New approach to dichloroindium amides

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Two different routes are presented for the synthesis of dichloroindium amides. On the one hand we prepared $(THF)_3Li(\mu\text{-}Cl)Cl_2InN(SiMe_3)(Dipp)$ (1) (Dipp = 2,6-diisopropylphenyl) by the reaction of indium trichloride with the lithiated aniline, on the other hand Cl_2InNEt_2 (2) by trimethylsilyl chloride elimination. Compound 1 was characterized by X-ray structural analysis.

Organoindium compounds were introduced by Rochow *et al.* in 1934.[1] In recent years interest in the synthesis of organoindium amides, phosphides, selenides and arsenides has increased owing to their application in the fields of CVD (Chemical Vapour Deposition) and MOCVD (Metal Organic Chemical Vapour Deposition) for the production of thin layers.[2–4] In this respect dimethylindium dimethylamide should be mentioned as a precursor for the synthesis of ceramics.[5,6]

Therefore new routes to indium compounds for use as single source precursors and their corresponding starting materials is an important target of current indium research. The syntheses of alkylindium dichlorides and dialkylindium amides have been thoroughly investigated.[7] Two pathways for the syntheses of these compounds were found to work in high yields: on the one hand the commutation reaction of trialkylindium compounds with $InCl_3$ for the preparation of alkylindium dichlorides, and on the other hand the reaction of trialkylindium derivatives with amines, with alkane elimination, for the synthesis of In–N compounds.[8,9] The alternative route to these compounds *via* the reaction of $InCl_3$ with lithiated alkyls or amides has been of no practical use until now. These reactions mostly lead to lower product yields due to metallic indium formation which is favoured in the presence of the lithiated amide or alkyl species.[10] In contrast to these observations the reaction of a lithiated tris(trimethylsilyl)methane with $InCl_3$ yields an alkylindium dichloride–lithium chloride adduct in 87% yield, which has been characterized by X-ray structural analysis.[11]

To the best of our knowledge a successful synthesis of dichloroindium amides, or rather their derivatives, has not been reported yet.

For the preparation of a dichloroindium amide we chose lithiated *N*-trimethylsilyl-2,6-diisopropylaniline for the reaction with $InCl_3$, owing to its high sterical demand. In our previous work we established *N*-trimethylsilyl-2,6-diisopropylanilide as a bulky ligand for the production of stable silanetriol and silanetriamide systems.[12] After the successful syntheses of gallium and aluminium amide systems using this ligand we are now interested in the corresponding indium compounds.

A solution of 2.49 g (10 mmol) lithiated *N*-trimethylsilyl-2,6-diisopropylaniline in THF (20 ml) was added to a solution of 2.21 g (10 mmol) $InCl_3$ in THF (50 ml) at 0 °C and stirred for an additional 1 h. The solution was allowed to reach room temperature, refluxed for 1 h and stirred at room temperature for another 6 h. THF was removed *in vacuo* and the remaining solid was dissolved in toluene. After filtration from the residue the solvent was removed *in vacuo* and **1** was isolated as a colourless solid in 83% yield (5.75 g). No reduction of In(III) was observed during the reaction (shown in Scheme 1). A sample of **1** was dissolved in *n*-hexane and kept for one week at room temperature. Single crystals suitable for X-ray crystallography were obtained from this solution.

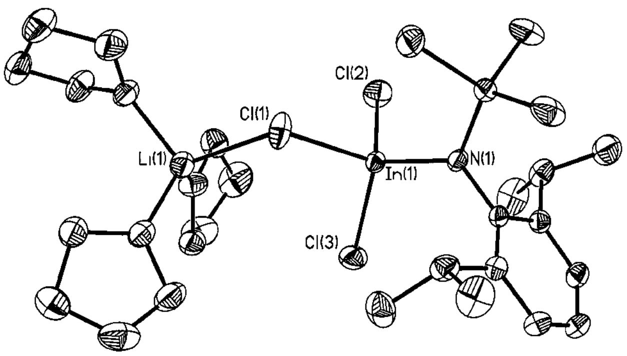
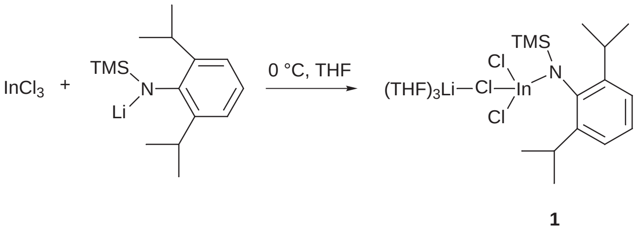


Fig. 1 X-Ray structure of **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: In(1)–N(1) 2.054(2), In(1)–Cl(1) 2.4152(8), In(1)–Cl(2) 2.3760(5), In(1)–Cl(3) 2.3614(8), Li(1)–Cl(1) 2.392(4); Cl(1)–In(1)–Cl(2) 104.56(3), Cl(1)–In(1)–Cl(3) 106.30(4), Cl(2)–In(1)–Cl(3) 105.31(3), Cl(1)–In(1)–N(1) 110.41(6), Cl(2)–In(1)–N(1) 115.12(6), Cl(3)–In(1)–N(1) 114.32(5), Li(1)–Cl(1)–In(1) 116.3(1).

