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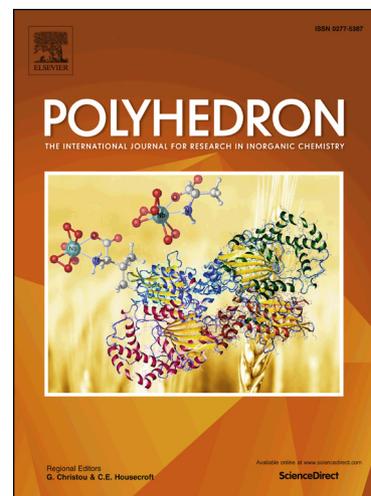
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Synthesis, Characterization and Reactivity of (Dithiolato)indium Complexes

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Abstract

We have synthesized indium complexes incorporating tetradentate dithiolate ligands. The 1:1 reaction of InX_3 ($\text{X} = \text{OAc}, \text{NO}_3$) and the corresponding dithiol or dithiolate yielded the compounds $[(\text{SOOS})\text{In}(\text{py})(\text{NO}_3)]$ (**1**), $[(\text{SNNS})\text{In}(\text{OAc})]$ (**2**), $[\text{In}(\mu\text{-SNNS})_2(\mu\text{-OMe})\text{In}][\text{NO}_3]$ (**3**), $[(\text{SNNSPr})\text{In}(\text{OAc})]$ (**4**), $(\text{NNS}_2)\text{In}(\text{OAc})$ (**5**) and $(\text{NNS}_2)\text{In}(\text{NO}_3)$ (**6**) [$\text{H}_2(\text{SOOS}) = 2,2'$ -(ethylenedioxy)diethanethiol; $\text{H}_2(\text{SNNS}) = N,N'$ -dimethyl- N,N' -bis(2-mercaptoethyl)ethylenediamine; $\text{H}_2(\text{SNNSPr}) = N,N'$ -diethyl- N,N' -bis(2-mercaptoethyl)propanediamine; $\text{H}_2(\text{NNS}_2) = N,N$ -diethyl- N',N' -bis(2-mercaptoethyl)ethanediamine]. The solid-state structures of **1**, **2** and **4-6** are mononuclear and show a tetradentate $\text{SOOS}/\text{SNNS}/\text{NNS}_2$ ligand and a distorted octahedral (**1**) or trigonal bipyramidal (**2**, **4-6**) coordination geometry at indium. Compound **3** is dinuclear, with the indium centres bridged by a -OMe oxygen atom and a thiolate sulfur atom of chelating tetradentate ligands, respectively. InX_3 ($\text{X} = \text{Cl}, \text{NO}_3$) were found to be useful Lewis acid catalysts for the aldol reaction of benzaldehyde and 1-(trimethylsiloxy)cyclohexene under ambient conditions, while compounds **1-6** show moderate activity as catalysts for the esterification of stearic acid and transesterification of methyl stearate and glyceryl trioctanoate.

1. Introduction

A major focus in green chemistry over the past two decades has been the development of synthetic methods that can be carried out in ambient atmosphere conditions and use benign solvents, notably water [[1]]. To this end, several inorganic metal salts have been recognized as useful water-tolerant Lewis acid catalysts for a variety of reactions [[2]]. Notable is the seminal work of Kobayashi et al., who employed the Mukaiyama aldol C-C bond formation reaction in thf:water to compare the utility of group 1-15 metal chlorides and triflates as water stable Lewis acids [[3],[4]] The most effective catalysts were rare earth triflates, with main group metal salts generally performing poorly due to their tendency to readily undergo hydrolysis reactions and form metal oxides.

Since this time, compounds of environmentally benign main group metals, such as indium salts (e.g. chloride, bromide, acetate, triflate), have been successfully employed as water tolerant Lewis acids for a variety of reactions [[5],[6],[7]]. However, very little work has been carried out with organometallic indium complexes, which provide possible tunability of catalytic activity through modification of organic ligands [[8]]. We have previously explored the ability of Lewis acidic methylindium dithiolates to facilitate the ring opening polymerization of cyclic esters [[9],[10]]. We now report the synthesis and characterization of a series of (dithiolato)indium acetate/nitrate compounds (**1-6**), which possess hydrolytically stable In-S bonds. We have screened these as potential water-tolerant Lewis acid catalysts using the Mukaiyama aldol reaction, and examined their ability to facilitate the esterification or transesterification of fatty acids or triglycerides, respectively, which are important reactions for the production of biodiesel from waste oils.

Structural drawings of (di)thiol proligands and **1-6** near here.

2. Results and discussion

2.1 Synthesis of **1-6**

Compounds **1-6** were prepared via the 1:1 metathesis reaction of the in situ generated sodium or potassium dithiolate ligand and indium nitrate, or the dithiol and indium acetate, in methanol. Reactions were stirred at 23°C for 18 h (**1**) or heated to reflux for 3 h (**2-6**), filtered, and the product crystallized from the reaction filtrate in 38-93 % yield. Six equivalents of pyridine were added to the reaction of H₂(SOOS) and In(NO₃)₃ in attempt to increase solubility of the product and promote crystallization, and resulted in formation of the pyridine adduct [(SOOS)In(py)(NO₃)] (**1**). The reaction of In(NO₃)₃ with H₂(SNNS) resulted in the isolation of the dinuclear product [(SNNS)In(μ-OMe)In(SNNS)][NO₃] (**3**), respectively. The compound incorporates a bridging -OMe ligand (vide infra), which results from deprotonation of a methanol solvent molecule. This appears to be a favorable process given that the reaction does not include the addition of base.

Despite several attempts, satisfactory elemental analysis data could not be obtained for **3** and **6**. Low mass percentage C, H and S values and high N values suggests contamination by alkali metal nitrate. However, a higher purity product was achieved using KOH versus NaOH as a base, which yields KNO₃ rather than NaNO₃ as byproduct. The former precipitates more readily from the reaction mixture, while the latter co-crystallizes with the product. Due to insolubility, compound **3** could not be characterized by solution NMR. However, X-ray powder diffraction

data confirm the identity of the bulk sample and the presence of a minor amount of amorphous impurity (see Supplementary data).

2.2 X-ray crystal structures

Crystals suitable for X-ray crystallographic analysis were isolated by cooling the corresponding reaction mixture at -15°C (**1**, **3-6**) or 4°C (**2**). X-ray crystal structures are presented in Figures 1-7. Selected bond distances and angles are included in the figure captions.

The structure of $[(\text{SOOS})\text{In}(\text{py})(\text{NO}_3)]$ (**1**) (Figure 1) shows indium bonded to a tetradentate $(\text{SOOS})^{2-}$ ligand, a pyridine nitrogen atom, and a chelating nitrato- $\kappa^2\text{O},\text{O}'$ group. The geometry at the metal is distorted octahedral if the nitrate group is considered to occupy one coordination site [$\text{S1-In1-S2} = 172.51(3)$, $\text{O1-In1-N1} = 144.55(6)$, $\text{O2-In1-N2} = 162.63(6)$]. The In1-O1 bond distance [$2.514(2)$ Å] is significantly longer than the In1-O2 bond distance [$2.468(2)$ Å], suggesting a weaker trans influence from the neutral pyridine ligand [$\text{O1-In1-N1} = 144.55(6)^{\circ}$] than the anionic nitrate ligand [$\text{O2-In1-O3} = 144.0(1)^{\circ}$; $\text{O2-In1-O4} = 155.8(1)^{\circ}$; $\text{O2-In1-N2} = 162.63(6)^{\circ}$]. The nitrate ligand is nearly symmetrically bonded to the indium centre [$\text{In1-O3} = 2.443(2)$, $\text{In1-O4} = 2.426(2)$ Å].

