Synthesis and Structural Characterization of Methylindium Imino/Aminophenolates: Comparison to Aluminum Analogues and Reactivity Toward the Coupling Reactions of Carbon Dioxide with Epoxides

Kori A. Andreaa, Adam R. Beckettb, Glen G. Briandb*, Sarah A. Martellb, Jason Masudac, Kathleen M. Morrisonb and Emilie M.T. Yammineb

a Department of Chemistry, Memorial University of Newfoundland, St. John’s, Newfoundland and Labrador, Canada A1B 3X7

b Department of Chemistry and Biochemistry, Mount Allison University, Sackville, New Brunswick, Canada E4L 1G8

c Department of Chemistry, Saint Mary’s University, Halifax Nova Scotia, Canada BH3 C3C

* To whom correspondence should be addressed. Tel: (506) 364-2346.
Fax: (506) 364-2313. E-mail: gbriand@mta.ca
Abstract

We have synthesized methylindium complexes containing a variety of amino- and iminophenolate ligands for structural comparison to their aluminum analogues. The reaction of Me₃In with the corresponding amino-/iminophenols resulted in the formation of MeIn(Et₂NCH₂CH₂-abp) (1), MeIn(PyCH₂-abp) (2), [MeIn(iPr-abp)]₂ (3), MeIn(Ph-salen) (4), MeIn(Et-salan) (5), MeIn(Cy-ip) (6) and MeIn(Mes-ip) (7) [H₂(Et₂NCH₂CH₂-abp) = Et₂NCH₂CH₂N(2-OH-3,5-C₆H₄tBu₂)₂, H₂(PyCH₂-abp) = (2-C₅H₄N)CH₂N(2-OH-3,5-C₆H₄tBu₂)₂, H₂(iPr-abp) = (CH₃)₂CHN(2-OH-3,5-C₆H₄tBu₂)₂, H₂(Ph-salen) = 1,2-(NCH-2-OH-3,5-C₆H₄tBu₂)₂C₆H₄, H₂(Et-salan) = 1,2-(NMeCH₂-2-OH-3,5-C₆H₄tBu₂)₂C₆H₄, H(Cy-ip) = (2-OH-3,5-tBu₂-C₆H₂)CHN(C₆H₁₁), and H(Mes-ip) = (2-OH-3,5-tBu₂-C₆H₂CHN(2,4,6-Me₃C₆H₂)). X-ray crystallography studies show monomeric structures and five-coordinate indium centres for 1 and 2, a dimeric structure via intermolecular In...O interactions and five-coordinate indium centres for 3, and monomeric structures and four-coordinate indium centres for 6 and 7. DFT calculations were used to rationalize the observed dimeric structure of 3 and monomeric structures of 6 and 7, and gauge the effect of ligand steric bulk and atomic radius in indium versus aluminum on dimerization. Compounds 2 and 5 are active catalysts for coupling reactions of carbon dioxide and propylene oxide to yield propylene carbonate and carbon dioxide with cyclohexene oxide to yield polycyclohexene carbonate. This work provides insight into controlling intermolecular bonding and hence reactivity in indium and aluminum amino-/iminophenolate complexes, and represent one of the first examples of indium complexes as catalysts for the formation of cyclic- or polycarbonates from carbon dioxide and epoxides.
1. Introduction

The synthesis of reactive species for use as improved alternatives to traditional transition metal-based catalysts in chemical processes is a primary focus of contemporary main group chemistry [1]. In this regard, alkylaluminum complexes supported by imino- and aminophenolate ligands (1-3) have found broad applicability as homogeneous catalysts in ring opening polymerizations (ROP) reactions, such as the ROP of cyclic esters to afford biodegradable aliphatic polyesters [2] and the co-polymerization of carbon dioxide (CO$_2$) and epoxides to afford polycarbonates or cyclic carbonates [3]. Although ROP catalysts based on the heavier group 13 congener indium have been found to exhibit high reactivity [4,5,6], there are comparably few studies of alkylindium imino- and aminophenolate complexes [7]. The first example of a diaminobis(phenolate) (salan) supported indium (chloride) complex has only recently been reported [8], as well as the first example of an indium-based catalyst for the ring-opening co-polymerization of epoxides and carbon dioxide [9].

Comparisons of analogous aluminum and indium catalysts have shown that their reactivities are affected by differences in the coordination sphere [10]. Indium possesses a much larger covalent radius than aluminum (1.42 vs 1.21 Å, respectively). This results in less steric crowding at the metal centre and more available coordination sites. In many cases, this leads to intermolecular bonding and the formation of dimeric or oligomeric species [11,12,13]. Dimerization has been shown to affect and sometimes improve catalytic activities, leading to proposed bimetallic mechanisms and further research into bimetallic systems [14,15,16], while in other cases a decrease in reactivity is observed [17]. A previous study comparing dimeric [(salen)InOEt]$_2$ with monomeric [(salen)InCHPyr] complexes containing the corresponding salen
ligands showed an initiation period for dimeric complexes but similar reactivity [18]. To gauge the structural effects of altering the metal centre, we now report the synthesis and solid-state structures of (di)methylindium aminobis(phenolate) (abp; 1-3), diiminobis(phenolate) (salen; 4), diaminobis(phenolate) (salan; 5) and imino(phenolate) (ip; 6-7) complexes for structural comparison to previously reported aluminum analogues. Further, we have used DFT calculations to rationalize structural differences in observed indium versus aluminum structures. Finally, we have performed preliminary screening of 2 and 5 for catalytic reactivity toward coupling reactions of carbon dioxide with epoxides to yield polycarbonates and cyclic carbonates for comparison to similar aluminum complexes.

**Structural Drawings of 1-7 near here**

2. Results and discussion

2.1 *Synthesis and spectroscopic characterization*

All compounds were prepared via the hydrocarbon elimination reaction between trimethylindium and one equivalent of the corresponding imino-/aminophenol. All reactions occurred at room temperature, some with the noticeable evolution of methane gas. Reaction mixtures were stirred for three hours. Crystalline materials were isolated by slow evaporation (1, 2, 4-6), solvent layering (3) or cooling (7) of reaction mixtures. Isolated yields of 1-7 were moderate to good (31-85%).

The FT-Raman spectra of compounds 1-5 show resonances at ~500 cm\(^{-1}\) corresponding to the \(\nu(\text{In-Me})\) vibrational mode, while 6 and 7 show a very strong resonance at ~485 cm\(^{-1}\).
corresponding to the $\nu_{\text{sym}}$ (Me-In-Me) vibrational mode [11]. All compounds show signals at 0.4 to -0.4 ppm in the $^1$H NMR spectra corresponding to the In-Me group [11], as well as the expected ligand resonances. Further, all compounds show a single set of sharp resonances for the corresponding aminophenolate ligand, indicating both that compound 3 is monomeric and that the trigonal bipyramidal metal bonding environment of 5 is fluxional in CDCl$_3$ solution at 23°C (vide infra).

2.2 X-ray crystal structures

The structure of 1 (Figure 1) shows one tetradeinate NNO$_2$ ligand and a five coordinate O$_2$N$_2$C bonding environment for indium. The In-O bond distances are similar [In1-O1 = 2.080(3), In1-O2 = 2.080(3) Å], while one nitrogen atom of the ligand is more weakly coordinated to the metal [In1-N1 = 2.357(3), In1-N2 = 2.403(3) Å]. The indium centre is in a distorted trigonal bipyramidal bonding environment, with the ligand O1, O2 and N2 in equatorial positions [O1-In1-O2 = 116.9(1), O1-In1-N2 = 127.45(9), O2-In1-N2 = 106.4(1)°], and the ligand N1 and the methyl carbon atom (C1) in axial positions [C1-In1-N1 = 165.4(1)°].

The structure of 2 (Figure S1) shows a similar structure to that of 1, with one tetradeinate NNO$_2$ ligand and a five coordinate O$_2$N$_2$C bonding environment for indium. The indium centre is in a distorted trigonal bipyramidal bonding environment, with the ligand O1, O2 and N2 in equatorial positions [O1-In1-O2 = 116.9(1), O1-In1-N2 = 127.45(9), O2-In1-N2 = 106.4(1)°], and the ligand N1 and the methyl carbon atom (C1) in axial positions [C1-In1-N1 = 165.4(1)°]. The In-O bond distances [In1-O1 = 2.092(2), In1-O2 = 2.081(2) Å] and the In1-N1 bond distance [2.369(3) Å] are similar to those in 1, while the In1-N2 [2.344(3) Å] bond distance is shorter than
that of 1 [2.403(3) Å]. This is presumably the result of the stronger electron donor ability of the pyridine nitrogen atom versus that of the tertiary amine group of 1.

