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# Synthesis and characterization of new monomeric dialkylindium amides

Kevin M. Simpson, Robert W. Gedridge, Jr. and Kelvin T. Higa

*Chemistry Division, Research Department, Naval Air Warfare Center Weapons Division, China Lake, CA 93555 (USA)*

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## Abstract

A series of organoindium amido compounds have been prepared for use as dopants in the organometallic vapor phase epitaxy (OMVPE) of II–VI semiconductor materials. Thus, reaction of $^t$Bu$_2$InCl or $^i$Pr$_2$InCl with the appropriate lithium or sodium dialkylamide afforded compounds of the type R$_2$InNR$'_2$ (where R = $^t$Bu, $^i$Pr, and R$'$ = Me, $^i$Pr, SiMe$_3$). Similarly, reaction of the N-lithiated derivative of NCMe$_2$(CH$_2$)$_3$CMe$_2$ gave $^i$Pr$_2$InNCMe$_2$(CH$_2$)$_3$CMe$_2$. All of the compounds are monomeric liquids, except for the compound where R = $^t$Bu, R$'$ = Me, which is a dimeric solid. The compounds have been characterized by $^1$H and $^{13}$C NMR, IR, molecular weight determination, and elemental analysis. In addition, properties relevant to the OMVPE process such as volatility and photosensitivity are presented and evaluated.

## 1. Introduction

Group III–V semiconductor layers for use in optoelectronic devices can be grown by the technique of organometallic vapor phase epitaxy (OMVPE) [1]. In OMVPE, volatile Group III organometallic compounds serve as the source for III–V semiconductors and as n-type dopants in II–VI semiconductor materials. Me$_3$In has been widely used as precursor for indium-containing semiconductor materials. However, transport problems associated with sublimation from solid Me$_3$In [1,2] and the pyrophoric nature of the trialkyls in general, have led to interest in developing suitable compounds with more benign characteristics. In addition, Me$_3$In does not lend itself well to controlled low level doping because of its high vapor pressure and residual presence in an OMVPE reactor after its use. The "memory effect" associated with the use of Me$_3$In as a dopant is believed to result from the formation of less volatile organoindium byproducts in the OMVPE reactor [3]. With these concerns in mind, compounds of the type R$_2$InNR$'_2$ were examined for use as alternatives to currently available organoindium dopants. By the judicious choice of alkyl groups on the metal and the amido nitrogen, compounds suitable for In doping have been obtained.

## 2. Results and discussion

### 2.1. *Synthesis and characterization of R$_2$InNR$'_2$ compounds*

Although many examples of R$_2$InNR$'_2$ compounds may be found in the literature [4], most are dimeric (or higher oligomers) solids which are not sufficiently volatile for use as precursors or dopants for the OMVPE of optoelectronic materials. However, ($^t$Bu)$_2$InNCMe$_2$(CH$_2$)$_3$CMe$_2$ has been reported as a monomeric compound [5]. Furthermore, a variety of intramolecularly stabilized monomeric organoindium compounds with *o*-[(dialkylamino)methyl]phenyl [6] and 3-[dialkylamino)propyl [7] ligands have been synthesized and used in OMVPE [8]. The goal of this study was to find the combination of alkyl groups on the indium and amido nitrogen that would lead to the formation of liquid monomers instead of oligomers.

The tert-butyl group was chosen as the substituent on indium since it possesses the greatest steric bulk of the alkyl groups. When $^t$Bu$_2$InCl, was treated with LiNMe$_2$, a white solid was obtained in 78% yield (eqn. (1)). The high sublimation temperature (100°C, 0.05 Torr) suggested that the compound was a dimer or trimer. Molecular weight measurements in pentane

$$(^t\mathrm{Bu}_2\mathrm{InCl})_2 + 2\ \mathrm{LiNMe}_2 \longrightarrow (^t\mathrm{Bu}_2\mathrm{InNMe}_2)_2 + 2\ \mathrm{LiCl} \quad (1)$$

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Correspondence to: Dr. R.W. Gedridge, Jr. or Dr. K.T. Higa.

