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Journal of Organometallic Chemistry 689 (2004) 3000–3004

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Cyclic dialkylindium amides: new structural information and ultra-purification using inorganic and inorgano–organic layered materials

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Received 1 September 2003; accepted 1 June 2004
Available online 31 July 2004

Abstract

New data on some cyclic dimethyl- and diethylindium-amides were obtained. X-ray structure of pyrrolidinodimethylindium was determined. The molecule is centrosymmetric with square–planar In_2N_2 base and distorted tetrahedral metal environment similar to that of known dialkylindium amides, the cyclic amido-ligands are present in an envelope conformation. A novel material- and energy-saving procedure for sorption ultra-purification of highly sensitive organometallic compounds in absolute non-polar media was developed. Advanced inorganic and inorgano–organic crystalline layered materials possessing enhanced affinity towards selected ions or molecules were applied for the sorption treatment.

Keywords: Ultra-purification; Indium; Layered materials; Nitrogen ligand; Crystal structure

1. Introduction

Many branches of modern science and technology are actually facing an acute problem of obtaining of high-purity degree substances and materials. Indium based materials represent a considerable part of III–V semiconductors obtained via metal-organic chemical vapour deposition (MOCVD), where a proper choice of the volatile precursor has a crucial significance [1]. Insufficient purity grade is the main factor restraining implementation of new challenging precursors, as total content of impurities should not exceed 10^{-4}–10^{-3}%, while their elimination constitutes a difficult problem, because the compounds are extremely sensitive to the atmospheric oxygen and moisture. Traditional methods of distillation or sublimation are accompanied by considerable losses of the end product, high energy and time consumption. Therefore, the development of new purification methods for organometallic compounds is of essential importance.

Recently, much attention was focused on structural and chemical properties of layered crystalline zirconium phosphates and phosphonates, especially those of α- and γ-type. These derivatives can be formulated as $\alpha\text{-Zr(O}_3\text{PR)}_2 \cdot nS$ and $\gamma\text{-ZrPO}_4\text{[O}_2\text{P(OH)R]} \cdot nS$, where R can be OH, H or an organic group, and S is an interlayer guest species. The interlayer space can be modulated in dimension and reactivity by the right choice of R and/or S species, in order to enhance the affinity

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doi:10.1016/j.jorganchem.2004.06.038

Table 1
Yields and spectroscopic data for cyclic dialkylindium amides

No.	Compound[a]	Yield (%)	Mw (Da)	^{14}N NMR δ (ppm)[b]
1	$(CH_3)_2InC_5H_{10}N$	81.0	458	−547.03 (−344.33)
2	$(CH_3)_2InC_4H_8N$	84.7	430	−546.95 (−344. 10)
3	$(CH_3)_2InC_3H_6N$	77.2	402	−548.93 (−354.98)
4	$(C_2H_5)_2InC_5H_{10}N$	75.1	514	
5	$(C_2H_5)_2InC_4H_8N$	76.5	486	−548.94 (−344. 10)
6	$(C_2H_5)_2InC_3H_6N$	73.9	458	

[a] $C_5H_{10}N$, C_4H_8N, and C_3H_6N stand for deprotonated moieties of piperidine, pyrrolidine, and azetidine, respectively.

[b] Data for the corresponding signals in the free ligands are given in parentheses.

toward selected ions or molecules, and to increase their sorption properties [2]. Furthermore, these layers can be dispersed on porous colloidal silica, in order to prepare composite materials with a large surface area [3].

It was of undoubted interest to study the performance of selected layered zirconium phosphates and phosphonates in ultra-purification of organoindium compounds.

2. Results and discussion

During several decades, various methods have been proposed to synthesise monoamides of dialkylindium [4–6]. In spite of a great number of publications in the area, some diethylindium amides were still unknown, and there was a lack of X-ray structural data on dialkylindium compounds containing alicyclic amido-ligands with one heteroatom [7].