The structure of 3 (Figure 2) shows the indium centre being chelated by one tridentate NO$_2$ ligand. Intermolecular In…O contacts involving one oxygen atom of the ligand results in a five coordinate O$_2$N$_2$C bonding environment for indium and a dimeric structure in the solid-state. The indium centre is in a distorted square pyramidal bonding environment, with the methyl carbon in the apical position and the two oxygen atoms and two nitrogen atoms of the abt ligand and the bridging oxygen atom in the basal positions [C1-In1-O1 = 99.86(6), C1-In1-O2 = 120.64(6), C1-In1-N1 = 111.62(6), C1-In1-O1$^*$ = 118.35(6)$^\circ$]. The In-O bond distance to the bridging oxygen atom [In1-O1 = 2.241(1) Å] is significantly longer than the In-O bond distance to the non-bridging oxygen [In1-O2 = 2.083(1) Å], as well as the intermolecular In…O contact to the neighbouring monomer [In1-O1$^*$ = 2.195(1) Å]. The In1-N1 [2.357(1) Å] and In1-C1 [2.141(2) Å] bond distances are similar to that observed for 1 and 2.

The structure of 4 (Figure 3) shows a tetradentate ONNO ligand and a five coordinate O$_2$N$_2$C bonding environment for indium. The In-O bond distances are similar [In1-O1 = 2.085(2), In1-O2 = 2.081(2) Å], while the In-N bond distances differ slightly [In1-N1 = 2.232(3), In1-N2 = 2.253(2) Å]. The indium centre is in a distorted square pyramidal bonding environment, with the methyl carbon in the apical position and the two oxygen atoms and two nitrogen atoms of the Ph-salen ligand in the basal positions [C1-In1-O1 = 113.7(1), C1-In1-O2 = 115.4(1), C1-In1-N1 = 113.3(1), C1-In1-N2 = 108.9(1)$^\circ$].

The structure of 5 (Figure 4) shows a tetradentate ONNO ligand and a five coordinate O$_2$N$_2$C bonding environment for indium. The In1-O2 bond distance [2.098(2) Å] is slightly larger than that of In1-O1 [2.059(1) Å], while the In1-N1 bond distance [2.420(2) Å] is significantly
larger than that of In1- N2 [2.293(2) Å]. This is a result of the distorted trigonal bipyramidal bonding environment at the indium centre, in which the ligand O2 and N1 atoms are in axial positions [N1-In1-O2 = 150.02(6)], and the methyl carbon atom (C1) and the ligand O1 and N2 atoms are in equatorial positions [C1-In1-O1 = 122.32(8), C1-In1-N2 = 116.0(1), O1-In1-N2 = 120.32(7)°]. The difference in the geometries at indium in 4 and 5 is presumably a result of the great flexibility of the ethyl backbone of the Et-salan versus Ph-salen ligand.

The structures of [Me2In(Cy-ip)] (6) (Figure 5) and [Me2In(Mes-ip)] (7) (Figure S2) are similar and show a bidentate NO iminophenolate ligand and a four coordinate ONC2 bonding environment for indium. The resulting geometry at indium is very distorted tetrahedral due to the acute bite angle of the iminophenolate ligand [6: N1-In1-O1 = 86.59(7); 7: N1-In1-O1 = 84.3(1)°].

2.3 Structural comparisons to aluminum analogues

The solid-state structures of 1, 2 and 4-7 are similar to those reported for the corresponding aluminum complexes or similar derivatives [19,20,21,22,23,24]. The formation of intermolecular In…O contacts and dimerization in 3 is presumably a result of the absence of a fourth donor atom for the aminobis(phenolate) ligand and the large atomic radius of indium. The latter is supported by the observed monomeric solid-state structures and distorted tetrahedral metal bonding environments for methylaluminum aminobis(phenolate) compounds 8 and 9 [20]. The replacement of an In-N bond in 1-2 with an In…O contact in 3 significantly distorts the geometry at indium from an ideal trigonal bipyramid [C1-In1-N1 = 111.62(6), O1-In1-O2 = 138.90(5), O1-In1-O1* = 69.71(5), O2-In1-O1* = 84.05(4)].
Dimerization is not observed for compounds 6 and 7, which, like 3, possess four coordinate indium centres and a non-crowded coordination sphere. However, dimerization is observed in the dimethylindium iminophenolate 10, yielding a five coordinate distorted trigonal bipyramidal coordination environment for indium [25]. This suggests that subtle changes in the steric bulk of pendent imine substituent and/or the addition of substituents to the phenolate ring affect intermolecular bonding in these compounds. Dimerization is not observed in the aluminum analogue 11 [25].

2.3 DFT Computational Studies

DFT calculations were performed to provide insight into the preference for the observed dimeric (d) and monomeric (m) solid-state structures in 3 and 6/7, respectively, and similar aluminum compounds. The energies associated with the dimerization ($E_{\text{dimerization}}$) may be calculated using Equations (1) or (2) for dimethylindium/aluminum iminophenolate and methylindium/aluminum aminobis(phenolate) compounds, respectively.

\[
\begin{align*}
2 \text{Me}_2\text{M(ip)} & \rightarrow [\text{Me}_2\text{M(ip)}]_2 & (1) & \text{M} = \text{Al, In} \\
2 \text{MeM(abp)} & \rightarrow [\text{MeM(abp)}]_2 & (2)
\end{align*}
\]

Calculated parameters for geometry optimized structures are given in Tables S1-S7. Representative structures are shown in Figure 6. Results from equations 1 and 2 are reported in Table 1.

For dimethylindium iminophenolate compounds $[\text{Me}_2\text{In(ip)}]_n$, the negative $E_{\text{dimerization}}$ value calculated for the unsubstituted iminophenolate derivative ($R = \text{H}, R' = \text{Ph}$; -41 kJ mol$^{-1}$)
indicates that dimerization is thermodynamically favourable in the gas phase. Increasing steric bulk at the pendant imine group (R = H, R’ = Mes) leads to no significant difference in $E_{\text{dimerization}}$ (-43 kJ mol$^{-1}$). However, substitution of a methyl group in the 5-position of the phenolate ring (R = Me, R’ = Ph) precludes geometry optimization of the dimeric structure (In…O = 4.51 Å; sum of van der Waals radii = 3.93 Å) [26], indicating that substitution in this position has a more significant effect on crowding at the metal centre. For corresponding aluminum compounds [Me$_2$Al(ip)]$_n$, the Al…O bond distance (3.86 Å) for the dimeric structure (n = 2) is larger than the sum of the van der Waals radii (3.75 Å) [26] suggesting no preference for dimerization. These results are in accordance with the observed monomeric structures of 6 and 7, which possess bulky tBu groups in the 5-position of the phenolate ring, and the unsubstituted dimethylaluminum phenyliminophenolate 11 [23,24,25].

The unsubstituted methylindium amino(bisphenolate) [MeIn(abp)]$_n$ (R, R’ = H) shows a large negative $E_{\text{dimerization}}$ (-155 kJ mol$^{-1}$), greater than that observed for [Me$_2$In(ip)]$_n$ (R = H, R’ = Ph). This suggests a stronger preference for dimerization in these compounds. As for the iminophenolate compounds, adding substituents in the 5-position of the phenolate ring decreases preference for dimerization. However, dimeric structures are still energetically favourable for R = Me (-145 kJ mol$^{-1}$) and R = tBu (-81 kJ mol$^{-1}$). The corresponding aluminum complex [MeAl(abp)]$_n$ (R = H) also shows a negative $E_d$ (-46 kJ mol$^{-1}$) Although, a dimeric structure is energetically favourable for R = Me (-22 kJ mol$^{-1}$), it is not for R = tBu (+77 kJ mol$^{-1}$). These results are in accordance with the observed dimeric indium (3) and monomeric aluminum (8) [20] solid-state structures. It is worth noting that the M…O bond distances in [MeM(abp)]$_2$ (R = H, Me, or tBu) does not increase with increased steric bulk despite the decreasing $E_{\text{dimerization}}$. 
2.5 Reaction of 2 and 5 as initiators for formation of cyclic- and polycarbonates

Carbon dioxide (CO₂) is a desirable C₁ feedstock due to its high abundance, low toxicity and low cost [27]. The use of highly reactive substrates such as epoxides to yield polycarbonates and cyclic carbonates allows high thermodynamic barriers associated with incorporating carbon dioxide into commercially viable chemicals to be overcome. However, the viability of the polymerization process is limited by catalyst activity and scope. The recent report of active indium-phosphasalen catalysts at atmospheric CO₂ pressures, for the controlled ring-opening co-polymerization of epoxides and carbon dioxide suggests potential for indium-based systems [9]. This is further supported by the use of InBr₃-Ph₃P and indium-porphyrin as catalysts for cyclic carbonate production from CO₂ and epoxides, though there are very few such studies reported in the literature [28].

