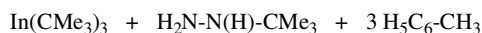

1 (C_{2h})   **2** (C_{2v})

Scheme 1.

The occurrence of *cis/trans* isomers of dimeric gallium hydrazides in solution was derived from some temperature dependent NMR spectroscopic investigations several times before [5,6,11,12]. However, structural evidence was missing, and the *trans* isomers crystallized in all cases and were detected by crystal structure determinations. Thus, the molecular structure of **2** represents the singular case where the *cis* isomer could be isolated in the solid state. It strongly supports the existence of that particular molecular form in solution. However, NMR spectra of **2** are quite simple and in absolute agreement with a centrosymmetric molecule. In order to get a better insight into the dynamic behaviour of the molecules in solution NMR experiments at low temperature were conducted in toluene. A general and significant low-field shift was detected with decreasing temperature (e.g., for In–Me: $\delta = 0.08$ at room temperature to $\delta = 0.27$ at -70 °C). Coalescence of the NH and Me–In resonances with very broad signals seem to occur at about -75 °C. Below that temperature (-80 °C) two sets of resonances were observed for each kind of N–H protons ($\delta = 2.79/2.53$ and $2.71/2.41$, pairs of resonances with equal intensity) and for the methyl groups attached to indium ($\delta = 0.41$ and 0.32). Thus, it seems to be clear that two different molecular forms exist at low temperature. But a concise interpretation of these observations is prevented by decomposition and by the occurrence of resonances which were caused by secondary products. As mentioned before, similar equilibria were detected for dimeric gallium hydrazides. However, the equilibration of their isomeric forms was observed at relatively high temperatures (>50 °C).

Low temperature ^{1}H NMR data of the indium hydrazide **1** show, however, that these equilibria may indeed involve more complicated mixtures of compounds and that the description by simple *cis/trans* isomers may be an oversimplification. At room temperature the expected simple spectrum resulted with a singlet for the methyl groups attached to indium and a singlet for each of the chemically different N–H protons. Coalescence of the methyl resonance occurred at about -25 °C. Below that temperature a splitting into five signals resulted ($\delta = 0.14$, 0.11, -0.03, -0.12 and -0.23) with temperature dependent intensity ratios of about 1.0/1.2/2.0/1.1/1.0 at -33 °C and 1.0/0.6/2.0/0.6/1.0 at -83 °C. Two methyl resonances are to be expected for the *cis* isomer, while the *trans* form should give one resonance only. Thus, it seems to be clear that further species are present here, which, however, could not be identified unambiguously, and all attempts to assign particular structures would be rather speculative. Same holds for the hydrazine resonances. The two signals observed at room temperature gave seven resonances at -23 °C [$\delta = 5.09$ (d, $J_{H-H} = 4.8$ Hz), 4.73, 4.42, 3.03, 2.92 (d, $J_{H-H} = 4.8$ Hz), 2.83 and 2.71]. Further cooling to -83 °C gave a completely different spectrum with eight resonances ($\delta = 5.32$, 4.85, 4.66, 4.57, 2.84, 2.71, 2.66, 2.65 and 2.52), the last six ones of which are of equal intensity.