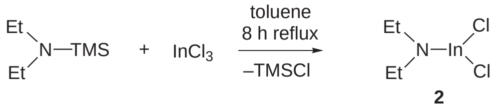


Scheme 1

The single crystal X-ray structural analysis shows **1** to crystallize in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The core of the structure consists of an indium centre which is tetrahedrally coordinated by three chlorine atoms and one *N*-trimethylsilyl-2,6-diisopropylaniline ligand. One of the chlorine atoms bridges the indium to a lithium cation whose tetrahedral coordination sphere is completed by three THF molecules (Fig. 1). As expected the bridging In(1)–Cl(1) bond length of 2.4152 Å is longer than the terminal ones (2.3760 and 2.3614 Å). The bond lengths and angles are comparable to those in $[Li(THF)_3(\mu\text{-}Cl)InCl_2\{C(SiMe_3)_3\}]$.[†][11]

The ^1H NMR data are consistent with **1**. The singlet (δ 0.28) is assigned to the protons of the $SiMe_3$ group. The expected doublets (δ 1.13 and 1.19) and septets (δ 2.86 and 3.65) for the isopropyl groups are found, whereas the aromatic protons give a multiplet (δ 6.98 to 7.06). Signals for the THF groups are observed in the expected range (δ 1.20 and 3.67). The consistency of the solid state structure also in solution of **1** can be proved by integration of the proton signals. In the ^7Li NMR spectrum of **1** a singlet is found (δ −0.21) assignable to Li coordinated to THF and the ^{29}Si NMR data result in a singlet (δ 4.07) for the $SiMe_3$ group. The mass spectrum shows fragments of **1** assigned to $DippNH_2$ (177; 30%), DippH (162; 100%), InCl (150; 48%) and In (115; 41%). The composition of **1** was confirmed by elemental analysis. We obtained dichloroindium amide as the LiCl adduct, which is in good agreement with the product proposed in Scheme 1.

For the synthesis of dichloroindium diethylamide an alternative approach proved to be applicable. To avoid reduction by any lithiated amine a trimethylsilyl chloride elimination reaction of the trimethylsilyl derivative of diethylamine with $InCl_3$ (Scheme 2) was carried out instead.



Scheme 2

A solution of 1.44 g (10 mmol) $(SiMe_3)NEt_2$ in toluene (20 ml) was added to a suspension of 2.21 g (10 mmol) $InCl_3$ in toluene (50 ml) at 0 °C. The suspension was allowed to reach room temperature and refluxed for 8 h. Toluene was removed *in vacuo* and the remaining solid was treated with *n*-hexane. After filtration the solvent was removed *in vacuo* and **2** was isolated as a colourless solid in 78% yield (2.01 g).

The ^1H NMR data show the expected signals for **2**. The triplet (δ 1.28) and the quartet (δ 3.11) are assigned to the protons of the ethyl group. The mass spectrum (EI) shows fragments of the monomer assigned to M (258 *m*/*z*; 53%) and InCl (150; 100%). The composition of **2** was confirmed by elemental analysis. The spectroscopic characterization established that the dimer of dichloroindium diethylamide was the product. This interpretation is supported by previous investigations of comparable alkylindium amides, as well as by infrared spectra, which reveal the nitrogen bridged dimeric system of **2**.‡

With these two routes for the synthesis of compounds **1** and **2** we have opened up the field of dichloroindium amides. Further investigations in our laboratory will focus on exchange reactions of the halides in these systems to obtain new single source precursors for the CVD process.

Acknowledgements

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Notes and references

† Crystal structure analysis of **1**: $C_{27}H_{50}Cl_3InLiNO_3Si$, $M_r = 692.88$, monoclinic, $P2_1/n$, unit cell dimensions: $a = 9.472(2)$ Å, $b = 24.866(5)$ Å, $c = 14.625(3)$ Å, $\beta = 91.58(3)°$, $V = 3444(1)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.336$ Mg m^{-3}, $\mu = 0.980$ mm^{-1}; total number of reflections measured 60120, unique 6753 ($R_{int} = 0.0512$). Final R indices: $R1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.0262$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.0627$ on data with $I > 2\sigma(I)$ and $R1 = 0.0316$, $wR2 = 0.0681$ on all data, goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2} = 1.161$. The crystal was mounted on a glass fibre in a rapidly cooled perfluoropolyether.[13] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K, with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), performing φ- and ω-scans. The structure was solved by direct methods using SHELXS-97[14] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The disordered $SiMe_3$ group in **1** was modelled with the help of similarity restraints for 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The occupancies for the disordered parts were refined and eventually set at the convergence value.

CCDC reference number 186/1505. See http://www.rsc.org/suppdata/dt/1999/2265/ for crystallographic files in .cif format.

‡ The infrared spectrum of **2** was recorded in CsI and shows the stretching of terminal In–Cl (279 and 259 cm^{-1}) and bending of In–μ-N (447 cm^{-1}). Owing to the air and moisture sensitivity of **2** cryoscopic measurements for the molecular weight determination were not successful.

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