Based on the reported reactivity of similar trivalent transition metal aminobis(phenolate) and salan compounds [29], compounds 2 and 5 were chosen for preliminary screening as catalysts for the formation of cyclic- or polycarbonates from CO₂ and epoxides. The formation of propylene carbonate from neat propylene oxide (PO) and CO₂ was carried out at 20 bar CO₂ at 100 °C for 24 h at a catalyst loading of 0.025 mol% indium and a bis(triphenylphosphine)iminium chloride (PPNCl) nucleophile cocatalyst (Table 2). After 24 h each reaction had reached >90% conversion. Further, the formation of poly(cyclohexane carbonate) from neat cyclohexene oxide (CHO) and CO₂ was carried out at 40 bar CO₂ at 60 °C for 24 h at a catalyst loading of 0.2 mol% indium and PPNCl cocatalyst (Table 3). After 24 h each reaction had reached ~70% conversion with >99% selectivity towards perfectly alternating polycyclohexene carbonate, and there was no evidence of formation of polyether or either the cis- or trans- cyclic byproduct. The obtained molecular
weights showed unimodal distributions with very well controlled with dispersities of 1.08 and 1.09, respectively. These indium catalysts have greater selectivity for carbonate linkages versus previously reported methyl- and chloroaluminum aminophenolate complexes, which sometimes afford mixtures of polycarbonate/polyether or cyclic carbonate depending on the specific aluminum catalyst or addition of cocatalyst [3c.d]. Selectivity is comparable to that of the 3-nitro-5-tert-butyl substituted (salen)AlCl complex in the presence of a Bu₄NN₃ cocatalyst, the most active of a series of (salen)AlX (X = Cl, Me) catalysts reported by Darensbourg, and superior to the corresponding 3,5-di-tert-butyl substituted analogues, which afford only cyclic carbonate in the presence of PPNCl cocatalyst [3d]. Finally, selectivity is comparable to previously reported phosophasalen indium complexes [9].

3. Conclusions

The hydrocarbon elimination reaction of trimethylindium and amino-/iminophenols is a high yield route to methylindium amino-/iminophenolate complexes. Solid-state structures of methylindium aminobis(phenolate) (1 and 2), salen (4) and salan (5) complexes and dimethylindium iminophenolates complexes (6 and 7) are similar to those observed for corresponding aluminum compounds. The indium isopropylaminobis(phenolate) (3) possesses a dimeric structure in contrast to similar aluminum compounds. Computational studies show that the dimerization is much more energetically favourable for indium versus aluminum complexes, though dimerization of aluminum compounds is also favourable in the absence of significant steric bulk on the phenolate rings. For iminophenolate complexes [Me₂M(ip)], addition of steric bulk at
the 5-position of the phenolate ring creates more crowing at the metal centre versus addition of bulkier imino-substituents. Preliminary studies show that compounds 2 and 5 are effective catalysts for the formation of propylene carbonate from PO and CO₂ and the formation of polycyclohexene carbonate from CHO and CO₂. In the latter case, >99% selectivity towards perfectly alternating polycyclohexene carbonate was observed, and there was no evidence of formation of polyether or either the cis- or trans- cyclic byproduct. This is comparable to previously reported indium phosphasalen catalysts and nitro-substituted salen aluminum complexes. This work provides insight into controlling intermolecular bonding and hence reactivity in indium and aluminum amino- / iminophenolate complexes, and represent one of the first examples of indium complexes as catalysts for the formation of cyclic- or polycarbonates from CO₂ and epoxides.

4. Experimental

4.1 General Considerations

Solution ¹H and ¹³C{¹H} spectra were recorded at 23°C on either a JEOL ECS-400 MHz + spectrometer (400 and 100 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 Guelph Chemical Laboratories, Guelph, Ontario, Canada. All coupling reactions were carried out in a 100 mL stainless-steel autoclave reactor (Parr Instrument Company) equipped with a motorized mechanical stirrer and a heating mantle. For the epoxide/carbon dioxide reactions, the pressure vessel was additionally equipped with a silicon ATR sensor (SiComp Sentinel) connected to a ReactIR 15 base unit (Mettler-Toledo) via a DS silver-halide Fiber-to-Sentinel conduit. Gel permeation chromatography (GPC) analysis was performed on a setup consisting of a miniDawn TREOS light-scattering detector, a Viscostar-II viscometer, and an Optilab T-rEX differential refractive index detector (Wyatt Technology) connected to an Agilent Infinity 1260 HPLC system equipped with two Phenogel 10 Å 300 × 4.60 mm columns with THF as eluent. Samples were prepared in THF at a concentration of 4 mg mL⁻¹, filtered through a 0.2 μm syringe filter, and analyzed at a flow rate of 0.3 mL min⁻¹ at 25 °C.

2,4-di-tert-butylphenol 99%, N,N-diethylethylenediamine ≥99%, paraformaldehyde 95%, 2-picolyamine 99%, isopropylamine 99%, 3,5-di-tert-butyl-2-hydroxybenzaldehyde 99%, o-phenylendiamine 99.5%, N,N'-dimethylethylenediamine 98%, cyclohexylamine ≥99.9% and 2,4,6-trimethylaniline 98% were used as received from Sigma-Aldrich. Trimethylindium 98+% was used as received from Strem. Propylene oxide, cyclohexene oxide and bis(triphenylphosphine)iminium chloride (PPNCl) were purchased from Alfa Aesar. Molecular sieves and sodium metal were added to toluene anhydrous 99.8%, hexanes anhydrous 95% and diethyl ether anhydrous ≥99% received from Sigma Aldrich. 36% formaldehyde solution was prepared by dissolving paraformaldehyde in distilled water with heat and stirring, H₂(Et₂CH₂CH₂-abp), H₂(Py-abp), H₂(iPr-abp) [30], H₂(Ph-salen) [31], H₂(Et-salan) [20], H(Cy-ip) [32] and H(Mes-ip) [33] were synthesized using modified literature procedures. All reactions were
performed under an atmosphere of inert dinitrogen using standard Schlenk techniques unless otherwise indicated. The epoxides were distilled from CaH$_2$ under N$_2$.