We adapted the method of Arif et al. [5] using Grignard reagents to generate the $InAlk_3$ that was brought into a reaction with an alicyclic amine.

$$InCl_3 + 3RMgCl = InR_3 + 3MgCl_2$$

$$InR_3 + R'{>}NH = R_2InN{<}R' + RH\uparrow,$$

where $R = –CH_3, –C_2H_5$; $R'{>}NH$ means a cyclic amine.

In such a way we synthesised readily volatile dimethyl- and diethylindium complexes, including new ones: **5** and **6**. All compounds were characterised by ^{1}H, ^{13}C, ^{14}N NMR-spectroscopy and mass-spectrometry. For **2** the X-ray structure was determined. The yields of the reactions and selected spectroscopic data are present in the Table 1.

The presence of In–N coordination was confirmed by the disappearance of N–H resonance in the proton spectra, and by the pronounced upfield shift ($\sim$200 ppm) of a sharp intense ^{14}N signal with respect to the free-ligand spectra. The ^{1}H and ^{13}C NMR signals of the hydrocarbon moieties are well-defined and were unambiguously assigned. Taking into a consideration the mass values of molecular ions, the complexes under discussion are dimers that corresponds to the literature data for similar compounds [4,6].

The dimeric structure of the complex **2** [1] was shown by X-ray structure analysis. Each of the eight molecules of the dimer inside the unit cell does not interact with the neighbouring molecules, providing favourable conditions for volatility of the compound. The molecular structure is shown on the Fig. 1, the numeration of atoms corresponds to that of the CIF file deposited at the CCDC. The mean values of chemical bond lengths and bonding angles are given in the Table 2. The centrosymmetric structure with square-planar In_2N_2 base and distorted tetrahedral metal environment is similar to that of known dialkylindium amides [7]. The rhombic distortion of the In_2N_2 in **2** is slightly greater, because the N-atom is a constituent of a five-member heterocyclic ligand and can not change its geometry *ad arbitrium*, while for acyclic dialkylindium amides the steric strain is distributed more evenly between the N and In atoms. The pyrrolidino-ligands are present in the molecule in an envelope conformation. Both heterocycles are equivalent and their methylene groups are in eclipsed conformation to each other.

The complex **5** was chosen for ultra-purification studies, as a volatile liquid more suitable for MOCVD applications then solid dimethylindium analogue. It is reasonable to suppose organomagnesium compounds and $MgCl_2$ as principal contaminants. They are difficult to remove by traditional sublimation or distillation, hence, the procedures have to be repeated in order to obtain the required purity grade. On the other hand, sorption is one of the most widespread techniques for the purification of gases and liquids. However, a treatment with activated carbon also does not achieve the goal [8], because the problem consists in elimination of more polar impurities with lower molecular weight from a less polar substance (organoindium compound).

To resolve the above problem inorganic sorbents possess several advantages over the organic ones: lower content of contaminants, easiness of dehydration, stability

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[1] CCDC No. 188477 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

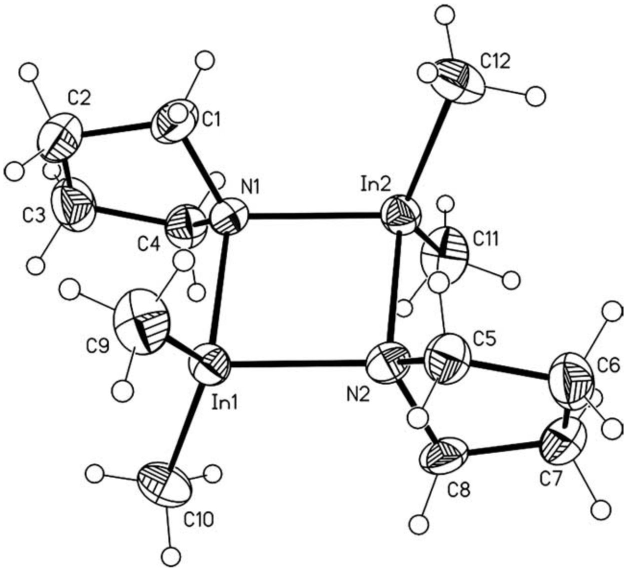

Fig. 1. X-ray structure of bis-pyrrolidinodimethylindium.