The structure of $[(\text{SNNS})\text{In}(\text{OAc})]$ (**2**) (Figure 2) shows indium bonded to a tetradentate $(\text{SNNS})^{2-}$ ligand and a chelating acetate- $\kappa^2\text{O},\text{O}'$ group. The geometry at the metal is distorted trigonal bipyramidal if the acetate group is considered to occupy one coordination site. An amine atom and a thiolate sulfur atom occupy axial positions [$\text{S2-In1-N1} = 158.36(7)^{\circ}$] and an amine nitrogen, a thiolate sulfur and the acetate group occupy equatorial positions [$\text{S1-In1-N2} = 109.01(8)$, $\text{S1-In1-C9} = 131.4(1)$, $\text{N2-In1-C9} = 117.0(1)^{\circ}$]. The assumption that the acetate

group occupies a single coordination site seems reasonable as the structure of [(SNNS)InMe] yields a very similar distorted trigonal bipyramidal structure with a monodentate methyl group substituted for the acetate group [Error! Bookmark not defined.]. The cis orientation of the sulfur atoms of the dithiolate ligand [$S1-In1-S2 = 108.62(3)^\circ$] is in contrast to the trans orientation in **1** [$S1-In1-S2 = 172.51(3)^\circ$] and similar to the related complexes (BAT-TM)InX [$H_2(BAT-TM) =$ tetramethylbis(aminoethanethiolate); X = Cl, NCS-*N*, $O_2CPh-\kappa^2O,O'$], in which the thiolate sulfur atoms of the tetradentate-SNN'S' ligand occupy cis positions [$S-In-S = 105.7(2)-107.5(1)^\circ$] [[11]] The axial bond distances [$In1-S2 = 2.479(1)$ and $In1-N1 = 2.386(3)$ Å] are larger than the corresponding equatorial bond distances [$In1-S1 = 2.451(1)$ and $In1-N2 = 2.296(3)$ Å], presumably as a result of trans influence in the former. The acetate ligand is asymmetrically bonded to the indium centre [$In1-O1 = 2.430(3)$ Å; $In1-O2 = 2.205(2)$ Å].

The structure of [$In(\mu-SNNS)_2(\mu-OMe)In$][NO₃] (**3**) (Figure 3) shows a dinuclear monocation with one crystallographically unique indium centre. The metal centres are each chelated by a tetradentate (SNNS)²⁻ ligand, and are bridged by one sulfur atom from each dithiolate and an -OMe ligand. This results in a distorted octahedral geometry at indium [$S1-In1-S2 = 176.33(4)$, $N1-In1-S1^* = 148.9(1)$, $N2-In1-O1 = 168.1(1)^\circ$]. Unlike **2**, the sulfur atoms of the (SNNS)²⁻ ligand are in trans positions. The In-S bond distance to the bridging sulfur atom (S1) is significantly larger [$In1-S1 = 2.696(1)$ versus $In1-S2 = 2.446(1)$ Å], and is larger than the $In1-S1^*$ bond distance [$2.614(1)$ Å].

The structure of [(SNNSPr)In(OAc)] (**4**) (Figure 4) is very similar to that of **2**, and shows small changes in metrics due to the propyl- versus ethyl- ligand backbone. The N1-In1-N2 bond angle increases from $76.8(1)^\circ$ in **2** to $89.3(2)^\circ$ in **4**, affecting an axial S2-In1-N1 bond angle increase from $158.36(7)^\circ$ in **2** to $172.7(1)^\circ$ in **4**. Also, In-S and In-N bond distances in **4** [$In1-S1$

= 2.492(1), In1-S2 = 2.460(1), In1-N1 = 2.414(4), In1-N2 = Å] are slightly longer than the corresponding values in **2**, and the acetate ligand is more symmetrically bonded to the indium centre [In1-O1 = 2.270(3), In1-O2 = 2.315(4) Å]. The asymmetric unit also contains the enantiomer as a crystallographically unique molecule. It exhibits similar bond distances and angles (see Table S1).

The structure of (NNS₂)In(OAc) (**5**) (Figure 5) shows indium bonded to a tetradentate (NNS₂)²⁻ ligand and a chelating acetate-κ²O,O' group. The geometry at the metal centre is distorted trigonal bipyramidal if the acetate group is considered to occupy one coordination site. The central ligand amine nitrogen atom and the acetate ligand occupy axial sites [N1-In1-C11 = 169.1(1)°] and two thiolate sulfur atoms and the ligand terminal amine nitrogen atom occupy equatorial positions [S1-In1-S2 = 135.34(5), S1-In1-N2 = 109.3(1), S2-In1-N2 = 106.7(1)°]. The In1-N1 bond distance [2.449(4) Å] is larger than the In1-N2 [2.353(4) Å], presumably as a result of the trans influence of the acetate ligand. The acetate ligand is asymmetrically bonded to the indium centre [In1-O1 = 2.162(4) Å; In1-O2 = 2.693(4) Å].

The structure of (NNS₂)In(NO₃) (**6**) (Figure 6) is very similar to that of **5**, and shows small changes in metrics due to the presence of the nitrate-κ²O,O' versus acetate ligand. The geometry at the metal centre is also distorted trigonal bipyramidal if the nitrate group is considered to occupy one coordination site. The geometry at indium in **6** is closer to an ideal trigonal bipyramid than in **5**, with an axial-axial bond angle closer to 180° [N1-In1-N3 = 174.1(1)°] and equatorial bond angles closer to 120° [S1-In1-S2 = 127.47(3), S1-In1-N2 = 116.96(6), S2-In1-N2 = 110.80(6)°]. The equatorial bond distances [In1-S1 = 2.4156(8), In1-S2 = 2.4077(9), In1-N2 = 2.329(2) Å] are slightly shorter than in **5**, while the axial In1-N1 bond distance [2.364(2)] is significantly shorter. This is a result of the more weakly coordinated nitrate

ligand [In1-O1 = 2.234(2), In1-O2 = 2.851(4) Å]. Compounds **1** and **6** are very rare examples of indium complexes containing a chelating nitrato- κ^2O,O' group [[12]].

The In-S bond distances in compounds **2-5** are in the range of previously reported indium bis- and tris(thiolates) [In-S = 2.4165(6)-2.543(2) Å] [Error! Bookmark not defined.,Error! Bookmark not defined.,[13],[14],[15]]. However, those of compounds **1** [In1-S1 = 2.4130(7), In1-S2 = 2.4109(7) Å] and **6** [In1-S1 = 2.4156(8), In1-S2 = 2.4077(9) Å] are at the low end of this range or are shorter. This is presumably a result of the weak interaction of the nitrate anion, yielding a more cationic indium centre and stronger In-S bonding interactions. The structure of **3** resembles those of a series of dinuclear [(NNO)InCl(μ -OEt)(μ -Cl)InCl(NNO)] complexes reported by Mehrkodavandi et al., which are efficient catalysts for the ring opening polymerization of cyclic esters [[16]]. Like **3**, these complexes incorporate a single bridging -OR group. However, compound **3** differs in that the indium centres are triply bridged and the dinuclear complex is cationic.

2.3 Aldol reactions

The Mukaiyama aldol reaction was chosen to screen InCl₃, In(OAc)₃, In(NO₃)₃ and (thiolato)indium compounds **1-6** as water stable catalysts due to the availability of data for a large number of group 1-15 chlorides and triflates for comparison [Error! Bookmark not defined.,Error! Bookmark not defined.]. Results are reported in Table 1. Kobayashi et al. reported a 68% product yield with 20 mol% InCl₃ catalyst in 9:1 thf:water [Error! Bookmark not defined.], while Loh et al. obtained a 79% product yield with addition of water only [[17]]. The latter procedure required "purification" of the InCl₃, which involved dissolution of InCl₃ in water,

filtration and removal of water in vacuo, and likely resulted in the formation of indium aqua/hydroxy chloride [[18]]. Our trials of the aldol reaction of benzaldehyde and 1-(trimethylsiloxy)cyclohexene with 20 mol% InCl_3 catalyst using the methods of both Kobayashi and Loh gave low product yields. We subsequently discovered that when the reaction using Loh's "purified" InCl_3 as catalyst was carried out neat, i.e. without addition of solvent or water, a quantitative yield of product was obtained. For comparison, analogous reactions using $\text{In}(\text{OAc})_3$ and $\text{In}(\text{NO}_3)_3$ were also carried out. $\text{In}(\text{OAc})_3$ gave a trace amount of product, while $\text{In}(\text{NO}_3)_3$ gave near quantitative conversion with a 10 mol% catalyst loading. Further, decreasing $\text{In}(\text{NO}_3)_3$ catalyst loading to 5 mol% gave only a trace amount of product. Decreasing the amount of 1-(trimethylsiloxy)cyclohexene to 1.5 equivalents did not affect yield significantly with 10 mol% $\text{In}(\text{NO}_3)_3$, while decreasing to 1 equivalent gave a 47% yield. With 10 mol% catalyst loading and 2 equivalents of 1-(trimethylsiloxy)cyclohexene, compounds **1-6** gave only trace amounts of product.