4.2 Preparation of $[\text{MeIn}(\text{Et}_2\text{NCH}_2\text{CH}_2\text{-abp})]$ (1)

H$_2$(Et$_2$NCH$_2$CH$_2$-abp) (0.325 g, 0.588 mmol) in diethyl ether (3 mL) was added dropwise to a solution of InMe$_3$ (0.094 g, 0.588 mmol) in diethyl ether (1 mL). The solution was stirred for 3 h at 23°C yielding a clear colorless solution. The solution was concentrated to 2 mL and allowed to sit at 23°C. After 18 h, colourless crystals of 1 were collected by filtration (0.339 g, 0.498 mmol, 85%). Anal. Calc. for C$_{37}$H$_{61}$InN$_2$O$_2$: C, 65.28; H, 9.03; N, 4.12. Found: C, 65.54; H, 9.05; N, 4.18. Mp = 219-222 °C. FT-IR (cm$^{-1}$): 2951br, 1601w, 1476s, 1468s, 1441s, 1412m, 1360m, 1302s, 1278m, 1240m, 1166m, 1128w, 1097w, 1072w, 1054w, 1006w, 912w, 875m, 833w, 809w, 726w, 686w. FT-Raman (cm$^{-1}$): 2945s, 2902s, 1601m, 1451m, 1301m, 1199m, 1097w, 926w, 835w, 809w, 612w, 558w, 504s v(In-Me), 482w, 220m, 174s, 134s. $^1$H NMR (CDCl$_3$, ppm): $\delta$ = 0.112 (s, 3H, InCH$_3$), 1.11 (t, $J$ = 7.0 Hz, 6H, CH$_3$), 1.25 (s, 18H, C(CH$_3$)$_3$), 1.40 (s, 18H, C(CH$_3$)$_3$), 2.59-2.83 (m, 8H, CH$_2$), 3.75 (s, 4H, CH$_2$), 6.80 (d, $J$ = 2.4 Hz, 2H, Ar-H), 7.19 (d, $J$ = 2.4 Hz, 2H, Ar-H). $^{13}$C($^1$H) NMR (CDCl$_3$, ppm): 9.4 (CH$_2$CH$_3$), 29.6 (C(CH$_3$)$_3$), 31.8 (C(CH$_3$)$_3$), 33.9 (C(CH$_3$)$_3$), 35.1 (C(CH$_3$)$_3$), 43.3 (CH$_2$CH$_3$), 47.4 (CH$_2$), 50.9 (CH$_2$), 61.3 (ArCH$_2$), 120.5 (Ar-C), 124.1 (Ar-C), 125.3 (Ar-C), 136.5 (Ar-C), 138.0 (Ar-C), 160.9 (Ar-C).

4.3 Preparation of $[\text{MeIn}(\text{PyCH}_2\text{-abp})]$ (2)
H₂(PyCH₂-abp) (0.324 g, 0.595 mmol) in diethyl ether (5 mL) was added dropwise to a solution of InMe₃ (0.095 g, 0.595 mmol) in diethyl ether (1 mL). The solution was stirred for 3 h at 23°C yielding a clear colorless solution. The solution was concentrated to 3 mL and allowed to sit at 23°C. After 18 h, colourless crystals of 2 were collected by filtration (0.135 g, 0.201 mmol, 34%). Anal. Calc. for C₃₇H₅₃InN₂O₂: C, 66.07; H, 7.94; N, 4.16. Found: C, 66.19; H, 8.05; N, 4.28. Mp = 196-198°C. FT-IR (cm⁻¹): 2950br, 1604m, 1478s, 1468s, 1462s, 1440s, 1413m, 1390m, 1359m, 1304m, 1249m, 1237s, 1202m, 1165m, 1132w, 1095w, 1053w, 1016w, 970w, 928w, 877m, 869m, 830w. FT-Raman (cm⁻¹): 3070w, 2949s, 2923s, 1603w, 1447w, 1304w, 1249w, 1200w, 1133w, 1095w, 1054w, 1017w, 923w, 844w, 615w, 544m, 486m (In-Me), 173s, 144m, 137m. ¹H NMR (CDCl₃, ppm): δ = 0.31 (s, 3H, InCH₃), 1.24 (s, 18H, C(CH₃)₃), 1.41 (s, 18H, C(CH₃)₃), 3.72-3.93 (m, 4H, CH₂), 4.02 (s, 2H, CH₂), 6.80 (d, J = 2.6 Hz, 2H, Ar-H), 7.16 (d, J = 2.6 Hz, 2H, Ar-H), 7.20-7.35 (m, 2H, py-H), 7.79 (m, 1H, py-H), 8.36 (d, J = 4.8 Hz, 2H, py-H). ¹³C{¹H} NMR (CDCl₃, ppm): 15.3 (InCH₃), 29.7 (C(CH₃)), 31.8 (C(CH₃)), 33.9 (C(CH₃)), 35.0 (C(CH₃)), 59.9 (py-CH₂), 61.9 (Ar-CH₂), 121.2 (Ar-C), 123.6 (py-C), 124.1 (Ar-C), 124.2 (py-C), 125.4 (Ar-C), 136.7 (Ar-C), 138.3 (Ar-C), 140.1 (py-C), 147.4 (py-C), 154.6 (py-C), 161.2 (Ar-C).

4.4 Preparation of [MeIn(iPr-abp)]₂ (3)

H₂(iPr-abp) (0.311 g, 0.627 mmol) in toluene (3 mL) was added dropwise to a solution of InMe₃ (0.100 g, 0.627 mmol) in toluene (1 mL). The solution was stirred for 3 h at 23°C yielding a clear colorless solution. The clear solution was concentrated to about 1 mL, layered with hexanes (3 mL) and allowed to sit at 23°C. After 18 h, colourless crystals of 3 were collected by filtration.
(0.125 g, 0.196 mmol, 31%). Anal. Calc. for C_{77}H_{122}In_{2}N_{2}O_{4}: C, 66.66; H, 9.22; N, 2.10. Found: C, 67.21; H, 9.11; N, 2.26. Mp = 204-206 °C. FT-IR (cm⁻¹): 2954br, 1605w, 1478s, 1468s, 1442s, 1304m, 1251m, 1239m, 1223s, 1203m, 1166m, 1127m, 998w, 912w, 874m, 825w, 805w, 781w, 726m. FT-Raman (cm⁻¹): 2959s, 2920s, 1605m, 1468m, 1383w, 1306w, 1269w, 1203w, 1159w, 1135w, 924w, 833w, 670w, 619w, 550m, 506s ν(In-Me), 485w, 183s, 134s.

1H NMR (CDCl₃, ppm): δ = 0.34 (s, 3H, InC₃H₃), 1.38 (d, J = 6.8 Hz, 6H, C₃H₃), 1.26 (s, 18H, C(CH₃)₃), 1.41 (s, 18H, C(CH₃)₃), 3.41 (septet, J = 6.8 Hz, 1H, C₃H), 3.84 (s, 4H, C₂H), 6.85 (d, J = 2.2 Hz, 2H, Ar-H), 7.25 (d, J = 2.2 Hz, 2H, Ar-H). 13C{¹H} NMR (CDCl₃, ppm): 17.4 (CH(C₃H₂)), 29.7 (C(CH₃)), 31.7 (C(CH₃)), 34.0 (C(CH₃)), 35.2 (C(CH₃)), 52.5 (CH(CH₃)₂), 53.0 (Ar-CH₂), 121.1 (Ar-C), 124.8 (Ar-C), 126.0 (Ar-C), 138.5 (Ar-C), 139.0 (Ar-C), 160.2 (Ar-C).

4.5 Preparation of [MeIn(Ph-salen)] (4)

H₂(Ph-salen) (0.300 g, 0.555 mmol) in toluene (3 mL) was added drop-wise to a stirring solution of InMe₃ (0.080 g, 0.555 mmol) in toluene (1 mL). The solution was stirred for 3 h at 23°C yielding a slightly cloudy yellow-orange solution. The solvent was removed under vacuum and the product was redissolved in diethyl ether (4 mL). The solution was allowed to sit at 23°C. After 18 h, red crystals of 4 were collected by filtration (0.187 g, 0.243 mmol, 47%). Anal. Calc. for C₃₇H₄₉InN₂O₂: C, 66.47; H, 7.39; N, 4.19. Found: C, 66.62; H, 7.34; N, 3.95. Mp = 283-291°C. FT-IR (cm⁻¹): 2954br, 2866w, 1600s, 1579s [υ(C=N)], 1523s, 1461w, 1428m, 1385m, 1357w, 1322w, 1253m, 1193w, 1161s, 1133m, 1026w, 968w, 910w, 869w, 834w, 789m, 743s, 697w, 637w. FT-Raman (cm⁻¹): 2958w, 1602m, 1577s [υ(C=N)], 1525m, 1483m, 1458w, 1427s, 1410s, 1353m, 1291m, 1212m, 1166m, 1134w, 1050w, 584w, 516w, 498w υ(In-Me), 307w, 161w, 129m.
NMR data (CDCl₃, ppm). ¹H NMR: -0.27 (s, 3H, InCH₃), 1.32 (s, 18H, C(CH₃)), 1.51 (s, 18H, C(CH₃)), 7.01 (d, J = 2.6 Hz, 2H, Ar-H), 7.36-7.39 (m, 2H, Ar-H), 7.49 (d, J = 2.6 Hz, 2H, Ar-H), 7.55-7.58 (m, 2H, Ar-H), 8.56 (s, 2H, N=CH). ¹³C{¹H} NMR: 29.5 (C(CH₃)), 31.3 (C(CH₃)), 33.9 (C(CH₃)), 35.6 (C(CH₃)), 116.7 (Ar-C), 118.3 (Ar-C), 127.9 (Ar-C), 129.1 (Ar-C), 131.0 (Ar-C), 136.6 (Ar-C), 139.4 (Ar-C), 142.5 (Ar-C), 164.7 (Ar-C), 169.5 (C=NH).