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TABLE 1. Spectroscopic data for $\mathrm{R_2InNR'_2}$ [a]

| Compound | NMR [b] | | IR [c] |
|---|---|---|---|
| | $^1$H | $^{13}$C | |
| $\mathrm{(^tBu_2InNMe_2)_2}$ | 1.38(s,$^t$Bu); 2.74(s, $\mathrm{NMe_2}$) | 34.04 ($\mathrm{C}\mathit{Me}_3$); 38.88 ($\mathrm{N}\mathit{Me}_2$); 49.48($\mathit{C}\mathrm{Me_3}$) | 2900 vs*, 2840vs, 1450s*, 1367s, 1252s, 1043 w, 1028 w, 1116 m, 1028s, 901s, 804 s, 798 w, 743 w, 714 w, 690 w, 584 w (*Nujol mull) |
| $\mathrm{(^tBu)_2InN(SiMe_3)_2}$ | 0.15 (s, $\mathrm{SiMe_3}$); 1.28 (s$^t$Bu) | 4.45 ($\mathrm{Si}\mathit{Me}_3$); 31.78($\mathrm{C}\mathit{Me}_3$); 48.55 ($\mathit{C}\mathrm{Me_3}$) | 2915 vs, 2805 vs, 2750 w, 2690 w, 1450 s, 1353 m, 1238 vs, 1170 m, 1147 m, 998 vs, 922 s, 863 s, 820 vs, 770 s, 744 m, 658 m, 605 m |
| $\mathrm{(^iPr)_2InN(^iPr)_2}$ | 0.86 (d, $\mathrm{NCH}\mathit{Me}_2$, $^3J_{(\mathrm{H-H})} = 6.4$); 1.13 (m, $\mathrm{InC}\mathit{H}\mathrm{Me_2}$); 1.61 (d, $\mathrm{InCH}\mathit{Me}_2$, $^3J_{(\mathrm{H-H})} = 7.7$); 2.74 (sept, $\mathrm{NC}\mathit{H}\mathrm{Me_2}$) | 24.60 ($\mathrm{NCH}\mathit{Me}_2$); 22.98 ($\mathrm{InCH}\mathit{Me}_2$) 28.38 ($\mathrm{In}\mathit{C}\mathrm{HMe_2}$); 45.89 ($\mathrm{N}\mathit{CH}\mathrm{Me_2}$) | 3000 s, 2620 m, 2681 m, 1345 s, 1378 s, 1363 s, 1333 m, 1294 w, 1168 m, 1147 s, 1132 s, 1080 m, 1057 m, 956 s, 897 s, 858 m, 785 m, 760 m |
| $\mathrm{(^iPr)_2In\overline{NCMe_2(CH_2)_3CMe_2}}$ | 1.04 (s, $\mathrm{C}\mathit{Me}_2$); 1.07–1.20 (br, m, $\mathrm{C}\mathit{H}_2$); 1.38 (m, $\mathit{H}\mathrm{CMe_2}$,); 1.49 (d, $\mathrm{HC}\mathit{Me}_2$, $^3J_{(\mathrm{H-H})} = 8.2$) | 18.16 ($\mathit{C}\mathrm{H_2}$); 23.53 ($\mathrm{C}\mathit{Me}_2$); 26.40 ($\mathrm{In}\mathit{C}\mathrm{HMe_2}$); 31.36 ($\mathrm{InCH}\mathit{Me}_2$); 38.94 ($\mathit{CH}_2$); 51.16 ($\mathrm{N}\mathit{C}\mathrm{Me_2}$) | 2910 s, 2840 s, 1458 s, 1370 s, 1352 s, 1238 s, 1172 m, 1133 m, 967 m, 920 m, 905 m, 870 w |
| $\mathrm{(^iPr)_2InN(SiMe_3)_2}$ | 0.132 (s, $\mathrm{SiMe_3}$, $^2J_{(\mathrm{Si-H})} = 6.4$; 1.26 (m, $\mathit{H}\mathrm{CMe_2}$); 1.39 (d, $\mathrm{HC}\mathit{Me}_2$, $^3J_{(\mathrm{H-H})} = 7.6$) | 4.36 ($\mathrm{Si}\mathit{Me}_3$); 22.42 ($\mathrm{C}\mathit{Me}_2$,); 28.92 ($\mathrm{H}\mathit{C}\mathrm{Me_2}$) | 2925 s, 2910 s, 2830 s, 1447 w, 1235 s, 1138 w, 1173 w, 1000 vs, 960 w, 922 w, 868 s, 830 s, 815 s, 772 m, 742 w, 660 m, 605 m |

[a] Abbreviations used: for NMR, s(singlet), d(doublet), sept(septet), m(multiplet); for IR, vs(very strong), s(strong), m(medium), w(weak). [b] Chemical shifts in ppm and coupling constants in Hz. All spectra recorded in benzene-$d_6$. [c] $\mathrm{cm^{-1}}$, recorded as neat liquids between NaCl windows, except where noted.

confirmed a dimeric composition. Thus, it appears that even with the bulky groups on indium, a more sterically demanding group on the amide nitrogen is necessary to prevent oligomerization.