2.2. Reaction of tri(tert-butyl)indium with tert-butylhydrazine

Tri(*tert*-butyl)indium did not react with *tert*-butylhydrazine by the release of methylpropane in *n*-pentane or *n*-hexane even after prolonged stirring of solutions at room temperature. Reaction was observed in boiling toluene over several hours. However, considerable quantities of elemental indium precipitated as a grey powder. After filtration all volatile components were removed in vacuum. A colorless solid remained which was recrystallized from cyclopentane. Surprisingly, the NMR spectroscopic characterization of the product (**3**) revealed a resonance of one sort of *tert*-butyl groups only, and benzyl groups could be identified by the signals of their phenyl and methylene protons. The hydrazine molecule seemed to be intact, and two resonances of N–H protons were detected in an integration ratio of 2 to 1. A coupling across the N–N bond was detected with a relatively large coupling constant of 5.8 Hz. In accordance with the results of a crystal structure determination an adduct of *tert*-butylhydrazine with tribenzylindium was formed in the course of that reaction, Eq. (2). Thus, interestingly the hydrazine molecule was not affected here, instead toluene was attacked, and a benzyl compound resulted by the probable release of methylpropane. It seems that caused by the influence of the alkyl group the acidity of the hydrazine molecule is considerably decreased [25]. Furthermore, steric shielding of the indium compound In(CMe$_3$)$_3$ may influence the particular course of this reaction. The yield of the finally isolated product **3** is 13% only. But no further compound could be identified by NMR spectroscopy, and the rough product after filtration showed only the resonances of **3**. Volatile products may be formed by the homolytic cleavage of In–C bonds, which were removed together with the solvent. The precipitate of elemental indium may be taken as an indication of such a decomposition reaction.

$$\text{In(CMe}_3)_3 \ + \ \text{H}_2\text{N-N(H)-CMe}_3 \ + \ 3\,\text{H}_5\text{C}_6\text{-CH}_3$$

$$\xrightarrow[\text{- 3 HCMe}_3]{} \quad \text{C}_6\text{H}_5\text{-H}_2\text{C} \overset{\overset{\displaystyle \text{CH}_2\text{-C}_6\text{H}_5}{|}}{\underset{\underset{\displaystyle \text{CH}_2\text{-C}_6\text{H}_5}{|}}{\text{In}}} \leftarrow \text{NH}_2\text{-N(H)-CMe}_3 \tag{2}$$

$$\mathbf{3}$$

Crystal structure determination verified the unexpected structure of **3** (Fig. 3). Three benzyl groups are attached to the central indium atom, which is further coordinated by the NH$_2$-nitrogen atom of a *tert*-butylhydrazine ligand. The molecules are located on crystallographic mirror planes. The methylene carbon atoms of the benzyl groups are almost ideally in a plane with the indium atom (sum of the C–In–C angles 358.2°). The hydrazine moiety is almost perpendicular to that group with C–In–N angles between 93.6° and 94.8°. This particular bonding situation
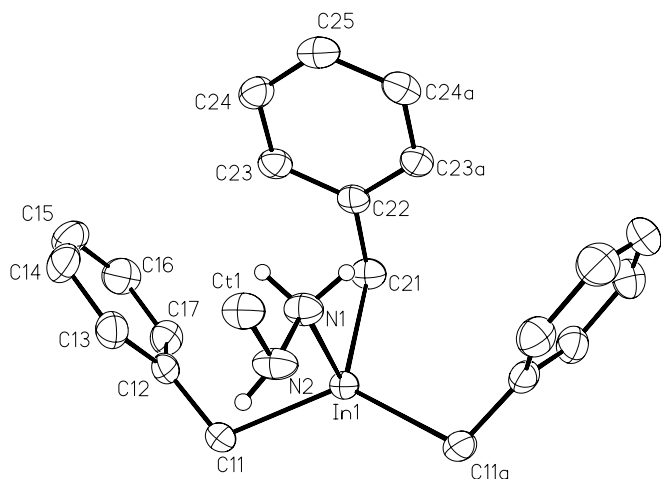
Fig. 3. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups of the *tert*-butyl group and hydrogen atoms of the benzyl groups are omitted. Important bond lengths (pm) and angles (°): In1–C11 220.2(2), In1–C21 220.8(2), In1–N1 235.1(2), N1–N2 143.3(3), C11–In1–C21 114.27(5), C11–In1–C11′ 129.66(9), C11–In1–N1 94.76(6), C21–In1–N1 93.63(7). C11′ generated by x, $-y + 1/2$, z.

