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Synthesis of a Diindacycle by Transmetalation of 1,8-Bis(trimethylstannyl)naphthalene with $InCl_3$

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Introduction

Group 13 polyfunctional Lewis acids are becoming useful in the field of catalysis,[1−7] molecular recognition,[8−14] and material synthesis.[15,16] While a large amount of work has focused on the use of boron[1−4,8,11,12] and aluminum[5−7,10,13,17] at the active site of these derivatives, recent efforts have been concerned with the preparation of derivatives containing several indium centers.[9,18−25] Such compounds are useful derivatives that can serve as selective molecular hosts[14] and supramolecular building blocks.[15] The discovery of high-yield syntheses leading to this class of compound has remained one of the main challenges. Initial efforts focused on the transmetalation reaction of organomercury derivatives with indium(I) halides.[9,18−22] In an effort to develop a general strategy for the preparation of group 13 polyfunctional Lewis acids, we have investigated the reaction of organostannanes with group 13 halides. Although organotin reagents have often been employed for the arylation, vinylation, and alkylation of boron halides,[26−29] the application of this method to the case of heavier group 13 derivatives appears much more limited.[30] Following some earlier work with aluminum,[5,17] we discovered that organostannanes react with gallium trichloride to yield organogallium species.[31] In an extension of these studies we have turned our attention to the case of organoindium and report the synthesis of a diindacycle. This note completes an account that appeared earlier in this journal.[21]

Experimental Section

General Methods. All experimental manipulations were carried out under a N_2 atmosphere using standard Schlenk procedures and a glovebox. NMR spectra were recorded on a Varian VXR-300 instrument at 298 K. The chemical shifts are reported in ppm relative to $SiMe_4$. Melting points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc. Pyridine, acetonitrile, and diethyl ether were dried over calcium hydride and distilled prior to use. 1,8-Bis(trimethylstannyl)naphthalene[32] and 1,8-dilithionaphthalene-tmeda[33] were prepared according to the literature procedures.

Synthesis of the Tetrakis(pyridine) Adduct of Bis(μ-1,8-naphthalenediyl)bis(chloroindium(III)) (1). Transmetalation. Indium trichloride (0.54 g, 2.4 mmol) was added to a suspension of 1,8-bis(trimethylstannyl)naphthalene (1.1 g, 2.4 mmol) in acetonitrile (12 mL). The mixture was stirred for 12 h, after which the starting materials became consumed and replaced by a fine powdery white solid. This solid was isolated by filtration, dried in a vacuum, and recrystallized from pyridine to afford **1** as a bis(pyridine) solvate in 65% yield (0.81 g, 0.79 mmol). Mp: 110−115 °C dec. Anal. Calcd for $C_{45}H_{37}N_5Cl_2In_2$ (loss of 1 interstitial pyridine): C, 57.0; H, 3.9. Found: C, 56.9; H, 4.0. ^{1}H NMR (300 MHz, pyridine-d_5, 25 °C): δ 7.70 (dd, $J = 7.5$ Hz, $J = 6.9$ Hz, 4H, *H*-3,6), 8.12 (d, $J = 7.5$, 4H, *H*-4,5), 9.50 (d, $J = 6.9$ Hz, 4H, *H*-2,7). ^{13}C NMR (75 MHz, pyridine-d_5, 25 °C): δ 125.0 (*C*-3,6), 130.7 (*C*-4,5), 136.6 (*C*-10), 140.7 (*C*-2,7), 146.5 (*C*-9), 159.3 (*C*-1,8).

Metathesis. To a suspension of indium(III) chloride (0.20 g, 0.90 mmol) in ether (5 mL) was added dropwise a solution of 1,8-dilithionaphthalene-tmeda (0.23 g, 0.90 mmol) in ether (5 mL) at −20 °C. The reaction mixture was stirred at room temperature for 30 min. Removal of the solvents followed by ^{1}H NMR analysis in pyridine-d_5 revealed a 25% yield in compound **1**.

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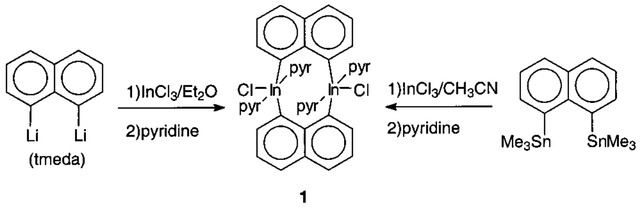
Table 1. Crystallographic Details for **1**·2(pyridine)

empirical formula	$C_{50}H_{42}Cl_2In_2N_6$
fw	1027.44
cryst size	0.13 × 0.19 × 0.28 mm^3
cryst color, shape	colorless
temp	110(2) K
cryst syst, space group	monoclinic, C2/*c*
unit cell dimens	$a = 11.2709(7)$ Å
	$b = 16.771(1)$ Å, $\beta = 99.268(1)°$
	$c = 22.942(1)$ Å
vol	4280.1(5) $Å^3$
Z, calcd density	4, 1.594 Mg/m^3
abs coeff	1.246 mm^{-1}
range for data collection	1.80−25.00
reflns collected/unique	14149/3761 [$R_{int} = 0.0309$]
abs corr	none
data/restraints/params	3761/0/273
final *R* indices [all data]^{a,b}	R1 = 0.0352, wR2 = 0.0927
largest diff peak and hole	2.348 and −0.775 e/$Å^3$

^{a} R1 = $F_o - F_c/F_o$. ^{b} wR2 = $\{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$.

