Supporting information

**Indium Catalysts for Low Pressure CO₂/Epoxide Ring Opening Copolymerization: Evidence for A Mononuclear Mechanism?**

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References.
Experimental section

All reactions were conducted under an inert atmosphere of dry nitrogen, either using standard Schlenk line or glovebox techniques. All solvents and reagents were obtained from commercial sources (Aldrich and Merck) and used as received, unless stated otherwise. Tetrahydrofuran, hexane and toluene were distilled from sodium/benzophenone, under dry argon ([H₂O] < 5 ppm). Dichloromethane and diethyl ether, used for ligands syntheses, were taken directly from an MBraun MB-SPS-800 solvent purification system. All dry solvents and reagents were stored under nitrogen and degassed by several freeze-pump-thaw cycles. Cyclohexeneoxide (CHO) was dried overnight over CaH₂, fractionally distilled and degassed. KO'Bu was sublimed prior to use. All other reagents used as received from suppliers.

NMR Spectroscopy

¹H (400.2 MHz) and ³¹P (162.0 MHz) NMR spectra were collected using a Bruker Advance III HD nanobay NMR equipped with a 9.4T magnet. ¹³C NMR, COSY, HMBC and HSQC NMR spectra were collected with a Bruker Avance NMR equipped with a 11.75T magnet and a ¹³C (125.8 MHz) detect cryoprobe.

DOSY

The Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed, at 298 K, on a Bruker 500 AVANCE III NMR spectrometer operating, at a frequency of 499.9 MHz for proton resonance and equipped with a z-gradient bbfo/5mm tuneable "SmartProbe™" probe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5 G/cm (5.35G/cmA). Diffusion ordered NMR data was acquired using the Bruker pulse program ledbpgp2s with a spectral width of 5500Hz (centred on 4.5 ppm) and 32768 data points. A relaxation delay of 12 s was employed along with a diffusion time (large delta) of 100 ms and a longitudinal eddy current delay (LED) of 5 ms. Bipolar gradients pulses (little delta/2) of 2.2 ms and homospoil gradient pulses of 0.6 ms were used. The gradient strengths of the 2 homospoil pulses were -17.13% and -13.17%. 32 experiments were collected with the bipolar gradient strength, initially at 5% (1st experiment), linearly increased to 95% (32nd experiment). All gradient pulses were smooth-square shaped (SMSQ10.100) and after each application a recovery delay of 200 µs used. The experiment was run with 24 scans per increment, employing one stimulated echo with two spoiling gradients. DOSY plots were generated by using the DOSY processing module of TopSpin. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression.²,³
**DOSY calibration plots**

A calibration plot was constructed through a series of DOSY analysis using a range of standards spanning molecular weight range 161.4-643.4 g mol⁻¹ {hexamethyldisilazane [HN(SiMe₃)₂], 161.4; Zn[N(SiMe₃)₂], 386.2; β-diketiminate ligand HC(C(Me)N-2,6-iPr₂C₆H₃)₂, (BDIH), 418.7; (BDI)Zn[N(SiMe₃)₂], 643.4 g mol⁻¹, Table S1}. From the diffusion coefficients of the external standards, linear calibration graphs were obtained by plotting logD vs logMW (Graph S1). Following DOSY analysis of the product, the diffusion coefficient obtained for the signals corresponding to the product allowed an estimate of the MW of the species present in solution.

Table S1. Diffusion coefficients of standards in d₈-THF solution compared to their molecular weight.

| Compound               | LogD  | MW (g mol⁻¹) | LogMW |
|------------------------|-------|--------------|-------|
| d₈-THF                | -8.568| 80.2         | 1.9040|
| HN(SiMe₃)₂            | -8.763| 161.4        | 2.2079|
| Zn[N(SiMe₃)₂]         | -8.943| 386.2        | 2.5868|
| BDIH                  | -8.990| 418.7        | 2.6219|

Graph S1. LogD vs LogMW representation from the ¹H DOSY NMR data obtained for the standards HN(SiMe₃)₂, Zn[N(SiMe₃)₂] and BDIH in d₈-THF solvent.

**MALDI-TOF MS**

MALDI ToF analysis was carried out on Micromass MALDI Micro MX spectrometer. The matrix used was dithranol. Potassium trifluoroacetate was used as an additive, as required. The samples were prepared in the following manner: 10 mg/mL THF solutions of the complex, matrix and additive were separately prepared. Then, 20 µL of the complex and 20 µL of the matrix solution were mixed, along with 10 µL of the additive solution, if required. This mixture (2 µL) was then spotted on the MALDI plate and allowed to dry.
**X-ray Diffraction**

The crystal sample was isolated in a glovebox, under a pool of fluorinated oil, and mounted on MiTeGen MicroMounts. The crystal was cooled to 150 K, with an Oxford Cryosystems Cryostream nitrogen cooling device. Data collection was carried out with an Oxford Diffraction Supernova diffractometer using Cu Kα (λ = 1.5417 Å) or Mo Kα (λ = 0.7107 Å) radiation. The resulting raw data was processed using CrysAlisPro. Structures were solved by SHELXT and Full-matrix least-squares refinements based on F2 were performed in SHELXL-14, as incorporated in the WinGX package. For each methyl group, the hydrogen atoms were added at calculated positions, using a riding model with U(H) = 1.5Ueq (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions, using a riding model with U(H) = 1.2Ueq (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion. All seven crystal structures have been registered with the Cambridge Structural Database: CCDC 1824209-1824215

**Elemental analysis**

Elemental analyses for all the complexes were determined by Stephen Boyer at London Metropolitan University.

**SEC**

Two Mixed Bed PSS SDV linear S columns were used in series, with THF as the eluent, at a flow rate of 1 mL/min, on a Shimadzu LC-20AD instrument at 40 °C. The instrument was calibrated using narrow \( M_n \) polystyrene standards and polymer \( M_n \) values are reported against polystyrene without correction. The polymer samples were dissolved in SEC grade THF and filtered prior to analysis.

**Low pressure CO\(_2\) line**

Low pressure copolymerization studies were performed using a triple manifold Young tap CO\(_2\)/N\(_2\)/vacuum Schlenk line. Research grade carbon dioxide (99.999 %) used was dried by flow through a Drierite column and two MC1 (Micro Torr) low pressure CO\(_2\) drying columns connected in series.

![Figure S1. Pictures of the drying columns (L.H.S.) and the triple manifold Young tap CO\(_2\)/N\(_2\)/vacuum Schlenk line used for the low CO\(_2\) pressure polymerization.](image)

**High pressure CO\(_2\) line**
High pressure copolymerization studies were performed in a 25 mL Parr 5500 HP Compact Reactor. Research grade carbon dioxide (99.999 %) was purified by passing through two high pressure drying columns, connected in series (VICI, Thames Restek).

Figure S2. Pictures of the drying columns (L.H.S. picture), the high pressure reactor disassembled (upper middle picture), the high pressure reactor assembled (R.H.S picture) and the controller unit (lower middle picture) used for high CO\textsubscript{2} pressure polymerization.