Table 2
Mean values of bond lengths (Å) and bond angles (°) for $[(CH_3)_2InN(CH_2)_4]_2$[a]

Bond lengths		*Bond angles*	
In···In	3.285(6)	N–In–N	84.7(1)
In–N	2.223(4)	In–N–In	95.3(2)
In–C	2.146(6)	C–In–C	129.5(3)
N–C_α	1.481(6)	N–In–C	108.4(2)
C_α–C_β	1.535(8)	In–N–C_α	115.4(3)
C_β–C_β	1.517(8)	N–C_α–C_β	105.2(4)
		C_α–C_β–C_β	104.5(4)
		C_α–N–C_α	101.1(4)

[a] Carbon atoms of the heterocycle are labelled as Cα and Cβ in the order of remoteness from the heteroatom.

to chemically aggressive media (e.g., organometallics) [9]. It was of interest to examine some layered crystalline zirconium phosphates and phosphonates with structures of α- and γ-type, known by their specificity to magnesium in aqueous media [2], for organometallic compound purification. Three materials were selected and prepared: a composite γ-zirconium phosphate–silica (hereafter γ-ZrP/SiO_2) exhibiting a large surface area [3]; an intercalation compound of γ-zirconium phosphate with decylamine, of a formula γ-$ZrPO_4(H_2PO_4) \cdot 0.5C_{10}H_{21}NH_2$ (hereafter γ-ZrP · 0.5DA) [10]; and a zirconium phosphite benzenephosphonate, with a layered structure of α-type, of a formula α-$Zr(O_3PH)(O_3P–C_6H_5)$ (hereafter α-ZrPHPF) [11].

The composite γ-ZrP/SiO_2 was prepared by rapid hydrolysis of tetraethylsilicate in the presence of exfoliated γ-ZrP (40% w/w of γ-ZrP). Simultaneous flocculation of silica and γ-ZrP nanoparticles prevented their reaggregation. After a calcination at 650 °C a composite exhibiting a large surface area (about 420 $m^2\,g^{-1}$) was obtained. The surface analysis by N_2 adsorption and desorption also showed the presence of mesopores (0.5 $cm^3\,g^{-1}$ in the range 40–100 Å diameter), while the micropore volume was negligible [3]. The intercalation of long chain alkylamines ($n \geqslant 6$) into γ-ZrP increases drastically the interlayer distance of the new phase (up to 25.0 Å at 75% r.h.). The composition of this phase was γ-$ZrPO_4(H_2PO_4) \cdot 0.5C_{10}H_{21}NH_2$-$nH_2O$ and it is able to incorporate alkanols from water–alkanol solutions, with the consequent increase of interlayer distance to 33.0 Å [10]. For this reason, the material could be a good candidate for sorption purification applications. The α-ZrPHPF was obtained by direct precipitation method [11], and its structure is composed of the packing of alternate layers of α-type, one richer in phenylphosphonate moieties, the other in phosphite ones. The defective arrangement of small and large groups in the two regions could favour the incorporation of guest species in a completely non-polar interlayer environment.

After a dehydration, layered inorganic and inorgano–organic materials were used for bis-pyrrolidinodiethylindium purification followed by activated carbon treatment to remove traces of non-polar contaminants. The procedure [2] was repeated if the required purity grade has not yet been achieved. The purification results are shown in the Table 3. Magnesium elimination after one cycle of treatment by γ-ZrP/SiO_2 makes up 60.1%, then for γ-ZrP · 0.5DA it does 51.9%, and for α-ZrPHPF it does 26.2%. Hence, the effectiveness of the sorbent principally depends on its specific surface area. A comparison of α-ZrPHPF and γ-ZrP · 0.5DA shows better affinity of the latter to remove organomagnesium impurities with aliphatic fragments, as it contains more polar groups and long aliphatic chains. The α-ZrPHPF is less-effective in this specific case, probably because the impurities do not contain any aromatic or conjugated fragments.