with a high s-character in the In–C bonds has been observed several times before, e.g., in adducts of gallane, GaH$_3$ [26]. Further narrow contacts to the indium atoms could not be detected, so that a higher coordination number with a trigonal bipyramidal geometry at the indium atoms can be excluded. The In–N bond of **3** (235.1 pm) is little lengthened by about 5 pm compared to those of adducts between dimethylindium chloride and hydrazines. This may be caused by the enhanced bulkiness of the benzyl groups compared to the methyl substituents and by the influence of the electronegative chlorine atom in the chloro compounds. The N–N bond length (143.3 pm) is in the normal range. The phenyl groups are oriented to the same side of the molecule and form a hollow in which the hydrazine ligand in enclosed. The N–N bond bisects the angle C11–In1–C11′, which is relatively large (129.7°) compared to the remaining two C–In–C angles (114.3°).

In summary, the synthesis of dialkylindium hydrazides seems to be rather difficult compared to the relatively facile syntheses of the aluminium or gallium analogues. The indium compounds could be isolated in low yields only. They tend to decompose in solution or in vacuum, and redox processes with the precipitation of elemental indium were observed in all synthetic procedures. This is in remarkable contrast to the properties of the aluminum or gallium hydrazides, which are accessible on high yield routes and can be sublimed in vacuum in many cases without decomposition. Furthermore, we did not observe the preferred attack of an E–C bond on solvent molecules in the presence of hydrazine molecules before.

3. Experimental

All procedures were carried out under purified argon. Toluene was dried over Na/benzophenone, *n*-hexane and cyclopentane over LiAlH$_4$, 1,2-difluorobenzene over molecular sieves (4 Å). Trimethylindium and tri(*tert*-butyl)indium were obtained according to the literature procedures [27,28]. Commercially available phenylhydrazine (Aldrich) was degassed, stored over molecular sieves and distilled in vacuum prior to use. MOCHEM GmbH (Marburg, Germany) kindly supported us with *tert*-butyl-hydrazine.

3.1. Synthesis of dimethylindium phenylhydrazide 1

Trimethylindium (0.895 g, 5.60 mmol) was dissolved in 45 ml of *n*-hexane and treated with 550 μl (0.605 g, 5.60 mmol) of phenylhydrazine at room temperature. Two liquid phases were formed owing to the insolubility of the hydrazine in *n*-hexane. The reaction started by gas evolution and precipitation of the colorless product after a few minutes. The suspension was stirred at room temperature for 1 h. Compound **1** was isolated in a pure form by filtration and short evacuation of the residue (maximum 10^{-2} Torr, 1 min). Yield: 0.835 g (59%), colorless powder, which adopts an intense yellow color on contact with traces of air. The melting point could not be determined; the color of the powder changed to brown at about 80 °C under argon, but the solid did not melt until 200 °C. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): $\delta = 7.11$ (4H, pseudo-t, *m*-H of phenyl), 6.74 (2H, pseudo-t, *p*-H of phenyl), 6.40 (4H, pseudo-d, *o*-H of phenyl), 4.75 (2H, d, $^3J_{\text{H}\cdots\text{H}} = 3.0$ Hz, N–H), 2.85 (2H, d, $^3J_{\text{H}\cdots\text{H}} = 3.0$ Hz, N–H), −0.18 (12H, s, InMe$_2$). ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K): $\delta = 152.1$ (N–C), 129.4, 119.5, 112.5 (all phenyl), −4.4 (InMe$_2$). IR (cm^{-1}; paraffin; CsBr): 3301 w br., 3256 w br., 3187 w br. νNH; 2954 vs, 2923 vs, 2853 vs (paraffin); 1699 vw, 1599 s, 1580 m, 1495 s (phenyl); 1462 vs, 1377 s (paraffin); 1306 w, 1263 w, 1207 w, 1177 w, 1156 w, 1074 w, 1023 w, 953 w, 881 w δCH$_3$, νCC, νNN, νNC; 799 s, 754 sh, 694 vs (phenyl); 676 sh, 615 w, 517 m, 467 m νInC, νInN.