**In situ ATR-IR measurements**

In situ ATR-IR measurements were performed on a Mettler-Toledo ReactIR ic.10 spectrometer equipped with a MCT detector and a silver halide DiComp probe.

**Typical Polymerization Procedure at 1 bar of CO\textsubscript{2}:**

In a glove box, the indium catalyst (1 equiv.) was dissolved in CHO (1 mL, 1000 equiv.), under a nitrogen atmosphere in a Schlenk tube with a magnetic stirrer bar. The Schlenk tube was sealed, brought outside of the glove box and connected to a vac-CO\textsubscript{2} line. The reaction mixture was subjected to three cycles of vac-CO\textsubscript{2} fill and then heated to the desired temperature (60 °C or 80 °C), under 1 bar of CO\textsubscript{2} pressure, for the desired time (24 h or 48 h). The crude polymer was isolated by evaporation of the excess CHO, under reduced pressure. Polymers were dissolved in THF (1 mL), then purified by precipitation using pentane (2 x 5 mL) to yield white powders.

**Typical Polymerization Procedure at high CO\textsubscript{2} pressure:**

In a glove box, the indium catalyst (1 equiv.) was dissolved in CHO (6 mL, 1000 equiv.), under a nitrogen atmosphere and added into a 25 mL Paar reactor (equipped with an overhead mechanical stirrer). The reactor was sealed, brought outside of the glove box and connected to a high pressure CO\textsubscript{2} line. The reactor was heated to 80 °C and pressurized. Polymerizations were stirred for 24 h, at 80 °C, at 10-40 bar of CO\textsubscript{2}. After the allotted time period, the reactor was cooled to ambient temperature over 5 min and depressurized. The crude polymer was isolated by evaporation of the
excess CHO, under reduced pressure. The crude polymer was dissolved in THF (5 mL) then purified by precipitation from pentane (2 x 20 mL) to yield a white powder.

**In-situ ATR-IR monitoring of CO\textsubscript{2}/CHO ROCOP, at 1 bar of CO\textsubscript{2}**

The ATR-IR probe was inserted into a dry Schlenk tube and dried overnight, under vacuum. In a glove box, the indium catalyst (1 equiv.) was dissolved in CHO (1.5 mL, 500-1200 equiv.) and the solution added to a dry Schlenk tube, equipped with a magnetic stirrer bar. The Schlenk tube was sealed, removed from the glove box and connected to a vac-CO\textsubscript{2}-N\textsubscript{2} line, where the reaction mixture was subjected to three cycles of vac-CO\textsubscript{2} fill. The IR probe was transferred from the empty Schlenk tube to the one containing the reaction mixture, under a dynamic flow of CO\textsubscript{2} gas. The IR probe was immersed in the reaction solution and the Schlenk tube was immersed in a pre-heated oil bath at 80 °C. As soon as the Schlenk tube was immersed in the oil-bath, data acquisition was started (at a rate of 1 scan/15 min). The reaction was maintained at 80 °C, under 1 bar of CO\textsubscript{2}, for the desired time (24 h or 48 h). When complete, an aliquot was removed and used to determine the polymer conversion (by \textsuperscript{1}H NMR spectroscopy). The crude polymer was isolated by evaporation of the excess CHO, under reduced pressure. The crude polymer was dissolved in THF (1 mL) then purified by precipitation using pentane (2 x 5 mL) to yield a white powder.

**Kinetic analyses**

The IR data acquired in the above experiments was used to determine initial rates. A brief outline of the methods used is provided and further information is available in Figs. S61, S78 and S79 (which show the plots of initial rates vs. time). The initial rates were monitored using in situ ATR-FTIR spectroscopy, by analysis of two IR vibrational modes: the C=O stretch (1787-1731 cm\textsuperscript{-1}) and the C-O stretch (O-C=O = 1014 cm\textsuperscript{-1}). An example of the data treatment is provided below:

**Monitoring of absorption at 1789 cm\textsuperscript{-1} and [In] = 20.24 mM.**

First the absorption vs. time data was collected, with absorption corresponding to the raw instrument data. Subsequently, the absorption data was normalized

\[
\text{(Normalized Absorption)}_t = (\text{Absorption})_t - (\text{Absorption})_i
\]

The monomer conversion was determined from the aliquot analysed by \textsuperscript{1}H NMR spectroscopy (at time = F). The absorption data was converted to conversion vs. time data using the following relationship:

\[
(\text{Conversion})_t = (\text{Normalized Absorption})_t x (\text{Conversion})_F / (\text{Normalized absorption})_F
\]

**[CHO]** (M): The variation of [CHO] over time was determined from:

\[
[\text{CHO}]_t = [\text{CHO}]_i - \text{Conversion}_t x [\text{CHO}]_i
\]

**[PCHC]** (M): The variation of [PCHC] over time was determined from:

\[
[\text{PCHC}]_t = [\text{CHO}]_i - [\text{CHO}]_i
\]

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$u$ (M.min$^{-1}$): The initial rate of the polymerization was determined by plotting [PCHC] (over the conversion range =0 -10 %) vs. time. A linear fit was applied to the data and the gradient corresponds to the initial rate.

$k_{obs}$ was determined by plotting [cat] (mM) against $u$ (mM.min$^{-1}$) and a linear fit was applied. The gradient is labelled, $k_{obs}$ (where $k_{obs}$ relates to $k_p$ according to the equation shown below):

$$k_{obs} (\text{min}^{-1}) = k_p[\text{CHO}]$$

$$k_p = k_{obs}/[\text{CHO}].$$

**In-situ ATR-IR monitoring of the CO$_2$ insertion reaction**

The ATR-IR probe was dried overnight, under reduced pressure, in a dry Schlenk tube. In a glove box, LiNtBu (100 mg, 0.1 mmol) was dissolved in THF (1.0 mL) and the solution was added into a two necked Schlenk tube equipped with a magnetic stirrer bar. The Schlenk tube was sealed, removed from the glove box and connected to a vac-CO$_2$-N$_2$ line, where the reaction mixture was subjected to three cycles of vac-N$_2$ fill. The IR probe was transferred from the empty Schlenck tube to the one containing the reaction mixture, under a dynamic flow of N$_2$. The mixture was degassed by a freeze-vac cycle, the reaction mixture was warmed to room temperature and the probe immersed into the de-gassed solution (at this moment the sealed flask is still under vacuum). As soon as the probe was immersed in the reaction solution, the data acquisition was started (1 scan/15 sec). After 5 minutes of data acquisition, CO$_2$ gas was added into the reaction solution and the reaction was monitored for 15 min. Next, a solution of DMAP (24 mg, 0.2 mmol, 2 equiv.) dissolved in THF (0.5 mL) was injected into the reaction mixture and the solution was monitored for a further 1 h. The final product was isolated by exposure of the solution to air, removal of the THF in vacuo and analysis of the residue by $^1$H NMR and $^{31}$P NMR spectroscopy (C$_6$D$_6$).