A portion of the crude substance was distilled three times for comparison. A substitution of distillations for sorption purification reduces considerably the energy consumption, providing a basis for a development of energy-saving technologies. Moreover, nearly 10% of the product are lost during each distillation, while the sorption treatment gives practically quantitative yield.

We successfully applied the purified precursor to obtain smooth n-type InP films in a low-pressure MOCVD reactor by a gas-phase reaction of **5** with phosphine.

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[2] Theoretically, one may also suppose a contamination by Zr from the sorbents. We controlled the content of the latter in each sample by AAS and no Zr was detected, i.e., its content was less then 0.079 ppm.

Table 3
Sorption purification of bis-pyrrolidinodiethylindium[a]

Sorbent used	No. of cycles	[Mg] (ppm)
γ-$ZrPO_4(H_2PO_4)/SiO_2$	1	112
	2	<0.062
α-$Zr(0_3PH)(0_3P\text{-}C_6H_5)$	1	386
	2	40
	3	<0.062
γ-$ZrPO_4(H_2PO_4) \cdot 0.5C_{10}H_{21}NH_2$	1	299
	2	9.15
	3	<0.062
Distillation[b]	1	137
	2	73
	3	54

[a] Initial [Mg] = 2947 ppm.
[b] For comparison.

3. Experimental

All manipulations were carried out in a nitrogen filled dry-box, and all reagents were from Aldrich. Grignard reagents and $InCl_3$ (99.999%) were used as supplied. Amines were stored over KOH pellets for several days before use. Solvents were purified according to standard procedures.

3.1. Syntheses

General procedure for synthesis of cyclic amides of dialkylindium was based on a procedure described in [5] with the following differences. $InCl_3$ (2.21 g, 10 mmol) was suspended in an absolute diethylether and stoichiometric quantity of 2M CH_3MgCl or C_2H_5MgCl solution in diethylether was added dropwise under continuous stirring during 2 h. After the addition of the Grignard reagent, the reaction mixture was allowed to stir for additional 2 h, then $MgCl_2$ was filtered off. Subsequently, the equimolar amount of an appropriate amine was added to the transparent solution, and left to stirr overnight. The solvent was removed in vacuo leaving either white crystals of dimethylindium derivatives or colourless or yellowish liquids of diethylindium ones. The compounds **1**–**4** described in [6] were identified by chemical analysis and spectroscopically. For **5**: colourless liquid. Anal. Calc. for $CgH_{18}lnN$: In, 47.24; C, 39.53; H, 7.46. Found: In, 47.14; C, 39.42; H, 7.59. ^1H NMR (δ, C_6D_6) (ppm): 2.43 (t, $C\alpha H_2$, 4H), 1.45 (t, CH_3, 6H), 1.07 (t, $C_\beta H_2$, 4H), 0.58 (q, CH_2, 4H). ^{13}C NMR (δ, C_6D_6) (ppm): 47.76 (C_α), 25.29 (C_β), 13.52 (C_{CH_3}), 3.59 (C_{CH_2}. For **6**: colourless liquid. Anal. Calc. for $C_7H_{16}InN$: In, 50.13; C, 36.71; H, 7.04. Found: In, 50.11; C, 36.53; H, 7.12. ^1H NMR (δ, C_6D_6) (ppm): 3.12 (t, $C_\alpha H_2$, 4H), 1.82 (t, $C_\beta H_2$, 2H), 1.54 (t, CH_3, 6H), 0.64 (q, CH_2, 4H). ^{13}C NMR (5, C_6D_6) (ppm): 48.25 (C_α), 21.55 (C_β), 13.70 (C_{CH_3}, 3.46 (C_{CH_2}).