3.2. Synthesis of dimethylindium tert-butylhydrazide 2

Trimethylindium (0.779 g, 4.875 mmol) was dissolved in 25 ml of *n*-hexane and treated with 521 μl (0.429 g, 4.875 mmol) of *tert*-butylhydrazine at room temperature. A solid precipitated which probably consists of the adduct Me$_3$In·NH$_2$N(H)-CMe$_3$. It was filtered off, dissolved in 25 ml of toluene and heated under reflux for 3 h. Elemental indium precipitated, which was filtered off. The solvent was removed in vacuum, and the residue was recrystallized with partial decomposition from 1,2-difluorobenzene (20/ −15 °C). A colorless waxy solid resulted, which even after prolonged evacuation included a considerable quantity of the solvent. Owing to the viscosity of the product the determination of a reasonable yield and the determination of the melting point failed. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 298 K): $\delta = 2.65$ (2H, d, $^3J_{\text{H}\cdots\text{H}} = 1.5$ Hz, N–H), 2.52 (2H, d, $^3J_{\text{H}\cdots\text{H}} = 1.5$ Hz, N–H), 0.82 (18H, s, CMe$_3$), 0.10 (6H, s, InMe$_2$). ^{13}C NMR (C$_6$D$_6$, 50 MHz, 298 K):

$\delta = 53.8$ (N–C), 26.8 (Me of CMe$_3$), −8.8 (InMe$_2$). IR (cm^{-1}; paraffin; CsBr): 3331 w, 3165 w νNH; 2954 vs, 2923 vs, 2853 vs, 1459 s, 1377 s (paraffin); 1305 w, 1229 w, 1211 w, 1174 w, 1109 vw, 1076 m, 1036 m, 954 w, 865 vw δCH$_3$, νCC, νNN, νNC; 720 sh, 691 s, 519 m, 442 m νInC, νInN, δC$_3$C.

3.3. Synthesis of tribenzylindium(tert-butylhydrazine) 3

Tri(*tert*-butyl)indium (1.079 g, 3.78 mmol) was dissolved in 50 ml of toluene and treated with 404 µl (0.333 g, 3.78 mmol) of *tert*-butylhydrazine at room temperature. The yellow color of the trialkylindium compound disappeared immediately. The solution was heated under reflux for 18 h, which resulted in the precipitation of a finely divided grey powder of probably elemental indium. Filtration and evaporation of the solvent yielded a colorless solid residue, which was recrystallized from cyclopentane. Yield: 0.239 g (13%), colorless crystals of **3**. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 298 K): $\delta = 7.03$ (6H, pseudo-t, *meta*-H of phenyl), 6.92 (6H, pseudo-d, *ortho*-H of phenyl), 6.77 (3H, pseudo-t, *para*-H of phenyl), 2.38 (2H, d, $^3J_{H\cdots H} = 5.8$ Hz, NH$_2$), 2.18 (6H, s, CH$_2$ of benzyl), 1.68 (1H, t, $^3J_{H\cdots H} = 5.8$ Hz, NH), 0.43 (9H, s, CMe$_3$). ^{13}C NMR (C$_6$D$_6$, 75 MHz, 298 K): $\delta = 148.7$ (*ipso*-C of phenyl), 128.9 and 126.3 (*ortho*- and *meta*-C of phenyl), 121.5 (*para*-C of phenyl), 53.1 (NC), 25.4 (CMe$_3$), 23.0 (In-CH$_2$). IR (cm^{-1}; paraffin; CsBr): 3311 m br. νNH; 3062

m, 3017 m (phenyl); 2955 vs, 2924 vs, 2854 vs (paraffin); 1937 vw, 1864 vw, 1806 vw, 1594 m, 1487 m (phenyl); 1455 s, 1377 m (paraffin); 1305 vw ρCH$_3$; 1207 m, 1178 w, 1151 w, 1038 s, 995 w, 899 w, 846 vw, 795 w νCC, νNN, νNC; 752 m, 698 m (phenyl); 536 vw, 520 vw, 463 m νInC, νInN, δC$_3$C.