**Typical Phosphasalen Ligand synthesis:**

![Scheme S1. Synthetic procedure to synthesise $^6$LH$_2$ (R =tBu, amyl, cumyl). i. NBS, CH$_3$CN, 18 h, 90% ii. 1.7M n-BuLi, -78 °C, Et$_2$O, 4 h iii. PPh$_3$Cl, -78 °C, Et$_2$O, 18 h, 60% vi. Br$_2$ (1 equiv.), CH$_2$Cl$_2$, -78 °C, 2 h v. Bu$_3$N (1 equiv.), NH$_2$(CH$_3$)$_2$NH$_2$ (0.5 equiv.), -78 °C, 18 h, 50 %.

| Step | Reaction Details |
|------|-----------------|
| i.   | NBS, CH$_3$CN, 18 h, 90% |
| ii.  | 1.7M n-BuLi, -78 °C, Et$_2$O, 4 h |
| iii. | PPh$_3$Cl, -78 °C, Et$_2$O, 18 h, 60% |
| iv.  | Br$_2$ (1 equiv.), CH$_2$Cl$_2$, -78 °C, 2 h |
| v.   | Bu$_3$N (1 equiv.), NH$_2$(CH$_3$)$_2$NH$_2$ (0.5 equiv.), -78 °C, 18 h, 50% |
**Compound S1:**

At 0 °C, N-bromosuccinimide (1 equiv.) was added to a solution of the desired phenol (5 g) in acetonitrile (~200 mL), under continuous stirring. The mixture was allowed to warm to 25 °C and left stirring for 12 h. After which time, a saturated solution of sodium sulphite (~100 mL) was added and the reaction mixture left to stir for 15 mins. The white suspension was then filtered and the product extracted using petroleum ether (3 x 100 mL). The combined organic fractions were dried (MgSO₄), filtered, and the solvent removed *in vacuo* (6 g, 90 %).

**t-Bu substituent S1**

$^1$H NMR (400 MHz, CDCl₃) δ (ppm): 7.31 (d, $4$J$_{HH} = 2.5$ Hz, 1H, tBu-C=CH-CBr), 7.23 (d, $4$J$_{HH} = 2.5$ Hz, 1H, tBu-C=CH-CBr), 5.65 (s, 1H, OHH), 1.40 (s, 9H, C(3)(CH₃)₃), 1.28 (s, 9H, C(3)(CH₃)₃);

Anal. Calc. for C$_{14}$H$_{21}$BrO: C, 58.95; H, 7.42 Found: C, 58.95; H, 7.41.

**Amyl substituent S1**

$^1$H NMR (400 MHz, CDCl₃, δ (ppm)): 7.28 (d, $J = 3.0$ Hz, 1H, CdH), 7.13 (d, $J = 2.2$ Hz, 1H, CbH), 5.63 (s, 1H, OH), 1.88 (q, $J = 7.5$ Hz, 2H, CH$_2$CH$_3$), 1.61 (q, $J = 7.4$ Hz, 2H, CH$_2$CH$_3$), 1.38 (s, 6H, C(CH$_3$)$_2$), 1.27 (s, 6H, C(CH$_3$)$_2$), 0.70 (t, $3$J$_{HH} = 7.4$ Hz, 3H, CH$_3$), 0.67 (t, $3$J$_{HH} = 7.4$ Hz, 3H, CH$_3$).

Anal. Calc. for C$_{16}$H$_{25}$BrO: C, 61.34; H, 8.04 %; Found: C, 61.24; H, 8.17 %.

**Cumyl substituent S1**

$^1$H NMR (400 MHz, CDCl$_3$, δ (ppm)): 7.34-7.17 (m, 12H, Ph), 5.17 (s, 1H, OH), 1.70 (s, 6H, C'(CH$_3$)$_2$Ph), 1.62 (s, 6H, C''(CH$_3$)$_2$Ph).

Anal. Calc. for C$_{24}$H$_{25}$BrO: C, 70.42; H, 6.16 %; Found: C, 70.36; H, 6.24 %.

**Compound S2**

Under a dry atmosphere of N₂, a solution of the desired bromo-phenol (3 g) in Et₂O (60 mL) was cooled to -78 °C, before a solution of n-BuLi (1.6 M in hexanes, 2 equiv.) was added. The reaction mixture, under continuous stirring, was allowed to warm to 25 °C. The mixture was left stirring at 25 °C, for 30 mins, after which time it was cooled again to -78 °C. Chlorodiphenylphosphine (1 equiv.) was added to the solution and the mixture allowed to warm to 25 °C. The solution formed a white suspension on warming and was left stirring, at 25 °C, for 15 h. The solution was extracted with aqueous solutions of Na$_2$H$_2$PO₄ (0.1 M, 2 x 100 mL) and the organic layer filtered to remove inorganic salts. The solution was then dried (MgSO₄), filtered and concentrated to ~10 mL. MeOH (5 mL) was then added and the solution left to crystallize the phosphate product (3 g, 70 %).
**Bu substituent S2

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$ (ppm)): 7.31-7.36 (m, 2H, $\text{Ph}$), 7.30 (d, $^3J_{\text{H,H}} = 2.8$ Hz, 1H, $\text{C}_6\text{H}$), 6.85-6.91 (m, 6H, $\text{Ph}$), 6.82 (dd, $^3J_{\text{H,H}} = 6.4$ Hz, $^4J_{\text{H,H}} = 2.4$ Hz, 1H, $\text{C}_6\text{H}$), 6.78 (d, $J = 2.8$ Hz, 1H, $\text{OH}$), 3.70 (s, 6H, OMe), 1.42 (s, 9H, C-$\text{CH}_3$), 1.13 (s, 9H, C-$\text{CH}_3$); $^{31}$C($^1$H) NMR (75 MHz, CDCl$_3$) $\delta$ (ppm): 156.3 (d, $^3J_{\text{P,C}} = 19.2$ Hz, OC$_{\text{oc}}$), 145.2 (d, $^3J_{\text{P,C}} = 3.0$ Hz, C$_{\text{olv}}$), 135.6 (d, $^3J_{\text{P,C}} = 3.0$ Hz, C$_{\text{olv}}$(PPh$_2$)), 135.5 (d, $^3J_{\text{P,C}} = 1.0$ Hz, C$_{\text{olv}}$), 133.6 (d, $^3J_{\text{P,C}} = 18.5$ Hz, $\alpha$-or m-CH(PPh$_2$)), 129.5 (d, $^3J_{\text{P,C}} = 3.5$ Hz, CH), 129.1 (s, p-CH(PPh$_2$)), 128.8 (d, $^3J_{\text{P,C}} = 7.5$ Hz, $\alpha$-or m-CH(PPh$_2$)), 126.6 (s, CH), 120.1 (s, C$_{\text{olv}}$-PPh$_2$), 35.4 (d, $^3J_{\text{P,C}} = 2.0$ Hz, C-C(CH$_3$)$_2$), 34.7 (s, C-C(CH$_3$)$_2$), 31.7 (s, C-C(CH$_3$)$_2$), 29.2 (s, C-C(CH$_3$)$_2$); $^{31}$P($^1$H) NMR (160 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): -50.7 (s, $P$); Anal. Calc. for $\text{C}_{26}\text{H}_{33}$PO: C, 79.96; H, 8.00 Found: C, 79.89; H, 8.03.