Layered materials were obtained according to earlier described procedures [3,11]. γ-$ZrPO_4H_2PO_4 \cdot 0.5C_{10}H_{21}$-$NH_2 \cdot nH_2O$ was obtained by adding 16.0 ml of a 0.1 M solution of *n*-alkyl amine in 1:1 water/ethanol to a 1 g portion of γ-$ZrPO_4H_2PO_4 \cdot 2H_2O$ dispersed in 100 ml of 1:1 water/ethanol. After a contact time of 6 h, the intercalation compound was separated from the solution by centrifugation, washed with water, and air-dried.

3.2. Purification

The sorbents were dried in vacuo at 60 °C for 2 h, and stored in an absolute and degassed hexane. 0.5 g of crude product were dissolved in 75 ml of the absolute hexane and treated in static conditions for 2 h with 0.25 g of the layered material. Subsequently, the liquid was filtered through 1 g of activated carbon Darco G-60 (100 mesh, preliminary dried and degassed in vacuo at 120 °C for 6 h). The Mg and Zr content was controlled by atomic absorption analysis.

3.3. Characterisation

NMR spectra were obtained at 293 K in C_6D_6 solutions in 5 mm ampoules with a Brucker AC-200 spectrometer. ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane at 200.13 and 50.33 MHz, respectively. ^{14}N spectra were measured in the same way at 14.462 MHz relative to nitromethane standard [12]. Mass-spectrometric data were obtained on VG ZAB 2F instrument (VG Analytical, Manchester, UK) and referred to ^{115}In isotope. X-ray powder diffraction patterns at room temperature were recorded with a computer controlled Philips PW1710 diffractometer using a graphite monochromated Cu Kα radiation (40 kV, 30 mA).

The amine content in the intercalation compound γ-$ZrPO_4H_2PO_4 \cdot 0.5C_{10}H_{21}NH_2 \cdot nH_2O$ was determined by thermogravimetry in air using a Stanton Redcroft Thermal Analyzer STA781 at a heating rate of 5 °C/min.

The MOCVD experiments were carried out in a horizontal quartz low-pressure hot-wall reactor. The deposition temperature was 610 °C using diffusion-purified H_2 as a carrier gas. Other deposition parameters were set up according to the procedure described in [13].

3.4. X-ray structure determination

Crystal data for: $C_{12}H_{28}N_2In_2$, Mw = 430.0, orthorhombic, space group *Pbca*, $a = 8.278(2)$ Å, $b = 16.670(3)$ Å, $c = 24.455(4)$ Å, $V = 3375(1)$ Å^3, $Z = 8$, $d_x = 1.693$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å,

μ(Mo Kα) = 27.2 cm^{-1}, $T = 293(2)$ K, No. reflections collected 2883 and conventional $R = 0.023$, based on the F values of 1541 reflections having $F_o^2 \leqslant 2\sigma(F_o^2)$.

A suitable air sensitive white crystal of **2** of dimensions 0.20 × 0.18 × 0.26 mm was obtained by sublimation at 80–85 °C and 9–11 Pa. It was lodged in a Lindemann glass capillary and centred on a four-circle Phillips PW 1100 (Febo System) diffractometer following standard procedures. The intensity data were corrected for Lorentz-polarisation effects and for absorption as described by North et al. [14]. No correction was made for extinction.

The structure was solved by direct method using SIR-92 [15]. Data processing and computations were carried out with SHELXL-97 using atomic scattering enclosed therein [16]. Geometrical calculations were made with PARST program [17,18], while the structure illustrations were from ORTEP II [19].

Acknowledgements

The authors are grateful to Prof. Giulio Alberti for helpful discussion and acknowledge the financial support of this research from INTAS (International Association for the Promotion of Co-operation with Scientists from the New Independent States of the Former Soviet Union), grant INTAS-UA-210. Some of us (I.G., A.G.) express their gratitude to Fundação de Amparo á Pesquisa do Estado do Rio de Janeiro (FAPERJ, Brazil) and NATO for visiting fellowships.

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