2.4 Esterification and transesterification reactions

Waste greases and oils are cheap and renewable sources of triglycerides that can be converted into fatty acid methyl esters (FAME), otherwise known as biodiesel [[19]]. Conventional transesterification processes usually involve strongly acidic or basic solutions as homogeneous catalysts [[20]]. However, free fatty acid (FFA) impurities react with basic solutions to form soaps, which makes separation of glycerol problematic [[21]]. Further, the presence of water leads to hydrolysis of oils and FAME in the presence of strong acids and bases [[22]]. Therefore, ideal homogeneous catalysts for biodiesel production from waste oils must

catalyze esterification reactions of carboxylic acids (fatty acids) with alcohol, as well as transesterification reactions of triglycerides. We have screened indium salts and compounds **1-6** as homogeneous catalysts for these reactions.

The esterification of stearic acid to methyl stearate was carried out in refluxing methanol for 4 hours using indium salts and compounds **1-6** as catalysts (Table 2). InCl_3 and $\text{In}(\text{NO}_3)_3$ gave moderate and high yields of 61% and 89%, respectively. Of the indium (di)thiolate compounds, compound **2** gave a moderate yield (41%), while low yields of 4-28% were found for **1** and **3-6**. The dithiolatoindium acetate compounds **2**, **4** and **5** all give higher yields than $\text{In}(\text{OAc})_3$, while the nitrate compounds **1**, **3** and **6** give lower yields than $\text{In}(\text{NO}_3)_3$.

The transesterification of methyl stearate to butyl stearate was carried out in refluxing n-butanol for 19 hours using indium salts and compounds **1-6** as catalysts (Table 3). Both InCl_3 and $\text{In}(\text{NO}_3)_3$ showed near quantitative conversions. Indium thiolate compounds **1-6** gave very high yields (84-100%), with the exception of compound **3**. The reaction was subsequently carried out for 4 hours with those compounds affording $\geq 90\%$ product yield, i.e. InCl_3 , $\text{In}(\text{NO}_3)_3$, **2** and **4-6**. Compound **2** gave the highest yield (81%), outperforming both indium salts.

Finally, the transesterification of glyceryl trioctanoate to methyl stearate was carried out in refluxing methanol for 19 hours using indium salts and compounds **1-6** as catalysts (Table 4). $\text{In}(\text{NO}_3)_3$ was the only salt that afforded any appreciable amount of product (23%). Indium thiolate compounds **1-6** gave very low yields (<1-13%), with the exception of compound **2**, which gave a moderate yield of 31%.

3. Conclusions

The stoichiometric reaction of indium salts with polydentate dithiol(ate)s in methanol is a facile route to the synthesis of mononuclear indium dithiolates or dinuclear indium dithiolates incorporating bridging –OMe groups. Our optimization of the Mukaiyama aldol reaction with (hydrolyzed) InCl_3 and $\text{In}(\text{NO}_3)_3$ showed that the reaction was best carried out neat in ambient conditions and without the addition of water or thf solvent, giving near quantitative yields. Indium dithiolates **1-6** were not effective catalysts for this reaction, but show moderate reactivity for esterification/transesterification reactions of fatty acids, fatty acid esters and triglycerides. InCl_3 and $\text{In}(\text{NO}_3)_3$ were found to give higher yields than **1-6** as catalysts for the esterification of stearic acid. However, compound **2** gave the highest yields for the transesterification of methyl stearate to butyl stearate and the transesterification of glyceryl trioctanoate to methyl octanoate. Although low overall, this shows that the reactivity of the indium complex can be altered significantly with the choice of thiolate ligand, affording complexes that are more effective Lewis acid catalysts than commonly employed indium salts. We are currently studying other thiolate ligand frameworks and catalyzed chemical reactions.

4. Experimental

4.1 General Considerations

Solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were recorded at 23°C on either a JEOL GMX 270 MHz + spectrometer (270 and 67.9 MHz, respectively), or a Varian Mercury 200 MHz + spectrometer (200 and 50 MHz, respectively), and chemical shifts are calibrated to the residual solvent signal. ATR FT-IR spectra were recorded on a Thermo Nicolet iS5 FT-IR spectrometer in the range of

4000-400 cm^{-1} . FT-Raman spectra were recorded on a Thermo Nicolet NXR 9600 Series FT-Raman spectrometer in the range 3900-70 cm^{-1} . Melting points were recorded on an Electrothermal MEL-TEMP melting point apparatus and are uncorrected. Elemental analyses were performed by Laboratoire d'analyse élémentaire, Université de Montréal, Montreal, Canada.

Indium(III) chloride (98%), indium (III) nitrate hydrate (99.9%), indium(III) acetate (99.99%), 2,2'-(ethylenedioxy)diethanethiol (95%), *N,N'*-dimethylethylenediamine 85%, *N,N'*-diethyl-1,3-propanediamine 97%, 2- *N,N*-diethylethylenediamine 99%, ethylene sulfide (98%), benzaldehyde (>99%), 1- cyclohexeneoxy(trimethylsiloxy) (99 %), stearic acid (98.5%), methyl stearate (99%), 1-butanol and glyceryl trioctanoate (≥ 99 %) were used as received from Sigma-Aldrich. Sodium hydroxide (97.0%) and potassium hydroxide (97.0%) was used as received from Caledon. $\text{H}_2(\text{SNNS})$, $\text{H}_2(\text{SNNSPr})$ [[23]], and $\text{H}_2(\text{NNS}_2)$ [[24]], were prepared according to literature methods.

4.2 Synthesis

4.2.1 [*(SOOS)In(py)(NO₃)*] (**1**).

Under a stream of dinitrogen, pyridine (0.528g, 6.68 mmol) and $\text{In}(\text{NO}_3)_3$ (0.427g, 1.11 mmol) were added to MeOH (15 mL). After 15 minutes, $\text{H}_2(\text{SOOS})$ (0.200 g, 1.10 mmol) was added and the reaction mixture was left to stir for 19 h. The solution was filtered and the filtrate was allowed to sit at -15°C . After 3 d the reaction mixture was filtered to yield **4** as colourless crystals of (0.429 g, 1.02 mmol, 93%). Anal. Calc. for $\text{C}_{11}\text{H}_{17}\text{InN}_2\text{O}_5\text{S}_2$: C, 30.29; H, 3.93; N, 6.42; S, 14.70. Found: C, 29.97; H, 3.87; N, 6.51; S, 13.82. M.p. = 166-169 $^\circ\text{C}$. FT-IR (cm^{-1}): 632 m, 669 s, 694 m, 755 m, 797 w, 811 w, 878 w, 932 w, 995 w, 994 w, 1026 m, 1065 w, 1159

w, 1192 w, 1203 w, 1217 w, 1262 m, 1275 w, 1345 m, 1470 s, 1603 m, 2856 w, 2936 w. FT-Raman (cm^{-1}): 120s, 140s, 214m, 284m, 340vs, 500vw, 649w, 671m, 1011s, 1037m, 1221w, 1278w, 1448w, 1603w, 2880w, 2940m, 3971w, 3071m. ^1H NMR ($\text{dms}\text{-}d_6$, ppm): 3.57 (m, 12H, CH_2), 7.37 (m, 2H, $m\text{-NC}_5\text{H}_5$), 7.77 (tt, $J_{\text{H-H}} = 7.8, 2.0$ Hz, 1H, $p\text{-NC}_5\text{H}_5$), 8.55 (dd, $J_{\text{H-H}} = 3.8, 1.6$ Hz, 2H $o\text{-NC}_5\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{dms}\text{-}d_6$, ppm): 25.7 (SCH_2), 66.2 ($\text{SCH}_2\text{CH}_2\text{O}$), 69.9 ($\text{OCH}_2\text{CH}_2\text{O}$), 123.6 ($m\text{-NC}_5\text{H}_5$), 135.8 ($p\text{-NC}_5\text{H}_5$), 149.2 ($o\text{-NC}_5\text{H}_5$).

4.2.2 [(SNNS)In(OAc)] (2).