Amyl substituent $^\text{Amyl}$S2

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$ (ppm)): 7.37-7.29 (m, 10H, PPh$_2$), 7.22 (d, $^3J_{\text{H,H}} = 2.4$ Hz, 1H, $\text{C}_6\text{H}$), 6.79 (dd, $^3J_{\text{H,H}} = 5.8$ Hz, $^4J_{\text{H,H}} = 2.4$ Hz, 1H, $\text{C}_6\text{H}$), 6.59 (d, $J = 10.0$ Hz, 1H, $\text{OH}$), 1.87 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2H, C(CH$_3$)$_2$CH$_2$CH$_3$), 1.46 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2H, C(CH$_3$)$_2$CH$_2$CH$_3$), 1.38 (s, 6H, C(CH$_3$)$_2$), 1.11 (s, 6H, C(CH$_3$)$_2$), 0.65 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3H, CH$_2$CH$_3$), 0.58 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3H, CH$_2$CH$_3$); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 155.8 (d, $^2J_{\text{P,C}} = 18.4$ Hz, C$_{\text{olv}}$-OH), 140.3 (d, $^3J_{\text{P,C}} = 2.7$ Hz, C$_{\text{olv}}$), 135.6 (d, $^3J_{\text{P,C}} = 3.4$ Hz, C$_{\text{olv}}$), 133.5 (s, Ph), 133.3 (d, $J_{\text{P,C}} = 20.5$ Hz, Ph), 130.0 (d, $^3J_{\text{P,C}} = 3.6$ Hz, $\text{C}_6\text{H}$), 128.8 (s, Ph), 128.6 (d, $J_{\text{P,C}} = 6.9$ Hz, Ph), 128.3 (s, $\text{C}_6\text{H}$), 119.5 (s, C$_{\text{olv}}$-P), 38.6 (s, C$_{\text{olv}}$(CH$_3$)$_2$), 37.5 (s, C$_{\text{olv}}$(CH$_3$)$_2$), 37.0 (s, CH$_2$), 33.0 (s, CH$_2$), 28.4 (s, C$_{\text{olv}}$(CH$_3$)$_2$), 27.7 (s, C$_{\text{olv}}$(CH$_3$)$_2$), 9.5 (s, CH$_2$CH$_3$), 9.0 (s, CH$_2$CH$_3$); $^{31}$P($^1$H) NMR (160 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): -30.0 (s, $P$); Anal. Calc. for $\text{C}_{28}\text{H}_{35}$OP: C, 80.35; H, 8.43 %; Found: C, 80.52; H, 8.56 %.

Cumyl substituent $^\text{Cumyl}$S2

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$ (ppm)): 7.31 (d, $^3J_{\text{H,H}} = 2.3$ Hz, 1H, $\text{C}_6\text{H}$), 7.30-7.12 (m, 20H, C$_{14}$(CH$_3$)$_2$Ph + PPh$_2$), 6.54 (dd, $^3J_{\text{H,H}} = 5.3$ Hz, $^4J_{\text{H,H}} = 2.3$ Hz, 1H, $\text{C}_6\text{H}$), 5.11 (d, $^2J = 1.9$ Hz, 1H, $\text{OH}$), 1.61 (s, 6H, C$_{14}$(CH$_3$)$_2$), 1.53 (s, 6H, C$_{14}$(CH$_3$)$_2$); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 154.1 (d, $^2J_{\text{P,C}} = 18.8$ Hz, C$_{14}$(OH)), 150.8 (s, C$_{14}$-$^\text{IV}$(CH$_3$)$_2$-$^\text{IV}$), 149.0 (s, C$_{14}$-$^\text{IV}$(CH$_3$)$_2$-$^\text{IV}$), 142.6 (s, C$_{14}$-$^\text{IV}$), 136.3 (d, $J_{\text{P,C}} = 7.1$ Hz, Ph), 134.7 (s, C$_{14}$-$^\text{IV}$), 133.7 (d, $J_{\text{P,C}} = 18.9$ Hz, Ph), 131.1 (s, C$_6$H), 128.9 (s, Ph), 128.7 (s, Ph), 128.5 (d, $J_{\text{P,C}} = 7.5$ Hz, Ph), 128.0 (s, Ph), 126.8 (s, Ph), 126.7 (s, C$_6$H), 126.0 (d, $J_{\text{P,C}} = 101.7$ Hz, C$_{14}$-P), 42.6 (s, C$_{14}$(CH$_3$)$_2$), 42.2 (s, C$_{14}$(CH$_3$)$_2$), 30.9 (s, C$_{14}$(CH$_3$)$_2$), 29.7 (s, C$_{14}$(CH$_3$)$_2$); $^{31}$P($^1$H) NMR (160 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): -20.5 (s, $P$); Anal. Calc. for $\text{C}_{30}\text{H}_{40}$OP: C, 84.02; H, 6.86 %; Found: C, 83.86; H, 6.76 %.
Phosphasalen ligand LH₂

At -78 °C, bromine (2 equiv.) was slowly added to a solution of 2-(diphenylphosphino)-4,6-di-tert-butylphenol (2.0 g) in dichloromethane (~50 mL). The cold bath was then removed and the solution left to stir for 2 h, at 25 °C. The solution was then cooled again to –78 °C. Once cool, tributylamine (2 equiv.) was added, followed by 2,2’(ethylenediamine) (1 equiv.). The solution left stirring for 16 h, at 25 °C. The solvent was removed in vacuo leaving a gelatinous semi-solid. THF (3 mL) was then added causing a white solid to form and the suspension was stirred for 30 mins. The white solid was isolated by filtration, washed with THF at 0 °C (5 x 3 mL) and then dried in vacuo (3.5 g, 3.5 mmol, 75 %).

¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 8.14 (s, 2H, 1), 7.72–7.50 (m, 20H, PPh₂), 6.93 (bs, 2H, NH), 6.43 (dd, 3J_H = 2.1 Hz, 3J_P,H = 15.2 Hz, 2H, 2), 3.70 (bs, 4H, NH-CH₂), 1.50 (s, 18H, o-¹Bu), 1.06 (s, 18H, p-¹Bu); ¹³C(¹H) NMR (126 MHz, CDCl₃, 298 K) δ (ppm): 155.8 (s, C⁻OH), 146.3 (d, J_P,C = 12.3 Hz, o-PhC⁴⁻o-¹Bu), 141.2 (d, J_P,C = 10.0 Hz, p-PhC⁴⁻p-P(Ph₂)), 134.4 (d, J_P,C = 4.2 Hz, p-PhC⁴⁻), 133.8 (d, J_P,C = 12.9 Hz, 1), 131.8 (s, p-CH(PPh₂)), 129.8 (d, J_P,C = 14.7 Hz, 2), 128.6 (d, J_P,C = 14.7 Hz, i-PPhC⁴⁻), 123.0 (s, o-PPh), 122.1 (s, o-PPh), 115.1 (s, m-PPh), 114.3 (s, m-PPh), 44.2 (dd, J_P,C = 2.2 Hz, J_P,C = 7.8 Hz, NH-CH₂), 35.3 (s, o-C⁴⁻(CH₃)₃), 34.7 (s, p-C⁴⁻(CH₃)₃), 32.2 (s, o-¹Bu), 30.8 (s, p-¹Bu); ³¹P(¹H) NMR (160 MHz, CDCl₃, 298 K) δ (ppm): 40.3 (s, P). Anal. Calc. for C₅₈H₅₆Br₂N₂O₂P₂ (998.21 g/mol): C, 66.03; H, 7.26; N, 2.66 %; Found: C, 65.94; H, 7.26; N, 2.62 %.