The new dialkylindium dialkylamido compounds were prepared by the metathesis reaction of the appropriate dialkylindium chloride with the lithium or sodium dialkylamide in pentane or diethyl ether at room temperature (eqn. (2). A slight excess of the lithium reagent is required in the case of $^i\text{Pr}_2\text{InN}^i\text{Pr}_2$; otherwise, a significant amount of unreacted $^i\text{Pr}_2\text{InCl}$ remains. Yields, based on the dialkylindium chloride, range from 45 to 78%.

$$(\text{R}_2\text{InCl})_2 + 2\ \text{MNR}'_2 \longrightarrow 2\ \text{R}_2\text{InNR}'_2 + 2\ \text{MCl} \quad (2)$$

where $\text{R} = {}^t\text{Bu}$, $\text{R}' = \text{Me}$ ($\text{M} = \text{Li}$), $\text{SiMe}_3$ ($\text{M} = \text{Na}$); $\text{R} = {}^i\text{Pr}$, $\text{R}' = {}^i\text{Pr}$, $\text{SiMe}_3$, and $\text{NR}'_2 = \overline{\text{NCMe}_2(\text{CH}_2)_3\text{C}}\text{Me}_2$, $\text{M} = \text{Li}$.

The indium amides were characterized by $^1$H-, $^{13}$C-NMR, and IR spectroscopy (Table 1), as well as by molecular weight measurements. It is noteworthy that, with the exception of $(^t\text{Bu}_2\text{InNMe}_2)_2$, these compounds are liquids and monomeric in solution. These compounds, though sensitive to oxygen and moisture, are not pyrophoric as are trimethylindium and other trialkylindiums. They also lack the extreme photosensitivity which presents problems in the synthesis, purification, and storage of many organoindium compounds. For example $^t\text{Bu}_2\text{In}\overline{\text{NCMe}_2(\text{CH}_2)_3\text{C}}\text{Me}_2$ deposits metallic indium on exposure to sunlight [5] while $^i\text{Pr}_2\text{In}\overline{\text{NCMe}_2(\text{CH}_2)_3\text{C}}\text{Me}_2$ appears to be much less photosensitive.

Although these compounds do not exhibit sufficient volatility to serve as replacements for conventional precursors in the atmospheric pressure OMVPE growth of bulk materials, they are liquids with low vapor pressures which makes them candidates for use in low-level n-type doping of II–VI materials grown by OMVPE. As a preliminary evaluation, $(^i\text{Pr})_2\text{InN}(^i\text{Pr})_2$ and $(^i\text{Pr})_2\text{InN}(\text{SiMe}_3)_2$ were pyrolyzed in our horizontal low pressure (70–100 mT) OMVPE reactor. Indium deposits consisting of 1–10 μm spheres were grown at 300°C on Si substrates. This demonstrates that these compounds are potential candidates for In doping in II–VI semiconductor materials grown by OMVPE.

## 3. Experimental section

### 3.1. General procedures

All manipulations were carried out under an atmosphere of purified argon or nitrogen using a Vacuum Atmospheres glovebox and standard Schlenk techniques. $(^t\text{Bu}_2\text{InCl})_2$ [5] and $(^i\text{Pr}_2\text{InCl})_2$ [9] were prepared by published procedures. $\text{LiNMe}_2$, $\text{LiN}(^i\text{Pr})_2$, and $\text{NaN}(\text{SiMe}_3)_2$ were purchased from Aldrich. $\text{LiNMe}_2$ and $\text{LiN}(^i\text{Pr})_2$ were purified by heating under vacuum and/or recrystallization from ether. $\text{H}\overline{\text{NCMe}_2(\text{CH}_2)_3\text{C}}\text{Me}_2$ was purchased from Aldrich and purified by distillation from Na at reduced pressure. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AMX 400 FT NMR spectrometer operating at 400.14 MHz and 100.61 MHz, respectively. Infrared spectra were recorded on a Perkin Elmer 1300 spectrophotometer. Microanalysis were performed by E + R Microanalytical Laboratories. Molecular weights were determined isopiestically in pentane using azobenzene as the standard [10].

### 3.1.1. *Tetra-tert-butylbis(μ-dimethylamido)diindium(III)*

To a stirred suspension of $(^t\text{Bu}_2\text{InCl})_2$ (2.00 g, 3.78 mmol) in 50 mL pentane was slowly added solid lithium dimethylamide (0.39 g, 7.6 mmol). After stirring at room temperature for 24 h, the mixture was filtered through a fine frit to obtain a colorless solution. Cooling the solution to −25°C afforded colorless crystals. These were sublimed at 100°C (0.05 Torr) to give pure $(^t\text{Bu}_2\text{InNMe}_2)_2$ as a white solid: yield 1.61 g, 78% based on $^t\text{Bu}_2\text{InCl})_2$. Anal. Calcd for $\text{C}_{20}\text{H}_{48}\text{N}_2\text{In}_2$ (546 g $\text{mol}^{-1}$); C, 43.98; H, 8.86; In, 42.04. Found: C, 43.76; H, 9.05; In, 41.72; mol wt.569 ($c = 0.012$ M).