4.6 Preparation of [MeIn(Et-salan)] (5)

H₂(Et-salan) (0.291 g, 0.560 mmol) in diethyl ether (3 mL) was added drop-wise to a stirring solution of InMe₃ (0.090 g, 0.560 mmol) in diethyl ether (1 mL). The solution was stirred for 3 h at 23°C yielding a slightly cloudy yellow solution. The reaction mixture was filtered and allowed to sit at 23°C. After 18 h, crystals of 5 were collected by filtration (0.236 g, 0.331 mmol, 59%). Anal. Calc. for C₃₅H₅₇InN₂O₂: C, 66.41; H, 8.80; N, 4.29. Found: C, 64.15; H, 9.05; N, 4.06. Mp = 261-263°C. FT-IR (cm⁻¹): 2952m, 2899w, 2864m, 1603w, 1465s, 1443m, 1412s, 1360w, 1319w, 1269s, 1245s, 1202m, 1166w, 1130w, 1090w, 1044w, 1028w, 997w, 921m, 880s, 829s, 808m, 779w, 737m, 692m. FT-Raman (cm⁻¹): 2957m, 2930m, 1605w, 1452w, 1307w, 1201w, 1162w, 1132w, 923w, 833w, 806w, 612w, 554w, 498m v(In-Me), 264w, 184m, 142s. NMR data (CDCl₃, ppm). ¹H NMR: -0.36 (s, 3H, InCH₃), 1.27 (s, 18H, C(CH₃)), 1.48 (s, 18H, C(CH₃)), 2.23 (s, 6H, NCH₃), 2.81 (m, 1H, NCH₂), 3.03 (d, J = 11.7 Hz, 1H, NCH₂), 3.17 (m, 1H, NCH₂), 4.74 (d, J = 11.7 Hz, 1H, NCH₂), 6.80 (d, J = 2.4 Hz, 2H, Ar-H), 7.25 (d, J = 2.4 Hz, 2H, Ar-H). ¹³C{¹H} NMR: 29.9 (C(CH₃)), 31.8 (C(CH₃)), 33.9 (C(CH₃)), 35.2 (C(CH₃)), 43.2 (NCH₃), 55.7 (NCH₂), 63.2 (ArCH₂), 121.5 (Ar-C), 124.2 (Ar-C), 125.1 (Ar-C), 136.4 (Ar-C), 139.0 (Ar-C), 161.5 (Ar-C).
4.7 Preparation of $[\text{Me}_2\text{In}($Cy-ip$)]$ (6)

H(Cy-ip) (0.274 g, 0.873 mmol) in diethyl ether (2 mL) was added dropwise to a solution of InMe$_3$ (0.139 g, 0.873 mmol) in diethyl ether (2 mL). The solution was stirred for 3 h at 23°C yielding a yellow solution. The reaction mixture was concentrated to 2 mL, which resulted in precipitation of a crystalline product. Yellow crystals of 6 were collected by filtration (0.216 g, 0.471 mmol, 54%). Anal. Calc. for C$_{23}$H$_{38}$InNO: C, 60.14; H, 8.34; N, 3.05. Found: C, 59.86; H, 8.18; N, 3.30. Mp = 149-152°C. FT-IR (cm$^{-1}$): 2946m, 2922m, 2852m, 1611s [(C=N)], 1532m, 1419m, 1361w, 1255m, 1176s, 1075s, 838w, 785m, 717m. FT-Raman (cm$^{-1}$): 2945m, 2924m, 2854w, 1611s [(C=N)], 1533m, 1460m, 1349w, 1156w, 919w, 797w, 631w, 552w, 521w, 488s [w$_{\text{sym}}$ (Me-In-Me)], 210m, 127s. $^1$H NMR (CDCl$_3$, ppm): $\delta = -0.13$ (s, 6H, InC$_3$H$_3$), 1.19–1.89 (m, 10H, Cy-H) 1.28 (s, 9H, C(CH$_3$)$_3$), 1.40 (s, 9H, C(CH$_3$)$_3$), 3.24 (m, 1H, Cy-H), 6.85 (d, $J = 2.4$ Hz, 1H, Ar-H), 7.41 (d, $J = 2.4$ Hz, 1H, Ar-H), 8.06 (s, 1H, N=CH). $^{13}$C($^1$H) NMR (CDCl$_3$, ppm): -5.3 (InCH$_3$), 21.5 (C$_6$H$_{11}$), 25.1 (C$_6$H$_{11}$), 29.4 (C(CH$_3$)$_3$), 31.4 (C(CH$_3$)$_3$), 33.8 (C(CH$_3$)$_3$), 34.9 (C$_6$H$_{11}$), 35.4 (C(CH$_3$)$_3$), 71.0 (C$_6$H$_{11}$), 117.9 (Ar-C), 125.3 (Ar-C), 129.9 (Ar-C), 135.6 (Ar-C), 141.3 (Ar-C), 166.9 (Ar-C), 169.6 (CH=N).

4.8 Preparation of $[\text{Me}_2\text{In}(\text{Mes-ip})]$ (7)

H(Mes-ip) (0.285 g, 0.807 mmol) in toluene (2 mL) was added dropwise to InMe$_3$ (0.130 g, 0.807 mmol) in toluene (2 mL), where bubbling occurred. The solution was stirred for 3 h at 23°C yielding a yellow solution. The reaction mixture was concentrated to 2 mL and stored at
15°C. After 48 h, yellow crystals of 7 were collected by filtration (0.192 g, 0.388 mmol, 48%).

Anal. Calc. for C$_2$H$_{38}$InNO: C, 63.04; H, 7.73; N, 2.83. Found: C, 62.78; H, 7.55; N, 3.07. Mp = 131-134°C. FT-IR (cm$^{-1}$): 2948 br, 1612 m, 1597 s [$\nu$(C=N)], 1526 s, 1459 w, 1425 m, 1382 m, 1323 m, 1238 m, 1160 m, 1132 s, 1032 w, 980 m, 848 w, 786 w, 718 m. FT-Raman (cm$^{-1}$): 2922 m, 1598 s [$\nu$(C=N)], 1528 m, 1459 m, 1426 s, 1343 w, 1209 w, 1158 w, 1133 m, 576 w, 524 w, 484 s [sym (Me-In-Me)], 192 w, 153 m, 134 m. $^1$H NMR (CDCl$_3$, ppm): $\delta$ = -0.13 (s, 6H, InCH$_3$), 1.28 (s, 9H, C(CH$_3$)$_3$), 1.43 (s, 9H, C(CH$_3$)$_3$), 2.19 (s, 6H, CH$_3$), 2.30 (s, 3H, CH$_3$), 6.84 (d, $J$ = 2.6 Hz, 1H, Ar-H), 6.93 (s, 2H, Ar-H), 7.49 (d, $J$ = 2.6 Hz, 1H, Ar-H), 7.87 (s, 1H, N=C=H). $^{13}$C [$^1$H] NMR (CDCl$_3$, ppm): -5.5 (InCH$_3$), 18.5 (CH$_3$), 20.8 (CH$_3$), 29.4 (C(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$), 33.8 (C(CH$_3$)$_3$), 35.5 (C(CH$_3$)$_3$), 117.9 (Ar-C), 125.3 (Ar-C), 129.0 (Ar-C), 129.3 (Ar-C), 130.3 (Ar-C), 131.1 (Ar-C), 135.6 (Ar-C), 141.8 (Ar-C), 145.5 (Ar-C), 167.7 (Ar-C), 173.8 (CH=N).

4.9 Catalysis Experiments

For all reactions, appropriate amounts of PPNCl and the corresponding indium complex were combined in 3 mL of dichloromethane in the glovebox. This solution was injected into the pressure vessel and solvent removed under vacuum. The appropriate amount of epoxide was then injected, the vessel was pressurized CO$_2$ and heated to the desired temperature for 24 h with mechanical stirring. In the case of polymer formation, the crude product was dissolved in dichloromethane and precipitated in cold acidified methanol.