Phosphasalen ligand AmylLH₂

¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 8.11 (s, 2H, OH), 7.72-7.51 (m, 22H, PPh₂ + 1), 6.90 (m, 2H, NH), 6.36 (dd, 3J_H = 16.0 Hz, 3J_H,N = 2.3 Hz, 2H, 2), 3.80-3.67 (m, 4H, NH-CH₂), 1.95 (q, 3J_H = 7.4 Hz, 4H, o-CH₂CH₃(CH₃)₂), 1.45 (s, 12H, o-CH₂CH₃(CH₃)₂), 1.38 (q, 3J_H = 7.4 Hz, 4H, p-CH₂CH₃(CH₃)₂), 1.00 (s, 12H, p-CH₂CH₃(CH₃)₂), 0.67 (t, 3J_H = 7.4 Hz, 6H, o-CH₂CH₃(CH₃)₂), 0.55 (t, 3J_H = 7.4 Hz, 6H, p-CH₂CH₃(CH₃)₂); ¹³C(¹H) NMR (126 MHz, CDCl₃, 298 K) δ (ppm): 155.7 (s, C⁴⁻OH), 143.6 (d, J_P,C = 13.5 Hz, o-PhC⁴⁻-o-Amyl), 141.2 (d, J_P,C = 10.0 Hz, p-PhC⁴⁻-p-Amyl), 134.4 (s, p-PPh), 133.8 (d, J_P,C = 7.2 Hz, 2), 133.8 (d, J_P,C = 10.0 Hz, o-PhC⁴⁻-o-PPh), 129.9 (d, J_P,C = 13.6 Hz, 1), 129.3 (s, 1-PPh₂), 123.2 (s, 0-Ph), 122.1 (s, o-Ph), 115.3 (s, m-Ph), 114.20 (s, m-Ph), 44.2 (dd, J_P,C = 6.8 Hz, J_P,C = 13.2 Hz, NH-CH₂), 39.0 (s, o-C⁴⁻CH₂(CH₃)₂), 37.8 (s, p-C⁴⁻CH₂(CH₃)₂), 36.7 (s, o-CH₂CH₃(CH₃)₂), 34.2 (s, p-CH₂CH₃(CH₃)₂), 28.8 (s, o-CH₂CH₃(CH₃)₂), 28.2 (s, p-CH₂CH₃(CH₃)₂), 9.7 (s, o-CH₂CH₃(CH₃)₂), 9.1 (s, p-CH₂CH₃(CH₃)₂); ³¹P(¹H) NMR (160 MHz, CDCl₃, 298 K) δ (ppm): 39.9 (s, P). Anal. Calc. for C₅₈H₅₆Br₂N₂O₂P₂ (1054.37 g/mol): C, 66.03; H, 7.26; N, 2.66 %; Found: C, 65.94; H, 7.26; N, 2.62 %.
Phosphasalen ligand Cumyl L'H$_2$

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.58 ($^1$J$_{HH}$= 2.1 Hz, 2H, 1), 7.57-7.53 (m, 8H, C-Ph), 6.96 (m, 2H, NH$_2$CH$_2$), 1.63 (s, 12H, o-Ph(CH$_3$)$_2$) 1.57 (s, 12H, p-Ph(CH$_3$)$_2$); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$, 298 K) δ (ppm): 154.8 (C IV-OH), 149.3 (o-PhC IV-o-Cumyl), 147.8 (o-PhC IV-o-Cumyl), 145.5 (o-PhC IV-o-Cumyl), 139.8 (p-PhC IV-PPh$_2$), 133.4 (2), 133.1 (p-PPh$_2$), 131.1 (i-PPh$_2$), 129.6 (1), 129.1 (o-a-Cumyl), 128.3 (m-o-Cumyl), 126.9 (o-a-Cumyl), 126.8 (m-p-Cumyl), 126.0 (p-o-Cumyl), 126.0 (p-p-Cumyl), 122.1 (o-PPh$_2$), 121.3 (o-PPh$_2$), 112.2 (m-PPh$_2$), 111.4 (m-PPh$_2$), 43.7 (NH$_2$CH$_3$), 43.0 (o-C IV-Cumyl), 42.2 (p-C IV-Cumyl), 30.8 (o-CH$_3$Ph(CH$_3$)$_2$), 29.9 (p-CH$_3$Ph(CH$_3$)$_2$); $^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$, 298 K) δ (ppm): 39.4 (s, P).

Anal. Calc. for C$_{74}$H$_{76}$Br$_2$N$_2$O$_4$P$_2$ (1247.29 g/mol): C, 71.27; H, 6.14; N, 2.25 %; Found: C, 70.88; H, 6.21; N, 2.26 %.

Salen ligand L’H$_2$

![Scheme S2. Synthetic procedure to synthesise L’H$_2$. i. H$_2$N-CH$_2$-CH$_2$-NH$_2$ (0.5 equiv.), MeOH, 25 °C, 4 h.](image)

A solution of ethylene diamine (257 mg, 4.27 mmol, 1 equiv.) in MeOH (3 mL) was added, dropwise, into a solution of 1-hydroxo-2,4-di-tert-butyl benzaldehyde (2 g, 8.54 mmols, 2 equiv.), at 25 °C, under air. The reaction was monitored by $^1$H NMR spectroscopy and stirred for 4 h. L’H$_2$ was isolated by removal of the solvent, under vacuum, and isolated as a yellow powder (2.1 g, 100 %).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 13.64 (s, 2H, OH), 8.39 (s, 2H, H=N), 7.36 (s, 1H, 1), 7.07 (s, 1H, 2), 3.92 (s, 4H, HC=NC$_2$H$_5$) 1.43 (s, 18H, o-^Bu), 1.28 (s, 17H, p-^Bu); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$, 298 K) δ (ppm): 167.7 (s, H=N), 158.2 (s, C IV-OH), 140.2 (s, C IV-HC=N), 136.7 (s, o-C IV(CH$_3$)$_2$), 127.2 (s, 2), 126.2 (s, 1), 117.9 (s, p-C IV(CH$_3$)$_2$), 59.8 (s, NH$_2$CH$_2$), 36.2 (s, o-C IV-Bu), 34.3 (s, p-C IV-Bu), 31.6 (s, o-^Bu), 29.6 (s, p-^Bu). Anal. Calc. for C$_{32}$H$_{48}$N$_2$O$_4$ (492.75 g/mol): C, 78.00; H, 9.82; N, 5.69 %; Found: C, 78.26; H, 9.84; N, 5.72%.
Salen catalyst L’InCl

\[
\begin{align*}
\text{LH}_2 & \quad \text{ii.} & \quad \text{L’InCl} \\
& \quad \text{i.} & \quad \text{K[N(SiMe}_3)_2] (2 \text{ equiv.}), \text{THF, 16 h, 25 °C, ii. InCl}_3 (1 \text{ equiv.}), \text{THF, 16 h, 25 °C} \\
\end{align*}
\]