### 3.1.2. *Di-tert-butyl(bis(trimethylsilyl)amido)indium (III)*

Solid sodium bis(trimethylsilyl)amide (1.42 g, 7.74 mmol) was added to a stirred suspension of $(^t\text{Bu}_2\text{InCl})_2$ (2.05 g, 3.88 mmol) in 50 ml ether. The mixture was stirred at room temperature for 24 h and filtered. Removal of solvent from the filtrate gave a yellow oil which was distilled under vacuum at 50°C and 0.20 Torr to give pure $(^t\text{Bu})_2\text{InN}(\text{SiMe}_3)_2$ as a pale yellow liquid: yield 0.91 g, 30% based on $(\text{R}_2\text{InCl})_2$. Anal. Calcd for $\text{C}_{14}\text{H}_{36}\text{NInSi}_2$ (389 g $\text{mol}^{-1}$): C, 43.18; H, 9.32; N, 3.60. Found: C, 42.98; H, 9.40; N, 3.74; mol wt. 395 ($c = 0.047$ M).

### 3.1.3. *Diisopropyl(diisopropylamido)indium(III)*

Solid lithium diisopropylamide (2.4 g, 22.4 mmol) was added to a stirred suspension of $(^i\text{Pr}_2\text{InCl})_2$ (5.00 g, 10.6 mmol) in 60 ml pentane. After stirring at room temperature for 24 h, the mixture was filtered and the pentane removed from the filtrate under reduced pressure. The resulting liquid was fractionally distilled and $^i\text{Pr}_2\text{InN}^i\text{Pr}_2$ was collected at 46°C (0.30 Torr) as a yellow liquid: yield 3.44 g, 54% based on $(^i\text{Pr}_2\text{InCl})_2$. Anal. Calcd for $\text{C}_{12}\text{H}_{28}\text{NIn}$ (301 g $\text{mol}^{-1}$): C, 47.86; H, 9.37; N, 4.65. Found: C, 47.73, H, 9.18; N, 4.45; mol wt. 330 ($c = 0.083$ M).

### *3.1.4. Diisopropyl(2,2,6,6-tetramethylpiperidino)indium(III)*

n-Butyllithium (11.0 ml of 1.6 M solution in hexanes, 17.6 mmol) was added to 2,2,6,6-tetramethylpiperidine (2.50 g, 17.7 mmol) in pentane (25 ml). The resulting off-white solid was collected by filtration, washed with two 10 ml portions of pentane, and dried under vacuum. The $\mathrm{Li\overline{NCMe_2(CH_2)_3C}Me_2}$ (2.45 g, 16.6 mmol) was added *via* powder funnel to a stirred suspension of $(^i\mathrm{Pr_2InCl})_2$ (3.92 g, 8.29 mmol) in 50 ml pentane. The mixture immediately turned yellow and deposited a white precipitate. After stirring at room temperature for 10 h, the mixture was filtered through a fine frit to obtain a yellow solution. Pentane was removed under reduced pressure to give a yellow-orange oil. This was distilled at 40°C (0.05 Torr) to give $^i\mathrm{Pr_2}$-$\mathrm{In\overline{NCMe_2(CH_2)_3C}Me_2}$ as a deep yellow liquid: yield 2.52 g, 44% based on $(^i\mathrm{Pr_2InCl})_2$. Anal. Calcd for $\mathrm{C_{15}H_{32}NIn}$ (341 g $\mathrm{mol^{-1}}$); C, 52.80; H, 9.45; N, 4.10. Found: C, 52.87; H, 9.56; N, 3.91.; mol wt. 298 ($c$ = 0.065 M).

### *3.1.5. Diisopropyl(bis(trimethylsilyl)amido)indium(III)*

The procedure used to prepare $(^t\mathrm{Bu})_2\mathrm{InN(SiMe_3)_2}$ was followed for the reaction of 3.38 g (7.15 mmol) $(^i\mathrm{Pr_2InCl})_2$ and 2.62 g (14.3 mmol) $\mathrm{NaN(SiMe_3)_2}$. Distillation of the product oil at 60°C (0.1 Torr) afforded $(^i\mathrm{Pr})_2\mathrm{InN(SiMe_3)_2}$ as a pale yellow liquid: yield 2.94 g, 57%. Anal. Calcd for $\mathrm{C_{12}H_{32}NInSi_2}$ (361 g $\mathrm{mol^{-1}}$): C, 39.88; H, 8.92; N, 3.88. Found: C, 40.09; H, 9.10; N, 3.78.; mol wt. 389 ($c$ = 0.049 M).

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