4.9 X-ray crystallography
Crystals of compounds 1-7 were mounted from Paratone-N oil on a MiTeGen MicroMount. The data were collected on a Bruker APEX II charge-coupled-device (CCD) diffractometer, with an Oxford 700 Cryocool sample cooling device. The instrument was equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å; 30 mA, 50 mV), with MonoCap X-ray source optics. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 5 second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). Data collection, unit cell refinement, data processing and multi-scan absorption correction were applied using the APEX2 [34] or APEX3 [35] software packages. The structures were solved using SHELXT [36] and all non-hydrogen atoms were refined anisotropically with SHELXL [37] using a combination of shelXle [38] and OLEX2 [39] graphical user interfaces. Unless otherwise noted, all hydrogen atom positions were idealized and ride on the atom to which they were attached. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. For compound 2, the crystal was found to be a non-merohedral twin. The two components refined to a 62:38 ratio. Details of crystal data, data collection, and structure refinement are listed in Table 4. All figures were generated using Diamond software [40].

4.10 Computational methods

DFT calculations were performed using Gaussian 09 at the B3LYP 6-31G* level of theory for all atoms except In, for which Stuttgart electron core pseudo-potentials (sdd) were employed [41]. All structures were geometry optimized and structural parameters for input files were derived from crystal structure data where possible. Frequency calculations were performed on all structures and gave no imaginary frequencies.
Acknowledgements

We thank the following: Dr. Fran Kerton and Dr. Chris Kozak (Memorial University of Newfoundland) for reactivity studies; Dan Durant for assistance in collecting solution NMR data; and the Natural Sciences and Engineering Research Council of Canada (RGPIN-2019-05965), the New Brunswick Innovation Foundation, the Canadian Foundation for Innovation (project No. 9211), Saint Mary’s University and Mount Allison University for financial support. A NSERC Vanier Canada Graduate Scholarship supports K.A.A.

Appendix A. Supplementary data

X-ray crystal structures of 2 and 7. Selected bond distances and angles for DFT geometry optimized structures. CCDC deposition numbers 1989068-1989074 contain the supplementary crystallographic data for 1-7. 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.
8, R = Me
9, R = Pr

10

11
Figure 1. X-ray crystal structure of 1 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): In1-C1 = 2.148(4), In1-O1 = 2.080(3), In1-O2 = 2.080(3), In1-N1 = 2.357(3), In1-N2 = 2.403(3), C1-In1-N1 = 169.2(1), O1-In1-O2 = 115.1(1), O1-In1-N2 = 116.3(1), O2-In1-N2 = 122.1(1).
Figure 2. X-ray crystal structure of 3 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Symmetry transformations used to generate equivalent atoms: (*) 1-x, -y, ½-z.

Selected bond distances (Å) and angles (deg): In1-C1 = 2.141(2), In1-O1 = 2.241(1), In1-O2 = 2.083(1), In1-O1* = 2.195(1), In1-N1 = 2.357(1), C1-In1-O1 = 99.86(6), C1-In1-O2 = 120.64(6), C1-In1-N1 = 111.62(6), C1-In1-O1* = 118.35(6)°.
Figure 3. X-ray crystal structure of 4 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): In1-C1 = 2.122(4), In1-O1 = 2.085(2), In1-O2 = 2.081(2), In1-N1 = 2.232(3), In1- N2 = 2.253(2), C1-In1-O1 = 113.7(1), C1-In1-O2 = 115.4(1), C1-In1-N1 = 113.3(1), C1-In1-N2 = 108.9(1).
Figure 4. X-ray crystal structure of 5 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): In1-C1 = 2.143(3), In1-O1 = 2.059(1), In1-O2 = 2.098(2), In1-N1 = 2.420(2), In1-N2 = 2.293(2), N1-In1-O2 = 150.02(6), C1-In1-O1 = 122.32(8), C1-In1-N2 = 116.0(1), O1-In1-N2 = 120.32(7).
Figure 5. X-ray crystal structure of 6 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): In1-C1 = 2.142(3), In1-C2 = 2.145(2), In1-O1 = 2.096(2), In1-N1 = 2.232(2), C1-In1-C2 = 132.31(9), N1-In1-O1 = 86.59(7).
Figure 6. Geometry optimized structures of $[\text{Me}_2\text{In(ip)}]_n$ and $[\text{MeIn(abp)}]_n$ ($n = 1, 2$). Hydrogen atoms are not shown for clarity.
Table 1. Calculated energies $E$ (kJ mol$^{-1}$) for geometry optimized $[\text{Me}_2\text{M(ip)}]_n$ and $[\text{MeM(abp)}]_n$ ($n = 1, 2$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>M</th>
<th>R</th>
<th>R'</th>
<th>$E_m$ (n = 1)</th>
<th>$E_d$ (n = 2)</th>
<th>$E_{\text{dimerization}}$ (Ed - 2Em)</th>
<th>M…O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Me}_2\text{M(ip)}]_n$</td>
<td>In</td>
<td>H</td>
<td>Ph</td>
<td>-1 871 647</td>
<td>-3 743 335</td>
<td>-41</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>H</td>
<td>Mes</td>
<td>-2 077 943</td>
<td>-4 155 929</td>
<td>-43</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>Me</td>
<td>Ph</td>
<td>-1 974 804</td>
<td>-3 949 609</td>
<td>-1</td>
<td>4.51</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>H</td>
<td>Ph</td>
<td>-2 503 299</td>
<td>-5 006 603</td>
<td>-5</td>
<td>3.86</td>
</tr>
<tr>
<td>$[\text{MeM(abp)}]_n$</td>
<td>In</td>
<td>H</td>
<td></td>
<td>-2 172 302</td>
<td>-4 344 759</td>
<td>-155</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>Me</td>
<td></td>
<td>-2 378 614</td>
<td>-4 757 373</td>
<td>-145</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>tBu</td>
<td></td>
<td>-2 997 422</td>
<td>-5 994 925</td>
<td>-81</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>H</td>
<td></td>
<td>-2 804 007</td>
<td>-5 608 060</td>
<td>-46</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>Me</td>
<td></td>
<td>-3 010 321</td>
<td>-6 020 664</td>
<td>-22</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>tBu</td>
<td></td>
<td>-3 629 129</td>
<td>-7 258 181</td>
<td>+77</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Table 2. Formation of propylene carbonate from carbon dioxide and propylene oxide using 2 and 5.

![Reaction mechanism diagram]

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Complex</th>
<th>% Conversion&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>&gt;99 %</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>90</td>
</tr>
</tbody>
</table>

<sup>a</sup>General reaction conditions: PO (3.00 g, 51.7 mmol), PPNCl (0.051 mmol), catalyst, 0.025 mol% (0.013 mmol), 100 °C, 20 bar CO<sub>2</sub>, 24 h. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy using the normalized integrals of the methylene resonances.
Table 3. Formation of poly(cyclohexane carbonate) from carbon dioxide and cyclohexene oxide using 2 and 5.