Scheme S3. Synthetic procedure for L’InCl. i. K[N(SiMe)_3]_2 (2 equiv.), THF, 16 h, 25 °C, ii. InCl_3 (1 equiv.), THF, 16 h, 25 °C

K[N(SiMe)_3]_2 (160 mg, 0.8 mmol) was added into a solution of LH_2 (200 mg, 0.4 mmol), in THF (10 mL), at 25 °C. The mixture was stirred for 16 h and the insoluble potassium salt was removed by filtration. The InCl_3 (90 mg, 0.4 mmol) was added to the reaction solution and the solution was stirred for 16 h, at 25 °C. The potassium chloride salt was removed by filtration and the solvent was evaporated, under reduce pressure, to afford L’InCl. (223 mg, 0.36 mmol, 86 %) The product was crystallized by the slow diffusion of hexane (2 mL) into a concentrated solution of L’InCl in toluene (0.1 mL), at -40 °C.

^1H NMR (400 MHz, CDCl_3, 298 K) δ (ppm): 8.38 (s, 2H, H-C=N), 7.51 (d, J_H-H = 2.56 Hz, 2H, 1), 6.95 (d, J_H-H = 2.46 Hz, 2H 2), 4.08 (m, 2H, N-CHH), 3.77 (m, 2H, N-CHH), 1.49 (s, 18H, o-tBu), 1.30 (s, 18H, p-tBu); ^13C(^1H) NMR (126 MHz, CDCl_3, 298 K) δ (ppm): 167.7 (s, H=C=N), 158.2 (s, C\text{IV}-O-In), 140.2 (s, C\text{IV}-HC=N), 136.7 (s, o-C\text{IV}(CH}_3)_2), 127.2 (s, 2), 126.2(s, 1), 117.9 (s, p-C\text{IV}(CH}_3)), 59.8 (s, N-CH_2), 35.2 (s, o-C\text{IV}Bu), 34.3 (s, p-C\text{IV}Bu), 31.6 (s, o-tBu), 29.6 (s, p-tBu). Anal. Calc. for C_32H_46ClInN_2O_2 (641.00): C, 59.96; H, 7.23; N 4.37 %. Found: C, 60.23; H, 7.35; N, 4.56%.

Phosphasalen catalysts

\[
\begin{align*}
\text{LH}_2^\text{R} & \quad \text{Br}^- & \quad \text{Br}^- \\
& \quad \text{i.} & \quad \text{ii.} & \quad \text{iii.} & \quad \text{R}\text{LH}_2 \\
\end{align*}
\]

Scheme S4. The synthesis of R\text{LInX}. i. K[N(SiMe)_3]_2 (2 equiv.), THF, 16 h, 25 °C, ii. InCl_3 (1 equiv.) or InBr_3 (1 equiv.), THF, 16 h, 25 °C, iii. KO\text{Bu} (1 equiv.) or KOAc (1 equiv.) or AgNO_3 (1 equiv.).

\text{LInCl}

K[N(SiMe)_3]_2 (160 mg, 0.80 mmol) was added into a slurry of LH_2 (200 mg, 0.20 mmol), in THF (10 mL), at 25 °C. The deprotonation reaction was monitored by ^31P(^1H) NMR spectroscopy (in C_6D_6) with
a clear resonance shift from 40.0 ppm (LH$_2$) to 25.4 ppm (LK$_2$). The insoluble potassium bromide salt was removed. InCl$_3$ (44 mg, 0.20 mmol) was added to the solution and it was stirred for 16 h, at 25 °C. The $^{31}$P($^1$H) NMR spectrum, in C$_6$D$_{16}$, confirmed formation of LinCl (a singlet at 42.1 ppm). The solvent was removed under reduced pressure. LinCl, insoluble in THF, was extracted from the potassium chloride salt with dichloromethane (2 x 10 mL). LinCl was isolated by solvent evaporation, under reduced pressure and was crystallized by the slow diffusion of hexane (2 mL) into a concentrated solution of LinCl in chloroform (0.1 mL), at -40 °C. The product was isolated as white crystals (166 mg, 0.17 mmol, 84 %).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.75 (d, $^2$J = 2.5 Hz, 2H, 1), 7.74 – 7.64 (m, 4H, o-PPh$_2$), 7.42 (dd, $^2$J$_{HH}$ = 11.7, 7.6 Hz, 4H, o-PPh$_2$), 7.11 – 6.93 (m, 8H, m- or p-PPh$_2$), 6.93 – 6.82 (m, 4H, m- or p-PPh$_2$), 6.63 (dd, $^2$J = 17.6, 2.5 Hz, 2H, 2), 3.23 – 2.91 (m, 2H, N-C$_2$H$_4$), 1.94 (s, 18H, m-1Bu), 1.12 (s, 18H, p-1Bu); $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$, 298 K) δ (ppm): 169.2 (d, $^2$J$_{PCM}$ = 14.9 Hz, C=O-In), 142.5 (d, $^2$J$_{PC}$ = 10.3 Hz, o-PhC$_{2}$N$_2$-o-1Bu), 136.2 (d, $^2$J$_{PC}$ = 14.8 Hz, p-PhC$_{2}$N$_2$-p-1Bu), 133.9 (d, $^2$J$_{PC}$ = 9.5 Hz, o-PPh$_2$), 132.8 (d, $^2$J$_{PC}$ = 9.2 Hz, o-PPh$_2$), 132.5 (s, p-PPh$_2$), 132.0 (s, p-PPh$_2$), 129.7 (s, C$_2$N$_2$-PPh$_2$), 129.0 (s, m-PPh$_2$), 128.9 (d, $^2$J$_{PC}$ = 4.3 Hz, 1), 128.3 (s, m-PPh$_2$), 126.74 (d, $^2$J$_{PC}$ = 15.3 Hz, 2) 107.7 (s, i-PPh$_2$), 106.8 (s, i-PPh$_2$), 46.3 (dd $^2$J$_{PC}$ = 5.2 Hz, $^2$J$_{PC}$ = 13.8 Hz, N-C$_2$H$_4$), 36.1 (s, o-C$_2$N$_2$(CH$_3$)$_2$), 34.0 (s, p-C$_2$N$_2$(CH$_3$)$_2$), 31.4 (s, o-1Bu), 30.3 (s, p-1Bu); $^{31}$P($^1$H) NMR (161 MHz, CDCl$_3$, 298 K): δ (ppm): 42.1 (s, P). Anal. Calc. for C$_{6}$H$_{16}$ClInN$_2$O$_2$P$_2$ (985.33): C, 63.69; H, 6.37; N 2.73 %. Found: C, 63.56; H, 6.65; N, 2.73 %.