Under a stream of dinitrogen, 0.350 g (1.20 mmol) $\text{In}(\text{OAc})_3$ was added to a solution of 0.250 g (1.20 mmol) $\text{H}_2(\text{SNNS})$ in MeOH (10 mL). The reaction mixture was heated to reflux for 20 h and hot filtered. The filtrate was allowed to sit at 4°C . After 6 d the solution was filtered to yield **3** as colorless crystals (0.266 g, 0.699 mmol, 58%) Anal. Calc. for $\text{C}_{10}\text{H}_{21}\text{InN}_2\text{O}_2\text{S}_2$: C, 31.59; H, 5.57; N, 7.37; S, 16.87. Found: C, 31.50; H, 5.62; N, 7.26; S, 16.72. M.p. = 155°C . FT-IR (cm^{-1}): 505 w, 627 m, 685 s, 709 w, 737 m, 946 w, 1014 m, 1043 m, 1095 w, 1198 w, 1447 s, 1526 m, 2930 w. FT-Raman (cm^{-1}): 124m, 187m, 231w, 261w, 311vs, 390w, 549w, 678m, 947m, 1052w, 1306w, 1454m, 2929s. ^1H NMR (CDCl_3 , ppm): 2.10 (s, 3H, InCO_2CH_3), 2.46 (s, 6H, NCH_3), 2.91 (m, 12H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 20.4 (CO_2CH_3), 22.2 (SCH_2), 52.2 ($\text{SCH}_2\text{CH}_2\text{N}$), 53.5 ($\text{NCH}_2\text{CH}_2\text{N}$), 181.9 (CO_2CH_3).

4.2.3 [(SNNS)In(μ -OMe)In(SNNS)][NO₃] (3).

Under a stream of nitrogen, 0.361 g (1.20 mmol) $\text{In}(\text{NO}_3)_3$ was added to a solution of 0.250 g (1.20 mmol) $\text{H}_2(\text{SNNS})$ and 0.134 g (2.40 mmol) KOH in MeOH (10 mL). The reaction mixture was heated to reflux for 20 h, then allowed to sit at -15°C . After 5 d the solution was

filtered to yield **3** as colorless crystals (0.162 g, 0.219 mmol, 37%). M.p. = 222 °C. FT-IR (cm^{-1}): 665 m, 754 s, 830 m, 958 s, 1007 s, 1043 s, 1076 m, 1281 s, 1313 s, 1449 m, 2889 w. FT-Raman (cm^{-1}): 111s, 185s, 240m, 255m, 318s, 341m, 364w, 457m, 667m, 757w, 940w, 959w, 1039m, 1136vw, 1232w, 1283w, 1444m, 2926s, 2947s. NMR data could not be obtained due to low solubility. Despite several attempts, satisfactory elemental analysis data could not be obtained.

4.2.4 [(SNNSPr)In(OAc)] (**4**).

Under a stream of dinitrogen, 0.291 g (0.998 mmol) $\text{In}(\text{OAc})_3$ was added to a solution of 0.250 g (0.998 mmol) $\text{H}_2(\text{SNNSPr})$ in MeOH (10 mL). The reaction mixture was heated to reflux for 19 h and hot filtered. The filtrate was allowed to sit at -15°C . After 2 d the solution was filtered to yield **4** as colorless crystals (0.291 g, 0.698 mmol, 70%). Anal. Calc. for $\text{C}_{13}\text{H}_{27}\text{InN}_2\text{O}_2\text{S}_2$: C, 36.97; H, 6.44; N, 6.63; S, 15.18. Found: C, 36.84; H, 6.54; N, 6.52; S, 15.53. M.p. = 191 °C. FT-IR (cm^{-1}): 455 w, 521 w, 627 m, 685 s, 709 w, 737 m, 946 w, 1015 w, 1043 m, 1095 w, 1198 w, 1448 s, 1527 m, 2930 w. FT-Raman (cm^{-1}): 144s, 172m, 204s, 284m, 316vs, 342s, 380m, 471m, 530w, 670s, 744w, 764w, 942m, 1211w, 1246w, 1279w, 1437w, 1456m, 2823w, 2921s, 3012w. ^1H NMR (CDCl_3 , ppm): 0.96 (t, $J_{\text{H-H}} = 8.2$ Hz, 6H NCH_2CH_3), 2.10 (s, 3H, InCO_2CH_3), 2.96 (m, 18H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 20.5 (CO_2CH_3), 22.2 (SCH_2), 30.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 52.2 ($\text{SCH}_2\text{CH}_2\text{N}$), 53.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 181.9 (CO_2CH_3).

4.2.5 (NNS_2)In(OAc) (**5**).

Under a stream of dinitrogen, 0.292 g (0.998 mmol) $\text{In}(\text{OAc})_3$ was added to a solution of 0.250 g (0.998 mmol) $\text{H}_2(\text{NNS}_2)$ in MeOH (10 mL). The reaction mixture was heated to reflux for 23 h, then allowed to sit at -15°C . After 1 d the solution was filtered to yield **2** as colorless crystals (0.223 g, 0.566 mmol, 57%). Anal. Calc. for $\text{C}_{12}\text{H}_{25}\text{InN}_2\text{O}_2\text{S}_2$: C, 35.30; H, 6.17; N, 6.68. Found: C, 35.34; H, 6.34; N, 6.87. M.p. = 172°C . FT-IR (cm^{-1}): 506 m, 599 w, 620 w, 670 s, 722 w, 743 m, 887 w, 930 w, 977 w, 1000 m, 1047 w, 1095 s, 1300 m, 1330 s, 1383 s, 1446 m, 1473 w, 1581 m, 2982 w. FT-Raman (cm^{-1}): 111s, 185vs, 240m, 256m, 318s, 339m, 363m, 458m, 543w, 667m, 757w, 941w, 1029m, 1232w, 1284w, 1443m, 2926s, 2947s. ^1H NMR (CDCl_3 , ppm): 1.25 (t, $J_{\text{H-H}} = 7.0$ Hz, 6H, NCH_2CH_3), 1.97 (s, 3H, InCO_2CH_3) 2.76 (m, 16H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 9.15 (NCH_2CH_3), 22.8 (SCH_2), 23.5 (CO_2CH_3), 44.5 (NCH_2CH_3), 49.5 ($\text{SCH}_2\text{CH}_2\text{N}$), 57.5 ($\text{NCH}_2\text{CH}_2\text{N}$) 181.7 (CO_2CH_3).

4.2.6 $(\text{NNS}_2)\text{In}(\text{NO}_3)$ (**6**).

Under a stream of dinitrogen, 0.300 g (0.998 mmol) $\text{In}(\text{NO}_3)_3$ and 0.250 g (0.998 mmol) $\text{H}_2(\text{NNS}_2)$ were added to a solution of 0.112 g (0.200 mmol) KOH in MeOH (10 mL). The reaction mixture was heated to reflux for 21 h, then allowed to sit at -15°C . After 2 d the solution was filtered to yield **3** as colorless crystals (0.223 g, 0.566 mmol, 57%). M.p. = 172°C . FT-IR (cm^{-1}): 663 w, 723 m, 745 m, 809 m, 824 w, 975 w, 1009 s, 1053 w, 1093 m, 1284 vs, 1354 m, 1444 m, 1477 m, 2853 w. FT-Raman (cm^{-1}): 183s, 208s, 240m, 318s, 341m, 364w, 458m, 544w, 676m, 758w, 958w, 1038m, 1136w, 1284w, 1443m, 297s, 2948s. ^1H NMR ($\text{dmsO-}d_6$, ppm): 1.28 (t, 6H, NCH_2CH_3), 2.92 (m, 16H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{dmsO-}d_6$, ppm): 10.19 (NCH_2CH_3), 20.2 (SCH_2), 44.5 (NCH_2CH_3), 51.1 ($\text{SCH}_2\text{CH}_2\text{N}$), 56.4 ($\text{NCH}_2\text{CH}_2\text{N}$). Despite several attempts, satisfactory elemental analysis data could not be obtained.

4.3 Catalysis

4.3.1 Aldol reaction

5, 10 or 20 mol % of the indium precatalyst and 0.106 g, 1 mmol benzaldehyde were stirred together for 30 minutes. 1, 2, or 3 mmol of 1-(trimethylsiloxy)cyclohexene was added and the reaction mixture was stirred at 23°C for 18 h. The resulting product was analyzed by ^1H NMR spectroscopy in CDCl_3 . Alternatively, 5 mL of water was added and the mixture stirred for 15 min. 15 mL CH_2Cl_2 was then added and the mixture stirred for 15 min. The organic layer was removed, dried over anhydrous magnesium sulfate, and filtered. The solution was washed through ~1-2 cm of silica gel (dessicant, 28-200 mesh) with 30 mL CH_2Cl_2 . The solvent was then removed in vacuo and the resulting product analyzed by ^1H NMR spectroscopy in CDCl_3 . Signals for the anti (5.40 ppm, d, $^3J = 2.5$ Hz) and syn (4.83 ppm, d, $^3J = 9.0$ Hz) products were integrated against that of benzaldehyde (10.00 ppm) to determine percent yield and isomeric ratio.