3.4. Crystal structure determinations of compounds 1–3

Single crystals were obtained on cooling of saturated solutions in different solvents (compounds **1**, 1,2-difluorobenzene, 20/+8 °C; compound **2**, pentafluorobenzene, 20/+8 °C; compound **3**, cyclopentane, +8 °C). The crystallographic data were collected with a STOE IPDS diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 [29] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters and structure refinement details are given in Table 1. The crystal of compound **2** proved to be a reflection twin in (0 0 1). Owing to the approach of the monoclinic angle to 90°, the small ratio of the twin domains of about 0.2, and the weak overall intensities, twin integration and refinement gave poor results only. Thus, reflection data integrated with the orientation matrix of the stronger domain only were used, and the 14 most impaired reflections were omitted. A possible additional inversion twinning could not be confirmed significantly (Flack parameter 0.34(11)). Due to remarkable deviations

Table 1
Crystal data and structure refinement for **1**, **2**, and **3**[a]

	1	2	3
Formula	C$_{16}$H$_{26}$In$_2$N$_4$	C$_{12}$H$_{34}$In$_2$N$_4$	C$_{25}$H$_{33}$InN$_2$
Temperature (K)	193(2)	193(2)	193(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group [30]	$P\bar{1}$ (no. 2)	$P2_1$ (no. 4)	$Pnma$ (no. 62)
a (pm)	888.34(8)	686.81(7)	915.99(4)
b (pm)	999.02(9)	1215.7(2)	1345.99(7)
c (pm)	1258.40(1)	1164.6(1)	1894.0(1)
α (°)	70.776(7)	90	90
β (°)	84.632(7)	90.80(1)	90
γ (°)	65.699(7)	90	90
V (10^{-30} m^3)	959.9(1)	972.3(2)	2335.1(2)
Z	2	2	4
D_{calc} (g cm^{-3})	1.744	1.585	1.355
μ (mm^{-1})	2.404	2.365	1.024
Crystal size (mm)	0.36 × 0.18 × 0.06	0.24 × 0.05 × 0.04	0.24 × 0.10 × 0.04
Radiation	Mo Kα; graphite-monochromator		
θ Range for data collection (°)	1.72 ⩽ θ ⩽ 26.06	1.75 ⩽ θ ⩽ 25.91	1.86 ⩽ θ ⩽ 26.19
Index ranges	−10 ⩽ h ⩽ 10	−8 ⩽ h ⩽ 8	−11 ⩽ h ⩽ 11
	−12 ⩽ k ⩽ 12	−14 ⩽ k ⩽ 14	−16 ⩽ k ⩽ 16
	−15 ⩽ l ⩽ 15	−14 ⩽ l ⩽ 14	−23 ⩽ l ⩽ 23
Reflections observed	3065	2554	2191
Independent reflections	3779 [$R_{int} = 0.0353$]	3513 [$R_{int} = 0.0610$]	2441 [$R_{int} = 0.0356$]
Parameters	219	174	149
$R = \sum ||F_o| − |F_c||/\sum |F_o|$ [$I > 2\sigma(I)$]	0.0201	0.0571	0.0201
$wR_2 = \{\sum w(|F_o|^2 − |F_c|^2)^2/\sum |F_o|^2\}^{1/2}$ (all data)	0.0479	0.1418	0.0541
Max./min. residual electron density (10^{30} e m^{-3})	0.404/−0.705	3.751[b]/−1.530	0.322/−0.821

[a] Program SHELXL-97 [29]; solutions by direct methods, full matrix refinement with all independent structure factors.
[b] Near the indium atoms.

of the dimer **2** from pseudo-symmetry C_{2v}, there is no choice to use the centrosymmetric space group $P2_1/m$.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 281041 (**1**), 281042 (**2**) and 281043 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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