LinBr

K[N(SiMe$_3$)$_2$] (29 mg, 0.80 mmol) was added into a slurry of LH$_2$ (200 mg, 0.20 mmol), in THF (10 mL), at 25 °C. The deprotonation reaction was monitored, by $^{31}$P($^1$H) NMR spectroscopy, in C$_6$D$_{16}$, by a resonance shift from 40.0 ppm (LH$_2$) to 25.4 ppm (LK$_2$). The insoluble potassium bromide salt was removed by filtration. InBr$_3$ (71 mg, 0.20 mmol) was added to the solution and was stirred, for 16 h, at 25 °C. The $^{31}$P($^1$H) NMR spectrum confirmed the formation of LinBr (singlet at 41.9 ppm). The potassium bromide salt was removed and the solvent was evaporated, under reduced pressure, to afford LinBr. LinBr was crystallized by the slow diffusion of hexane (2 mL) into a concentrated solution of LinBr in toluene (0.1 mL), at -40 °C. The product was isolated as white crystals (183 mg, 0.18 mmol, 89 %).
c = 14.9 Hz, C\text{\textsuperscript{16}}O-In), 142.3 (d, J_{P-C} = 10.5 Hz, o-PhC\text{\textsuperscript{16}}O-\text{\textsuperscript{1}Bu}), 136.0 (d, J_{P-C} = 15.3 Hz, p-PhC\text{\textsuperscript{16}}O-\text{\textsuperscript{3}Bu}), 133.8 (d, J_{P-C} = 9.4 Hz, o-PhH\textsubscript{2}), 132.6 (d, J_{P-C} = 12.4 Hz, o-PhH\textsubscript{2}), 132.4 (s, p-PhH\textsubscript{2}), 131.8 (s, p-PhH\textsubscript{2}), 129.7 (s, C\text{\textsuperscript{16}}O-PPh\textsubscript{2}), 129.1 (s, m-PhH\textsubscript{2}), 129.0 (s, m-PhH\textsubscript{2}), 128.7 (d, J_{P-C} = 12.4 Hz, 1), 126.6 (d, J_{P-C} = 13.6 Hz, 2), 107.2 (s, i-PhH\textsubscript{2}), 106.3 (s, i-PhH\textsubscript{2}), 45.9 (dd, d, J_{P-C} = 5.6 Hz, J_{P-C} = 13.1 Hz, N-CH\textsubscript{2}), 36.0 (s, o-C\text{\textsuperscript{16}}O(CH\textsubscript{2})\textsubscript{2}), 36.0 (s, p-C\text{\textsuperscript{16}}O(CH\textsubscript{2})\textsubscript{2}), 31.3 (s, o-\text{\textsuperscript{1}Bu}), 30.2 (s, p-\text{\textsuperscript{1}Bu}); \textsuperscript{31}P\textsuperscript{[\text{\textsuperscript{1}H}]} NMR (161 MHz, CDCl\textsubscript{3}, 298 K) \delta (ppm): 41.9 (s, P). Anal. Calc. for C\textsubscript{59}H\textsubscript{62}BrInN\textsubscript{2}O\textsubscript{2}P\textsubscript{2} (1028.27 g/mol): C, 62.98; H, 6.26; N 2.72 %. Found: C, 62.80; H, 6.38; N, 2.83 %.

\textbf{LinO'Bu\textsuperscript{5}}

K[N(SiMe\textsubscript{3})\textsubscript{2}] (160 mg, 0.80 mmol) was added into a slurry of ligand LH\textsubscript{2} (200 mg, 0.20 mmol), in THF (10 mL), at 25 °C. The deprotonation reaction was monitored, by \textsuperscript{31}P\textsuperscript{[\text{\textsuperscript{1}H}]} NMR in C\textsubscript{6}D\textsubscript{6}. After 16 h, the deprotonated product was obtained with a characteristic resonance at 25.4 ppm (LK\textsubscript{4}). The cloudy solution was filtered to remove the insoluble potassium bromide salt. InCl\textsubscript{3} (71 mg, 0.20 mmol) was added to the filtrate and the solution was stirred, for 16 h, at 25 °C. The \textsuperscript{31}P\textsuperscript{[\text{\textsuperscript{1}H}]} NMR spectrum, in C\textsubscript{6}D\textsubscript{6}, confirmed the formation of the In-Cl complex (singlet at 42.0 ppm). KO'Bu (23 mg, 0.20 mmol) was added and the solution was stirred for 4 h, at 25 °C. The \textsuperscript{31}P\textsuperscript{[\text{\textsuperscript{1}H}]} NMR spectrum, in C\textsubscript{6}D\textsubscript{6}, confirmed the formation of the complex (singlet at 40.3 ppm). The potassium chloride salt was removed by filtration and the filtrate was evaporated under reduced pressure. LinO'Bu was isolated as a white powder, after crystallization by the slow diffusion of hexane (2 mL) into a concentrated solution of LinO'Bu in THF (0.1 mL), at -40 °C (130 mg, 0.13 mmol, 63 %).

\textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) \delta (ppm): 7.78-7.75 (m, 4H, o-Ph), 7.74 (d, J_{H-H} = 2.4 Hz, 2H, 1), 7.50-7.42 (m, 4H, o-Ph), 7.11-7.05 (m, 6H, m-Ph or p-Ph), 7.00-6.85 (m, 6H, m-Ph or p-Ph), 6.59 (dd, J_{H-H} = 2.3 Hz, J_{H-P} = 17.00 Hz, 2H, 2), 3.11 (m, br, 2H, 3), 2.82 (m, br, 2H, 2H, 4), 1.97 (s, 18H, o-\text{\textsuperscript{1}Bu}), 1.44 (s, 9H, O'Bu), 1.12 (s, 18H, p-\text{\textsuperscript{1}Bu}); \textsuperscript{13}C\textsuperscript{[\text{\textsuperscript{1}H}]} NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) \delta (ppm): 171.1 (d, J_{P-C} = 15.1 Hz, C\text{\textsuperscript{16}}O-In), 142.9 (d, J_{P-C} = 12.4 Hz, o-PhC\text{\textsuperscript{16}}O-\text{\textsuperscript{1}Bu}), 135.7 (d, J_{P-C} = 14.9 Hz, p-PhC\text{\textsuperscript{16}}O-\text{\textsuperscript{3}Bu}), 134.3 (d, J_{P-C} = 9.4 Hz, o-PhH\textsubscript{2}), 132.9 (d, J_{P-C} = 9.5 Hz, o-PhH\textsubscript{2}), 132.2 (d, J_{P-C} = 13.5 Hz, C\text{\textsuperscript{16}}O-PPh\textsubscript{2}), 131.4 (s, p-PhH\textsubscript{2}), 130.9 (s, p-PhH\textsubscript{2}), 129.2 (s, m-PhH\textsubscript{2}), 128.8 (d, J_{P-C} = 4.2 Hz, 1), 128.6 (s, m-PhH\textsubscript{2}), 126.8 (d, J_{P-C} = 15.3 Hz, 2), 108.2 (s, i-PhH\textsubscript{2}), 107.2 (s, i-PhH\textsubscript{2}), 69.2 (dd, J_{P-C} = 10.4 Hz, J_{P-C} = 14.3 Hz, N-CH\textsubscript{2}), 46.6 (s, In-C\text{\textsuperscript{16}}O'Bu), 36.6 (s, o-C\text{\textsuperscript{16}}O(CH\textsubscript{2})\textsubscript{2}), 35.0 (s, O-(CH\textsubscript{2})\textsubscript{2}), 34.2 (s, p-C\text{\textsuperscript{16}}O(CH\textsubscript{2})\textsubscript{2}), 31.6 (s, o-\text{\textsuperscript{1}Bu}), 31.0 (s, p-\text{\textsuperscript{1}Bu}); \textsuperscript{31}P\textsuperscript{[\text{\textsuperscript{1}H}]} NMR (161 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) \delta (ppm): 40.3 (s, P). Anal. Calc. for C\textsubscript{59}H\textsubscript{62}BrInN\textsubscript{2}O\textsubscript{2}P\textsubscript{2} (1022.41 g/mol): C, 68.10; H, 7.19; N 2.74 %. Found: C, 67.87; H, 7.32; N, 2.82 %.
**LInOAc**