4.3.2 Esterification of stearic acid

To a solution of stearic acid (0.100 g, 0.352 mmol) in MeOH (1 mL) was added 10 mol % of the desired catalyst (0.035 mmol). The resulting solution was heated to reflux for 4 h, after which the excess methanol was removed under reduced pressure. The residue was extracted with diethyl ether and the solvent was removed under vacuum to yield the crude product. Samples were analyzed by ^1H NMR spectroscopy in CDCl_3 to determine conversion of stearic acid to methyl stearate.

4.2.3 Transesterification of methyl stearate

Methyl stearate (0.100g, 0.335 mmol) was dissolved in 1-butanol (1 mL) with subsequent addition of 10 mol % of the desired catalyst (0.035 mmol). The resulting solution was heated at reflux for 4-18 h, after which the solvent was removed under vacuum. The residue was extracted with diethyl ether and the solution washed with distilled water (5 mL). The organic layer was then dried over anhydrous sodium sulfate and the solvent removed under vacuum to yield the crude product. Samples were analyzed by ^1H NMR spectroscopy in CDCl_3 to determine conversion of methyl stearate to methyl stearate.

4.3.4 Transesterification of glyceryl trioctanoate

Glyceryl trioctanoate (0.150g, 0.319 mmol) was dissolved in MeOH (1 mL) with subsequent addition of 10 mol % of the desired catalyst (0.032 mmol). The resulting solution was refluxed for 4-18 h, after which excess alcohol was removed under vacuum. The residue was extracted with diethyl ether, washed with distilled water (5 mL), dried over anhydrous sodium sulfate, and the solvent removed under vacuum to yield the crude product. Samples were analyzed by ^1H NMR spectroscopy in CDCl_3 to determine conversion of glyceryl trioctanoate to methyl stearate.

4.4 X-ray crystallography

Crystals of **1-** were isolated from the reaction mixtures as indicated above. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS

P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [[25]] and corrected for absorption (SADABS) [[26]]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [[27]]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model, except for the methanol hydrogen atoms that were omitted (**6**). Crystallographic data are found in Table 5.

For **2**, all of the C atoms were disordered over two positions and the site occupancies determined using an isotropic model as 0.7 [C(1)-C(8)] and 0.3 [C(1A)-C(8A)] and fixed in subsequent refinement cycles. Thermal parameters for the disordered pairs were constrained and the bond distances within the equivalent bonds restrained. For **3**, the methanol molecule was disordered and the site occupancies determined using an isotropic model as 0.5 (C(10), C(11), O(10), O(11)) and fixed in subsequent refinement cycles. For **4**, the crystal was a multiple twin and the orientation matrix of the major component was determined (CELL_NOW) [[28]]. For **5** and **6**, the crystal was twinned and the orientation matrixes for two components were determined (CELL_NOW).

4.5 X-ray powder diffraction

X-ray powder diffraction (XRD) measurements were carried out in reflection with a custom built theta/theta diffractometer equipped with a pyrolytic graphite monochromator and analyzer crystals. Cu K-alpha radiation ($1/4 \cdot 0.154178$ nm) was used for the measurements, in the $5-100^\circ$ 2θ range with a 0.1° step size and 10 s count time. Air-scattering was avoided by

evacuating the sample space and signal originating from the substrate was minimized by placing the powder on a Si (511) crystal. The data are shown as a function of the modulus of the scattering vector, $q = 4\pi/\lambda \sin \theta$, where 2θ is the scattering angle. The power pattern was calculated from single crystal data using Diamond 3.1 software [[29]]. The experimental data was fit using a Rietveld refinement [[30]].

Appendix A. Supplementary data

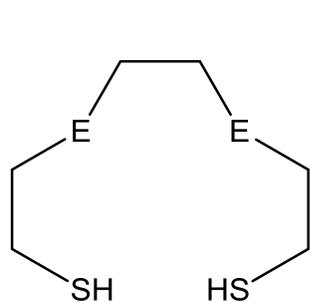
Selected bond distances for both crystallographically unique molecules of **4**. Experimental and calculated X-ray powder diffraction (XRD) pattern for **3**. CCDC 1526658-1526660 and 1526662-1526664 contains the supplementary crystallographic data for **1-6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

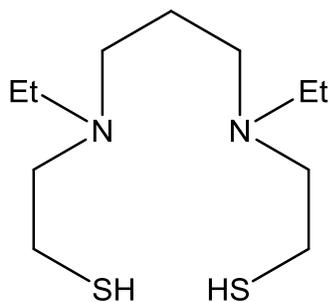
We thank the following: Dan Durant for assistance in collecting solution NMR data; Delilah Brown for XRD data collection; and the Natural Sciences and Engineering Research Council of Canada, the New Brunswick Innovation Foundation, the Canadian Foundation for Innovation and Mount Allison University for financial support.

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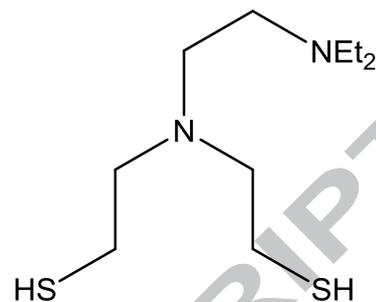
Structural drawings of dithiol proligands.



$H_2(SOOS)$, E = O
 $H_2(SNNS)$, E = NMe

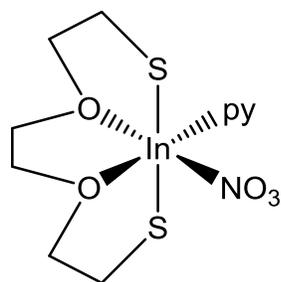


$H_2(SNNSPr)$

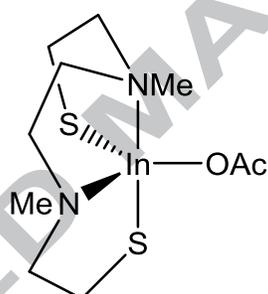


$H_2(NNS_2)$

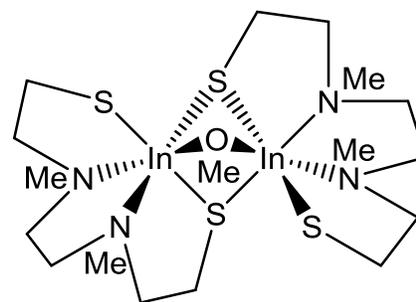
Structural drawings of **1-6**.



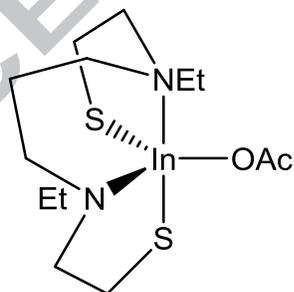
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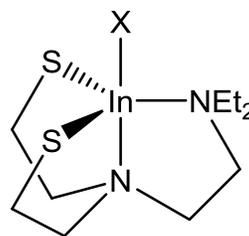
2