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion</th>
<th>% CO₃</th>
<th>$M_n$ (g mol⁻¹)</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>73</td>
<td>&gt;99</td>
<td>5 260</td>
<td>1.08</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>71</td>
<td>&gt;99</td>
<td>7 940</td>
<td>1.09</td>
</tr>
</tbody>
</table>

---

aGeneral reaction conditions: CHO (2.50 g, 25.5 mmol), PPNCl (0.510 mmol), catalyst, 0.5 mol% (0.510 mmol), 60 °C, 40 bar CO₂, 24 h. bDetermined by ¹H NMR spectroscopy using the normalized integrals of the methylene resonances. cPercent carbonate = (copolymer carbonate linkages)/(copolymer + ether linkages). d$D$, dispersity = $M_w/M_n$. Determined in THF by GPC equipped with a multiangle light-scattering detector.
Table 4. Crystallographic Data for 1-7.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{37}$H$</em>{61}$InN$_2$O$_2$</td>
<td>C$<em>{37}$H$</em>{53}$InN$_2$O$_2$</td>
<td>C$<em>{68}$H$</em>{108}$In$_2$N$_2$O$_4$·C$<em>6$H$</em>{14}$</td>
<td>C$<em>{37}$H$</em>{49}$InN$_2$O$_2$</td>
<td>C$<em>{35}$H$</em>{57}$InN$_2$O$_2$</td>
<td>C$<em>{23}$H$</em>{38}$InNO</td>
<td>C$<em>{26}$H$</em>{38}$InNO</td>
</tr>
<tr>
<td>fw</td>
<td>680.69</td>
<td>672.63</td>
<td>1333.37</td>
<td>668.60</td>
<td>652.64</td>
<td>459.36</td>
<td>495.39</td>
</tr>
<tr>
<td>crystal system</td>
<td>Orthorhombic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>Triclinic</td>
<td>Trigonal</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>Pca$_2_1$</td>
<td>C2/c</td>
<td>C2/c</td>
<td>P-1</td>
<td>R-3</td>
<td>P2$_1$/n</td>
<td>P2$_1$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>28.748(3)</td>
<td>33.576(3)</td>
<td>30.550(4)</td>
<td>9.8481(2)</td>
<td>30.495(3)</td>
<td>11.8446(9)</td>
<td>12.341(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.818(1)</td>
<td>8.9410(9)</td>
<td>9.528(1)</td>
<td>12.5610(3)</td>
<td>30.495(3)</td>
<td>9.1537(7)</td>
<td>8.688(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.445(1)</td>
<td>23.063(2)</td>
<td>26.037(3)</td>
<td>15.1097(3)</td>
<td>22.368(2)</td>
<td>21.436(2)</td>
<td>12.874(3)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>87.005(1)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>90</td>
<td>93.219(2)</td>
<td>110.285(1)</td>
<td>79.765(1)</td>
<td>90</td>
<td>91.748(1)</td>
<td>113.828(2)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>67.543(1)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>3559.2(7)</td>
<td>6913(1)</td>
<td>7109(2)</td>
<td>1699.62(6)</td>
<td>18014(3)</td>
<td>2323.0(3)</td>
<td>1262.6(4)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>18</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>18</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>F(000)</td>
<td>1448</td>
<td>2832</td>
<td>2840</td>
<td>700</td>
<td>6228</td>
<td>960</td>
<td>516</td>
</tr>
<tr>
<td>(\rho_{\text{calcd}, \text{g cm}^{-3}})</td>
<td>1.270</td>
<td>1.293</td>
<td>1.246</td>
<td>1.306</td>
<td>1.083</td>
<td>1.313</td>
<td>1.303</td>
</tr>
<tr>
<td>(\mu, \text{mm}^{-1})</td>
<td>0.697</td>
<td>0.717</td>
<td>0.695</td>
<td>0.728</td>
<td>0.617</td>
<td>1.028</td>
<td>0.951</td>
</tr>
<tr>
<td>(T, \text{K})</td>
<td>125(2)</td>
<td>125(2)</td>
<td>125(2)</td>
<td>125(2)</td>
<td>125(2)</td>
<td>421(2)</td>
<td>125(2)</td>
</tr>
<tr>
<td>(\lambda, \text{Å})</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>(R_1)^{a}</td>
<td>0.0345</td>
<td>0.0398</td>
<td>0.0250</td>
<td>0.0464</td>
<td>0.0369</td>
<td>0.0317</td>
<td>0.0383</td>
</tr>
<tr>
<td>(wR_2)^{b}</td>
<td>0.0750</td>
<td>0.1025</td>
<td>0.0619</td>
<td>0.0872</td>
<td>0.0837</td>
<td>0.0662</td>
<td>0.0651</td>
</tr>
</tbody>
</table>

^{a} R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|} \text{ for } [F_o^2 > 2\sigma(F_o^2)].

^{b} \text{ wR}_2 = \left\{\frac{\Sigma w(F_o^2-F_c^2)^2}{\Sigma w(F_o^4)}\right\}^{1/2}.
References


Supplementary material for

Synthesis and Structural Characterization of Methylindium
Imino/Aminophenolates: Comparison to Aluminum Analogues and Reactivity
Toward the Coupling Reactions of Carbon Dioxide with Epoxides

Kori A. Andrea\textsuperscript{a}, Adam R. Beckett\textsuperscript{b}, Glen G. Briand\textsuperscript{b}\textsuperscript{*}, Sarah A. Martell\textsuperscript{b}, Jason
Masuda\textsuperscript{c}, Kathleen M. Morrison\textsuperscript{b} and Emilie M.T. Yammine\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, Memorial University of Newfoundland,
St. John’s, Newfoundland and Labrador, Canada  A1B 3X7
\textsuperscript{b}Department of Chemistry and Biochemistry, Mount Allison University,
Sackville, New Brunswick, Canada  E4L 1G8
\textsuperscript{c}Department of Chemistry, Saint Mary’s University, Halifax Nova Scotia, Canada  BH3 C3C

Page
S3  \textbf{Figure S1.} X-ray structure of 2.
S4  \textbf{Figure S2.} X-ray structure of 7.
S5  \textbf{Table S1.} Selected bond distances (Å) and angles (°) for the X-ray crystal
structure of 7 and DFT calculated values for geometry optimized
[Me\textsubscript{2}In(ip)].
S6  \textbf{Table S2.} Selected bond distances (Å) and angles (°) for the X-ray crystal
structure of 10 and DFT calculated values for geometry optimized
[Me\textsubscript{2}In(ip)]\textsubscript{2}.
Table S3. Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 11 and DFT calculated values for geometry optimized [Me$_2$Al(ip)]$_n$ (n = 1, 2).

Table S4. Selected DFT calculated bond distances (Å) and angles (°) for geometry optimized [MeIn(abp)].

Table S5. Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 3 and DFT calculated values for geometry optimized [MeIn(abp)].

Table S6. Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 8 and DFT calculated values for geometry optimized [MeAl(abp)].

Table S7. Selected DFT calculated bond distances (Å) and angles (°) for geometry optimized [MeAl(abp)].
Figure S1. X-ray crystal structure of 2 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): In1-C1 = 2.150(4), In1-O1 = 2.092(2), In1-O2 = 2.081(2), In1-N1 = 2.369(3), In1-N2 = 2.344(3), C1-In1-N1 = 165.4(1), O1-In1-O2 = 116.9(1), O1-In1-N2 = 127.45(9), O2-In1-N2 = 106.4(1).
Figure S2. X-ray crystal structure of 7 (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): In1-C1 = 2.141(4), In1-C2 = 2.138(6), In1-O1 = 2.094(4), In1-N1 = 2.237(4), C1-In1-C2 = 138.2(2), N1-In1-O1 = 84.3(1).
Table S1. Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 7 and DFT calculated values for geometry optimized [Me₂In(ip)].

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>R = H</th>
<th>R’ = Ph</th>
<th>R = H</th>
<th>R’ = Mes</th>
<th>R = Me</th>
<th>R’ = Ph</th>
<th>R = Me</th>
<th>R’ = Mes</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-C1</td>
<td>2.141(4)</td>
<td>2.15</td>
<td>2.16</td>
<td>2.15</td>
<td>2.16</td>
<td>2.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In-C2</td>
<td>2.138(6)</td>
<td>2.16</td>
<td>2.16</td>
<td>2.16</td>
<td>2.16</td>
<td>2.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In-O</td>
<td>2.094(4)</td>
<td>2.08</td>
<td>2.08</td>
<td>2.08</td>
<td>2.08</td>
<td>2.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In-N</td>
<td>2.237(4)</td>
<td>2.27</td>
<td>2.27</td>
<td>2.26</td>
<td>2.26</td>
<td>2.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-In-C2</td>
<td>138.2(2)</td>
<td>129.2</td>
<td>125.5</td>
<td>129.1</td>
<td>125.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-In-O</td>
<td>84.3(1)</td>
<td>86.0</td>
<td>85.9</td>
<td>85.3</td>
<td>85.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Table S2.** Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 10 and DFT calculated values for geometry optimized [Me₂In(ip)]₂.