Scheme 1



Crystal Structure Determination for 1. Data were collected on a Siemens SMART-CCD area detector diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å). A specimen of suitable size and quality was selected and mounted onto a glass fiber with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Further crystallographic details can be found in Table 1 and in the Supporting Information.

Results and Discussion

The reaction of 1,8-bis(trimethylstannyl)naphthalene[32] and $InCl_3$ in acetonitrile at 25 °C yields after 12 h an insoluble solid (Scheme 1) as well as Me_3SnCl, which could be recovered from the supernatant. This solid is insoluble in solvents of low polarity as well as in acetonitrile, but dissolves in pyridine to yield the tetrakis(pyridine) adduct of bis(μ-1,8-naphthalenediyl)bis(chloroindium(III)) (**1**). It is interesting to note that the tetrakis(thf) adduct of this diindacycle has been previously isolated in trace amount in the reaction between InCl and 1,8-bis(chloromercurio)naphthalene.[21] The present synthesis appears therefore as a worthy alternative since it affords the diindacyclic species in a 65% yield. Attempts to prepare this diindacycle by metathesis have also been pursued. As shown by ^{1}H NMR spectroscopy, treatment of indium trichloride with an equimolar amount of 1,8-dilithionaphthalene-tmeda in Et_2O also affords the diindacycle. Integration of the ^{1}H NMR spectrum of the product mixture revealed the formation of the diindacycle in a 25% yield based on naphthalene. However, the presence of LiCl complicates the isolation of the product.

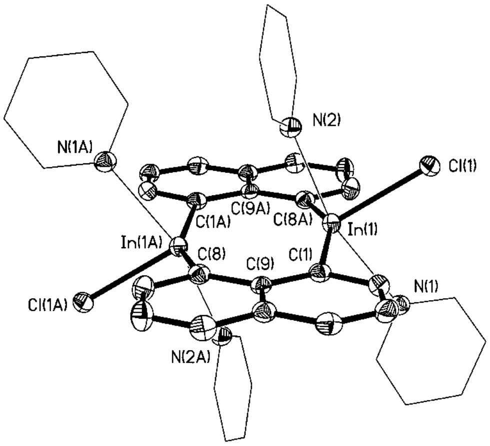


Figure 1. Structure of **1** in the crystal. ORTEP drawing (50%). Selected bond lengths [Å] and angles [deg]: In(1)−C(1) 2.163(3), In(1)−C(8A) 2.174(3), In(1)−N(2) 2.468(2), In(1)−Cl(1) 2.4968(6), In(1)−N(1) 2.524(2), C(1)−C(2) 1.382(4), C(1)−C(9) 1.440(4), C(7)−C(8) 1.379(5), C(8)−C(9) 1.442(4); C(1)−In(1)−C(8A) 153.3(1), C(1)−In(1)−Cl(1) 105.95(8), C(8A)−In(1)−Cl(1) 100.76(8), N(2)−In(1)−N(1) 163.48(7), N(2)−In(1)−Cl(1) 81.98(5), Cl(1)−In(1)−N(1) 82.49(5).

Compound **1** crystallizes in the monoclinic space group *C*2/*c* with two interstitial solvate pyridine molecules (Table 1). The molecular structure of this adduct is similar to that determined for the tetrakis(thf) adduct.[21] Molecules of **1** are centrosymmetrical (Figure 1). The indium centers are pentacoordinated in an approximate trigonal bipyramidal fashion with pyridine ligands occupying the axial sites. The indium coordination sphere undergoes strong distortions which are especially noticeable in the equatorial ligand plane (C(1)−In(1)−C(8A) = 153.3°). As previously observed in analogous dimetallacycles, the *peri*-substituted naphthalenediyl backbone is sterically crowded, as indicated by the increased C(9)−C(1)−In(1) and C(9)−C(8)−In(1A) angles (128.6° and 129.7°). Other deviations from the ideal trigonal bipyramidal geometry include contracted C(1)−In(1)−Cl(1) (106.0°), C(8A)−In(1)−Cl(1) (100.8°), N(1)−In(1)−Cl(1) (82.5°), and N(2)−In(1)−Cl(1) (82.0°) angles.

Conclusion

These results are significant because they indicate that organostannanes are useful starting materials for the preparation of indium derivatives. We are presently investigating the scope of this synthetic methodology by screening the reactions of $InCl_3$ with different organostannanes.

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Supporting Information Available: A crystallographic information file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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