3



4



5, X = OAc
6, X = NO₃

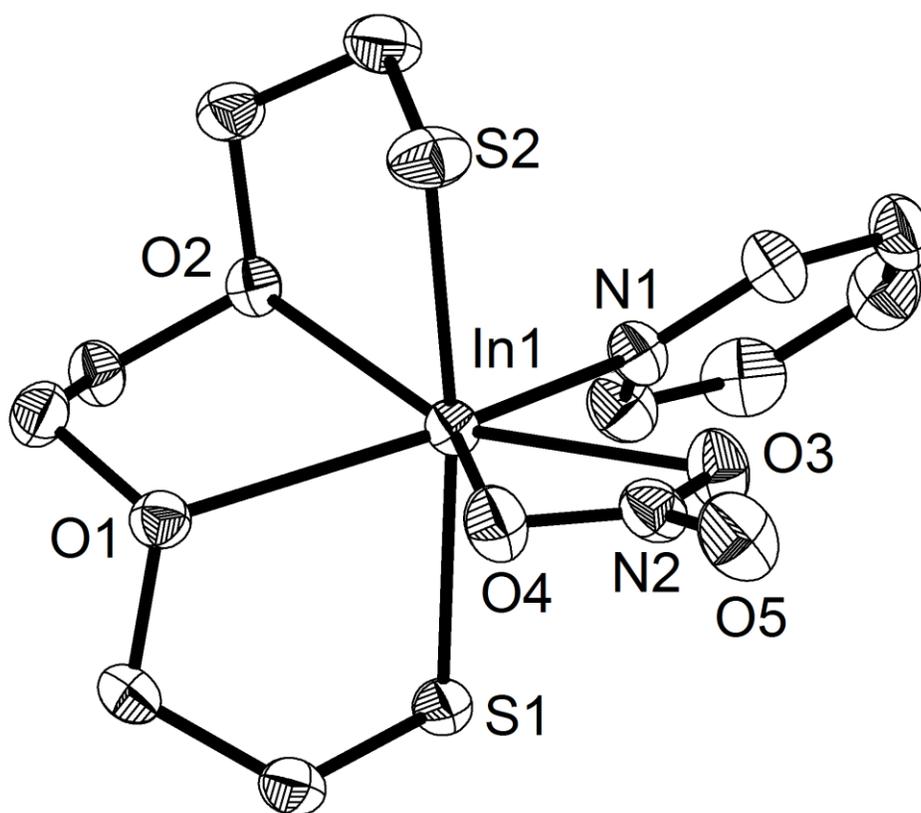


Figure 1. X-ray structure of **1** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (°): In1-S1 = 2.4130(7), In1-S2 = 2.4109(7), In1-O1 = 2.514(2), In1-O2 = 2.468(2), In1-N1 = 2.340(2), In1-O3 = 2.443(2), In1-O4 = 2.426(2), S1-In1-O1 = 76.40(4), S2-In1-O2 = 77.73(4), O3-In1-O4 = 52.71(6), O1-In1-O2 = 69.54(5), S1-In1-S2 = 172.51(3), O1-In1-N1 = 144.55(6), O2-In1-N2 = 162.63(6).

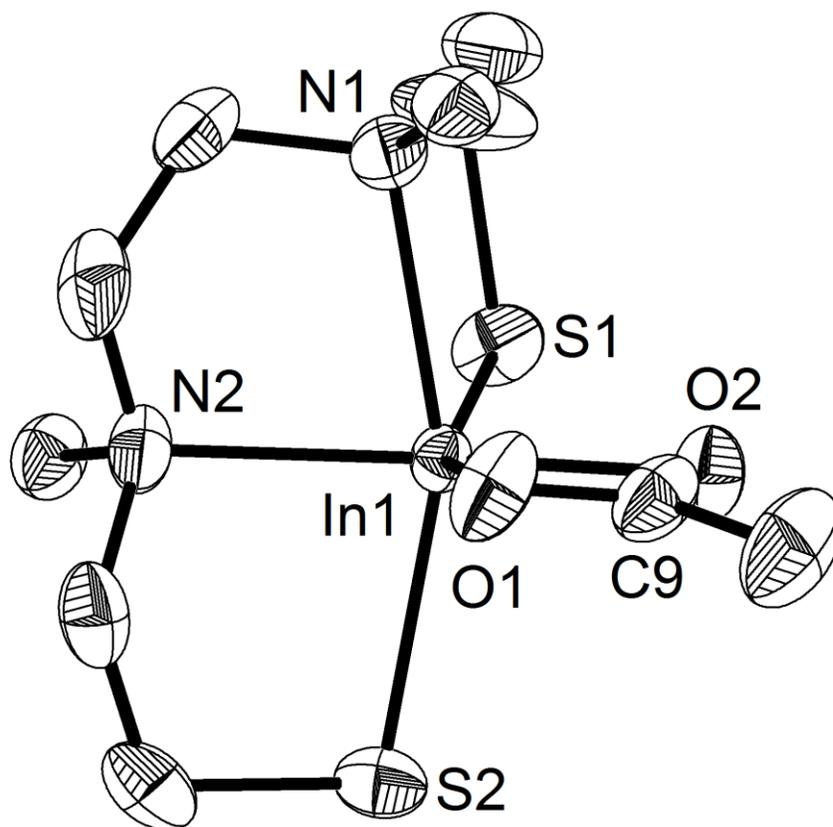


Figure 2. X-ray structure of **2** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (°): In1-S1 = 2.451(1), In1-S2 = 2.479(1), In1-N1 = 2.386(3), In1-N2 = 2.296(3), In1-O1 = 2.430(3), In1-O2 = 2.205(2), S1-In1-N1 = 82.90(8), S2-In1-N2 = 82.02(8), N1-In1-N2 = 76.8(1), S1-In1-N2 = 109.01(8), S1-In1-C9 = 131.4(1), N2-In1-C9 = 117.0(1), S2-In1-N1 = 158.36(7).

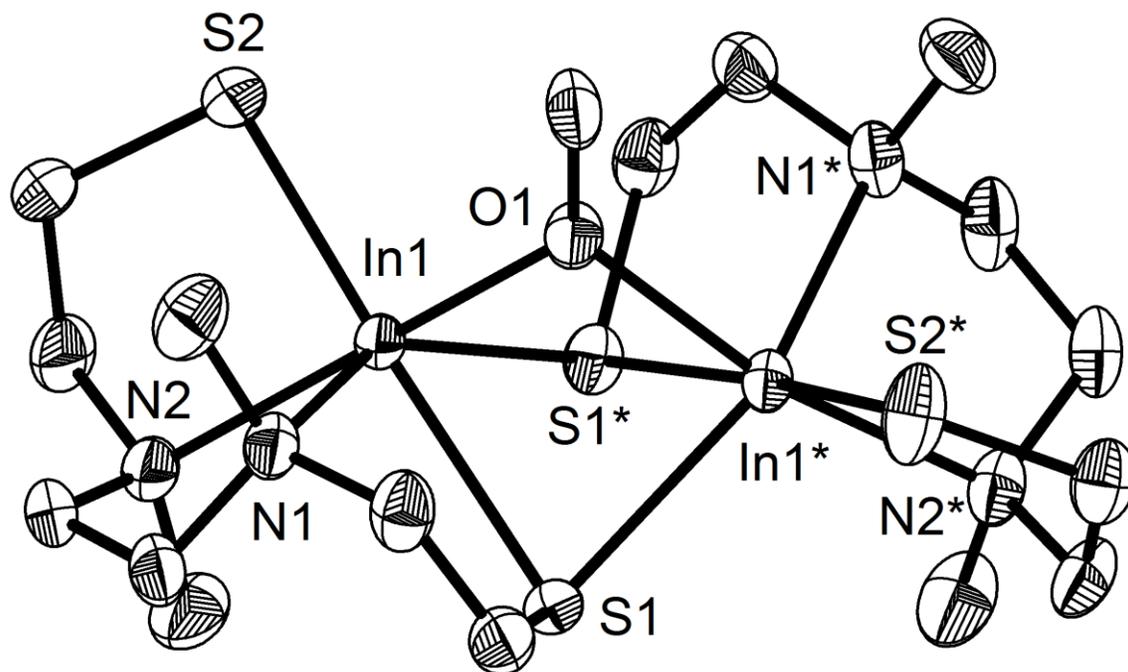


Figure 3. X-ray structure of the cation of **3** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Symmetry transformations used to generate equivalent atoms (*): $-x, -y+1, z$. Selected bond distances (Å) and angles (°): In1-S1 = 2.696(1), In1-S2 = 2.446(1), In1-S1* = 2.614(1), In1-N1 = 2.345(4), In1-N2 = 2.333(4), In1-O1 = 2.174(4), S1-In1-N1 = 76.4(1), S2-In1-N2 = 84.5(1), N1-In1-N2 = 77.9(1), S1-In1-S2 = 176.33(4), N1-In1-S1* = 148.9(1), N2-In1-O1 = 168.1(1).