![Chemical structure](image)

<table>
<thead>
<tr>
<th></th>
<th>10²⁵ R = H R’ = Ph</th>
<th>R = H R’ = Mes</th>
<th>R = Me R’ = Ph</th>
<th>R = Me R’ = Mes</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-C1</td>
<td>2.137(5)</td>
<td>2.16</td>
<td>2.17</td>
<td>2.15</td>
</tr>
<tr>
<td>In-C2</td>
<td>2.133(5)</td>
<td>2.16</td>
<td>2.16</td>
<td>2.16</td>
</tr>
<tr>
<td>In-O</td>
<td>2.158(3)</td>
<td>2.15</td>
<td>2.17</td>
<td>2.09</td>
</tr>
<tr>
<td>In-N</td>
<td>2.366(3)</td>
<td>2.38</td>
<td>2.41</td>
<td>2.26</td>
</tr>
<tr>
<td>In…O</td>
<td>2.477(3)</td>
<td>2.40</td>
<td>2.36</td>
<td>4.51</td>
</tr>
<tr>
<td>C1-In-C2</td>
<td>140.3(2)</td>
<td>137.6</td>
<td>133.8</td>
<td>130.6</td>
</tr>
<tr>
<td>N-In-O</td>
<td>82.0(1)</td>
<td>82.5</td>
<td>79.4</td>
<td>85.9</td>
</tr>
<tr>
<td>O-In-O*</td>
<td>74.5(1)</td>
<td>75.7</td>
<td>71.7</td>
<td>93.4</td>
</tr>
<tr>
<td>In-O-In*-<em>-O</em></td>
<td>0.0</td>
<td>0.0</td>
<td>16.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>
**Table S3.** Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 11 and DFT calculated values for geometry optimized \([\text{Me}_2\text{Al(ip)}]_n\) (n = 1, 2).

![Chemical structures](image)

<table>
<thead>
<tr>
<th></th>
<th>11\textsuperscript{25}</th>
<th>R = H, R’ = Ph (n = 1)</th>
<th>R = H, R’ = Ph (n = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al1-C1</td>
<td>1.946(3)</td>
<td>1.99</td>
<td>1.99</td>
</tr>
<tr>
<td>Al1-C2</td>
<td>1.943(3)</td>
<td>1.98</td>
<td>1.98</td>
</tr>
<tr>
<td>Al1-O</td>
<td>1.772(2)</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>Al1-N</td>
<td>1.963(2)</td>
<td>2.04</td>
<td>2.05</td>
</tr>
<tr>
<td>Al1…O</td>
<td></td>
<td>3.86</td>
<td></td>
</tr>
<tr>
<td>C1-Al1-C2</td>
<td>119.1(1)</td>
<td>120.9</td>
<td>121.7</td>
</tr>
<tr>
<td>N-Al1-O</td>
<td>95.14(9)</td>
<td>93.0</td>
<td>92.8</td>
</tr>
<tr>
<td>O-Al1-O*</td>
<td>-</td>
<td>-</td>
<td>74.0</td>
</tr>
<tr>
<td>Al-O-Al* -AlO*</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table S4. Selected DFT calculated bond distances (Å) and angles (°) for geometry optimized [MeIn(abp)].

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Bond</th>
<th>R = H</th>
<th>R = Me</th>
<th>R = tBu</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-C</td>
<td>2.14</td>
<td>2.14</td>
<td>2.14</td>
</tr>
<tr>
<td>In-O1</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
</tr>
<tr>
<td>In-O2</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
</tr>
<tr>
<td>In-N</td>
<td>2.30</td>
<td>2.30</td>
<td>2.28</td>
</tr>
<tr>
<td>C-In-N</td>
<td>116.2</td>
<td>116.4</td>
<td>116.4</td>
</tr>
<tr>
<td>C-In-O1</td>
<td>118.2</td>
<td>118.1</td>
<td>118.8</td>
</tr>
<tr>
<td>C-In-O2</td>
<td>118.3</td>
<td>118.1</td>
<td>118.8</td>
</tr>
</tbody>
</table>
Table S5. Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 3 and DFT calculated values for geometry optimized [MeIn(abp)]₂.

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>R = H</th>
<th>R = Me</th>
<th>R = tBu</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-C</td>
<td>2.141(2)</td>
<td>2.14</td>
<td>2.15</td>
<td>2.15</td>
</tr>
<tr>
<td>In-O1</td>
<td>2.241(1)</td>
<td>2.15</td>
<td>2.15</td>
<td>2.21</td>
</tr>
<tr>
<td>In-O2</td>
<td>2.083(1)</td>
<td>2.05</td>
<td>2.05</td>
<td>2.06</td>
</tr>
<tr>
<td>In-N</td>
<td>2.357(1)</td>
<td>2.43</td>
<td>2.42</td>
<td>2.38</td>
</tr>
<tr>
<td>In...O</td>
<td>2.195(1)</td>
<td>2.18</td>
<td>2.18</td>
<td>2.20</td>
</tr>
<tr>
<td>C-In-N</td>
<td>111.62(6)</td>
<td>107.2</td>
<td>106.7</td>
<td>102.8</td>
</tr>
<tr>
<td>C-In-O1</td>
<td>99.86(6)</td>
<td>112.1</td>
<td>108.9</td>
<td>106.7</td>
</tr>
<tr>
<td>C-In-O2</td>
<td>120.64(6)</td>
<td>119.6</td>
<td>118.7</td>
<td>113.3</td>
</tr>
<tr>
<td>C-In-O*</td>
<td>118.35(6)</td>
<td>115.4</td>
<td>119.8</td>
<td>127.9</td>
</tr>
<tr>
<td>In-O1-In*-O1*</td>
<td>-23.50(5)</td>
<td>-21.8</td>
<td>-21.9</td>
<td>-25.1</td>
</tr>
</tbody>
</table>
Table S6. Selected bond distances (Å) and angles (°) for the X-ray crystal structure of 8 and DFT calculated values for geometry optimized [MeAl(abp)].

<table>
<thead>
<tr>
<th></th>
<th>8&lt;sup&gt;20&lt;/sup&gt;</th>
<th>R = H</th>
<th>R = Me</th>
<th>R = tBu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-C</td>
<td>1.919(3)</td>
<td>1.96</td>
<td>1.97</td>
<td>1.97</td>
</tr>
<tr>
<td>Al-O1</td>
<td>1.735(2)</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>Al-O2</td>
<td>1.740(2)</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>Al-N</td>
<td>1.988(2)</td>
<td>2.06</td>
<td>2.06</td>
<td>2.04</td>
</tr>
<tr>
<td>C-Al-N</td>
<td>113.6(1)</td>
<td>112.4</td>
<td>112.8</td>
<td>113.1</td>
</tr>
<tr>
<td>C-Al-O1</td>
<td>117.2(1)</td>
<td>117.0</td>
<td>116.7</td>
<td>117.1</td>
</tr>
<tr>
<td>C-Al-O2</td>
<td>113.4(1)</td>
<td>114.7</td>
<td>114.6</td>
<td>114.6</td>
</tr>
</tbody>
</table>
Table S7. Selected DFT calculated bond distances (Å) and angles (°) for geometry optimized [MeAl(abp)]₂.

<table>
<thead>
<tr>
<th></th>
<th>R = H</th>
<th>R = Me</th>
<th>R = tBu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-C</td>
<td>1.98</td>
<td>1.98</td>
<td>1.98</td>
</tr>
<tr>
<td>Al-O1</td>
<td>1.91</td>
<td>1.97</td>
<td>2.10</td>
</tr>
<tr>
<td>Al-O2</td>
<td>1.81</td>
<td>1.82</td>
<td>1.84</td>
</tr>
<tr>
<td>Al-N</td>
<td>2.29</td>
<td>2.22</td>
<td>2.21</td>
</tr>
<tr>
<td>Al1…O1</td>
<td>1.97</td>
<td>1.94</td>
<td>1.95</td>
</tr>
<tr>
<td>C-Al-N</td>
<td>103.5</td>
<td>107.4</td>
<td>104.2</td>
</tr>
<tr>
<td>C-Al-O1</td>
<td>107.1</td>
<td>100.1</td>
<td>101.2</td>
</tr>
<tr>
<td>C-Al-O2</td>
<td>115.2</td>
<td>110.2</td>
<td>106.8</td>
</tr>
<tr>
<td>C-Al-O1*</td>
<td>114.4</td>
<td>122.0</td>
<td>126.6</td>
</tr>
<tr>
<td>Al-O1-Al*-O1*</td>
<td>-10.0</td>
<td>-6.4</td>
<td>-18.5</td>
</tr>
</tbody>
</table>