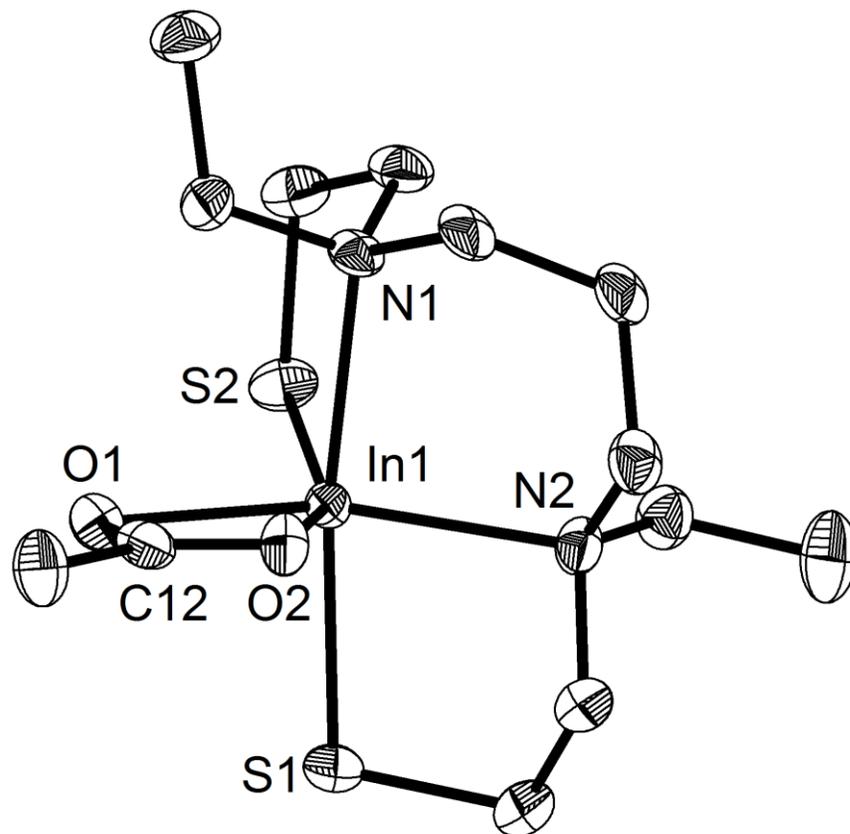


Figure 4. X-ray structure of **4** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (°): In1-S1 = 2.492(1), In1-S2 = 2.460(1), In1-N1 = 2.414(4), In1-N2 = 2.352(4), In1-O1 = 2.270(3), In1-O2 = 2.315(4), S1-In1-N1 = 172.7(1), S2-In1-N2 = 114.2(1), S2-In1-C12 = 129.7(1), N2-In1-C12 = 114.8(2), N1-In1-N2 = 89.3(2), S1-In1-N2 = 83.5(1), S2-In1-N1 = 81.7(1).

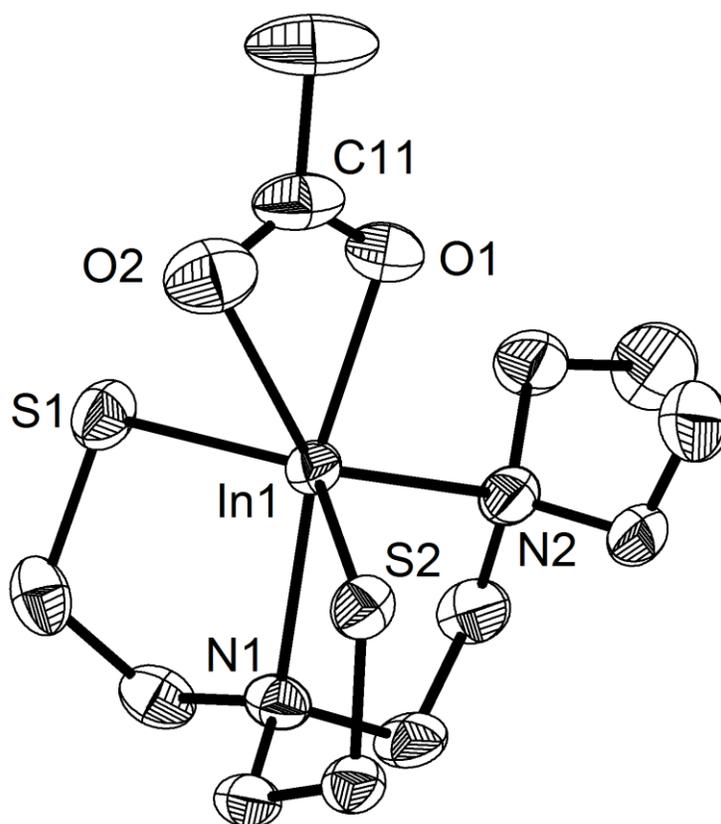


Figure 5. X-ray structure of **5** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (°): In1-S1 = 2.425(1), In1-S2 = 2.439(1), In1-N1 = 2.449(4), In1-N2 = 2.353(4), In1-O1 = 2.162(4), In1-O2 = 2.693(4), S1-In1-S2 = 135.34(5), S1-In1-N2 = 109.3(1), S2-In1-N2 = 106.7(1), N1-In1-C11 = 169.1(1).

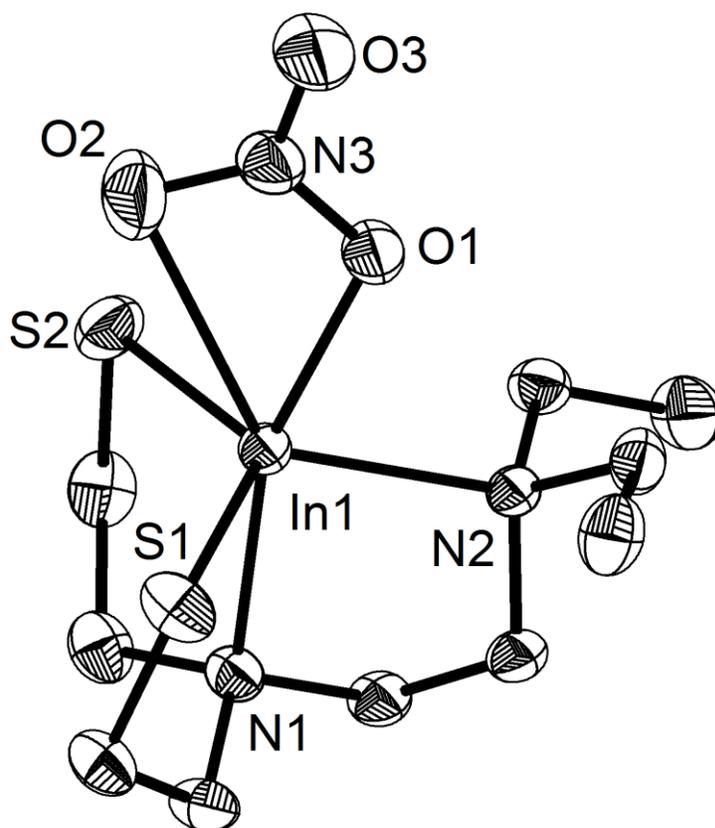
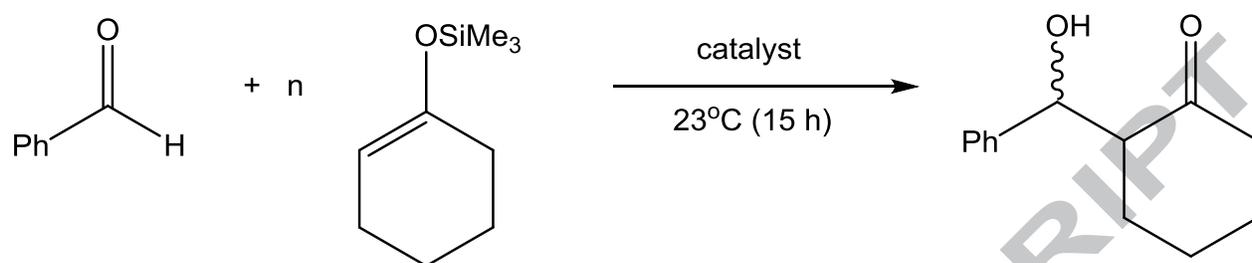


Figure 6. X-ray structure of **6** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (°): In1-S1 = 2.4156(8), In1-S2 = 2.4077(9), In1-N1 = 2.364(2), In1-N2 = 2.329(2), In1-O1 = 2.234(2), In1-O2 = 2.851(4), S1-In1-S2 = 127.47(3), S1-In1-N2 = 116.96(6), S2-In1-N2 = 110.80(6), N1-In1-N3 = 174.50(7).

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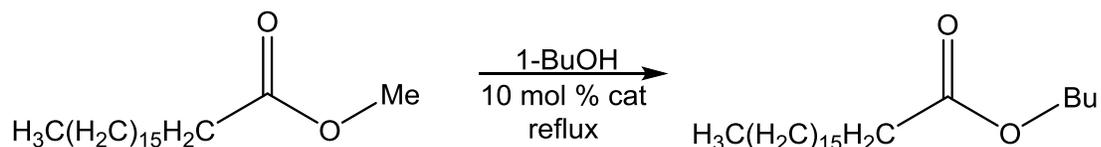
Table 1. Catalyzed aldol reaction of benzaldehyde and 1-trimethylsilyloxycyclohexene.

Catalyst	n	mol% catalyst	Yield (%) (<i>anti:syn</i>)
InCl ₃ (purified)	2	20	100 (73:27)
In(OAc) ₃	2	20	<1
In(NO ₃) ₃	2	10	95 (56:44)
In(NO ₃) ₃	2	5	<1
In(NO ₃) ₃	1.5	10	93 (46:54)
In(NO ₃) ₃	1	10	47 (45:55)
1-6	2	10	<1

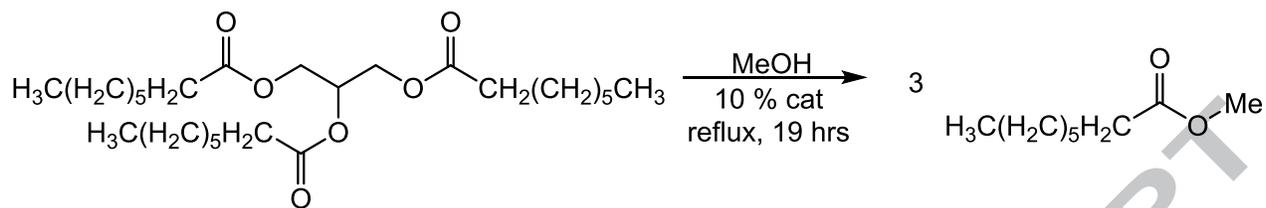
Table 2. Catalyzed conversion of stearic acid to methyl stearate.

$$\text{H}_3\text{C}(\text{H}_2\text{C})_{15}\text{H}_2\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \xrightarrow[\text{reflux, 4 h}]{\text{MeOH, 10 mol \% cat}} \text{H}_3\text{C}(\text{H}_2\text{C})_{15}\text{H}_2\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Me}$$

Catalyst	Conversion (%)
None	< 1
InCl ₃	61
In(OAc) ₃	< 1
In(NO ₃) ₃	89
1	4
2	41
3	10
4	22
5	11
6	28

Table 3. Catalyzed conversion of methyl stearate to butyl stearate.

Catalyst	Time (h)	Yield (%)
None	19	4
InCl ₃	19	99
In(OAc) ₃	19	33
In(NO ₃) ₃	19	95
1	19	84
2	19	90
3	19	14
4	19	92
5	19	100
6	19	91
InCl ₃	4	6
In(NO ₃) ₃	4	43
2	4	81
4	4	2
5	4	24
6	4	<1

Table 4. Catalyzed conversion of glyceryl trioctanoate to methyl octanoate.

Catalyst	Conversion (%)
None	<1
InCl ₃	<1
In(OAc) ₃	2
In(NO ₃) ₃	23
1	<1
2	31
3	13
4	2
5	12
6	2

Table 5. Crystallographic data for **1-6**.

	1	2	3·MeOH	4	5	6
formula	C ₁₁ H ₁₇ InN ₂ O ₅ S ₂	C ₁₀ H ₂₁ InN ₂ O ₂ S ₂	C ₁₈ H ₄₃ In ₂ N ₅ O ₅ S ₄	C ₁₃ H ₂₇ In N ₂ O ₂ S ₂	C ₁₂ H ₂₅ InN ₂ O ₂ S ₂	C ₁₀ H ₂₂ InN ₃ O ₃ S ₂
fw	436.21	380.23	767.45	422.31	408.28	411.25
crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
space group	P-1	P2(1)/n	A m a 2	P-1	P2(1)/n	P2(1)/n
<i>a</i> (Å)	7.483(2)	8.700(2)	25.632(9)	8.438(2)	7.6549(10)	9.5567(19)
<i>b</i> (Å)	8.575(2)	11.210(3)	14.169(4)	13.614(3)	8.5532(10)	13.857(3)
<i>c</i> (Å)	13.160(3)	15.426(4)	7.922(2)	15.522(3)	25.906(3)	11.713(2)
<i>α</i> (deg)	82.466(3)	90	90	92.074(2)	90	90
<i>β</i> (deg)	87.640(3)	101.281(3)	90	92.169(3)	94.516(3)	91.090(3)
<i>γ</i> (deg)	72.672(3)	90	90	101.550(2)	90	90
<i>V</i> (Å ³)	799.1(3)	1475.4(7)	2877.1(15)	1744.1(6)	1690.9(4)	1550.8(5)

Z	2	4	4	4	4	4
F(000)	436	768	1552	864	832	832
ρ_{calcd} , g cm ⁻³	1.813	1.712	1.772	1.608	1.604	1.761
μ , mm ⁻¹	1.760	1.878	1.930	1.597	1.645	1.800
T, K	188(1)	188(1)	188(2)	188(1)	223(1)	223(1)
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
reflections collected	5449	9692	9584	9354	3274	3447
unique reflections	3445	3279	3296	6599	3276	3447
R(int)	0.0165	0.0307	0.0453	0.0209		
parameters	190	189	168	367	176	174
GooF	1.044	1.057	1.063	1.089	1.109	1.147
Largest diff. peak and hole (e.Å ⁻³)	1.129 and -0.719	1.102 and -0.658	0.653 and -0.461	1.454 and - 0.795	0.808 and -0.626	0.741 and -0.379
R ₁ ^a	0.0248	0.0288	0.0309	0.0398	0.0288	0.0249
wR ₂ ^b	0.0663	0.0737	0.0705	0.1057	0.0769	0.0702

^a $R_1 = [\sum ||F_o| - |F_c||] / [\sum |F_o|]$ for $[F_o^2 > 2\sigma(F_o^2)]$. ^b $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^4)]\}^{1/2}$.

References

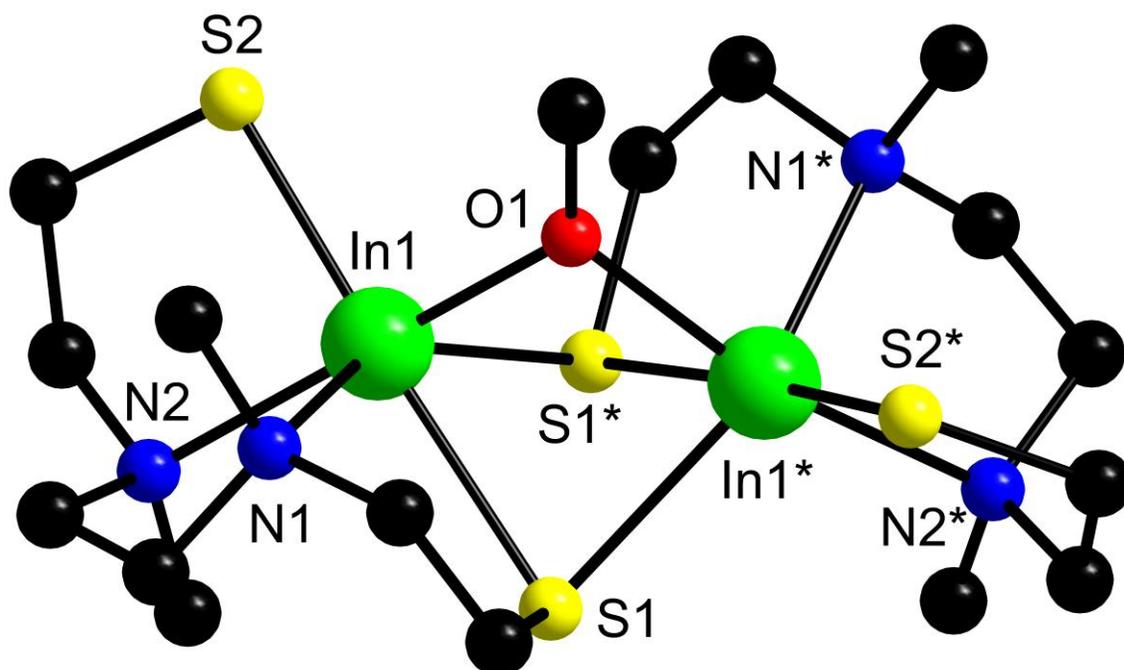
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ACCEPTED MANUSCRIPT

Graphical abstract

Graphical Abstract (Synopsis)

The reaction of indium(III) salts with polyfunctional dithiolates afforded mono- and dinuclear (dithiolato)indium complexes that show moderate reactivity as Lewis acid catalysts.