K[N(SiMe₃)₂] (160 mg, 0.80 mmol) was added into a slurry of LH₂ (200 mg, 0.20 mmol), in THF (10 mL), at 25 °C. The deprotonation reaction was monitored, by ³¹P{¹H} NMR in C₆D₆. After 16 h, the deprotonated product was obtained with a characteristic resonance at 25.4 ppm (LK₂). The insoluble potassium bromide salt was removed by filtration. InBr₃ (71 mg, 0.20 mmol) was added to the solution and it was stirred for 16 h, at 25 °C. The ³¹P{¹H} NMR spectrum, in C₆D₆, showed formation of LInBr (singlet at 41.9 ppm). The insoluble potassium bromide salt was removed by filtration and KOAc (25 mg, 0.25 mmol) was added to the filtrate. The solution was stirred for 16 h, at 25 °C. The ³¹P{¹H} NMR spectrum, in C₆D₆, confirmed the formation of LInOAc (singlet at 38.7 ppm). The potassium bromide salt was removed and the solvent was evaporated under reduced pressure. LInOAc was isolated as a white powder, after crystallization by the slow diffusion of hexane (2 mL) into a concentrated solution of LInOAc in THF (0.1 mL), at -40 °C (165 mg, 0.16 mmol, 72 %).

³¹H NMR (400 MHz, C₆D₆, 298 K) δ (ppm): 7.76 (d, ²J_H-H = 2.54 Hz, 2H, 1), 7.64 (bs, 8H, o-Ph), 6.95-7.10 (m, 12H, m+p-Ph), 6.71 (dd, ²J_H-H = 2.58 Hz, ³J_H-P = 17.07 Hz, 2H, 2), 3.01 (bs, 2H, N-C₄H₉), 2.84 (bs, 2H, N-CH₂), 1.87 (s, 9H, o-tBu), 1.85 (s, 3H, OAc), 1.13 (s, 18H, p-tBu); ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K) δ (ppm): 182.7 (s, CIV-O₂Me), 171.1 (d, J_P-C = 4.3 Hz, CIV-O-In), 109.3 (s, i-PPh), 108.3 (s, o-PPh), 47.1 (dd, J_P-C = 5.2 Hz, d, J_P-C = 11.5 Hz, N-CH₂), 36.2 (s, o-CIV(CH₃)₂), 34.0 (s, p-CIV(CH₃)₂), 31.7 (s, o-tBu), 30.5 (s, p-tBu), 20.2 (s, CIV₂Me); ³¹P{¹H} NMR (161 MHz, C₆D₆, 298 K) δ (ppm): 38.7 (s, P). Anal. Calc. for C₅₆H₆₇InN₂O₄P₂ (1008.83 g/mol): C, 63.63; H, 7.41; N, 3.59 %. Found: C, 63.78; H, 7.53; N, 3.49 %.

**LInNO₃**

K[N(SiMe₃)₂] (160 mg, 0.80 mmol) was added into a slurry of LH₂ (200 mg, 0.20 mmol), in THF (10 mL), at 25 °C. The deprotonation reaction was monitored, by ³¹P{¹H} NMR in C₆D₆. After 16 h, the deprotonated product was obtained with a characteristic resonance at 25.4 ppm (LK₂). The insoluble potassium bromide salt was removed by filtration. InCl₃ (71 mg, 0.20 mmol) was added to the solution and it was stirred for 16 h, at 25 °C. The ³¹P{¹H} NMR spectrum, in C₆D₆, showed formation of LInCl (singlet at 41.9 ppm). AgNO₃ (34 mg, 0.20 mmol) was added and the mixture was stirred, for 16 h, at 25 °C. The ³¹P{¹H} NMR spectrum, in C₆D₆, confirmed the formation of LInNO₃ (singlet at 40.8 ppm). The silver bromide salt was removed and the solvent was evaporated under reduced pressure. LInNO₃ was isolated as a white powder, after crystallization by the slow diffusion of hexane.
(2.0 mL) into a concentrated solution of LinNO₃ in THF (0.10 mL), at -40 °C (143 mg, 0.14 mmol, 68 %).

¹H NMR (400 MHz, C₆D₆, 298 K) δ (ppm): 7.75 (d, ³J_H-H = 2.62 Hz, 2H, 1), 7.54 (bs, 8H, o-Ph), 7.04 (bs, 4H, p-Ph), 6.98 (bs, 8H, m-Ph), 6.67 (dd, ³J_H-H = 2.57 Hz, ³J_H-p = 17.17 Hz, 2H, 2), 2.96 (bs, 2H, N-CH(H)), 2.76 (bs, 2H, N-CH(H)), 1.81 (s, 9H, o-²Bu), 1.12 (s, 18H, p-²Bu); ¹³C(¹H) NMR (126 MHz, C₆D₆, 298 K) δ (ppm): 169.7 (d, J_H-C = 3.6 Hz, CIV-O-In), 142.7 (d, J_H-C = 10.3 Hz, o-PhCIV-o-²Bu), 136.5 (d, J_H-C = 15.0 Hz, p-PhCIV-p-²Bu), 133.7 (bs, o-PPh), 132.8 (bs, o-PPh), 132.5 (bs, m-PPh), 131.35 (bs, m-PPh), 129.3 (d, J_H-C = 2.0 Hz, 1), 128.4 (s, p-PPh), 127.5 (s, p-PPh), 126.6 (d, J_H-C = 13.7 Hz, 2), 108.8 (s, i-PPh), 107.9 (s, i-PPh), 46.5 (dd, J_H-C = 4.6 Hz, d, J_H-C = 11.3 Hz N-Ch₂), 35.9 (s, o-CIV(CH₃)₂), 33.9 (s, p-CIV(CH₃)₂), 31.2 (s, o-²Bu), 29.8 (s, p-²Bu); ³¹P(¹H) NMR (161 MHz, C₆D₆, 298 K) δ (ppm): 40.9 (s, P). Anal. Calc. for CₙHₙLinNₙOₕP (1011.89 g/mol): C, 64.10; H, 6.38; N 4.15 %. Found: C, 63.96; H, 6.47; N, 4.28%.

AnvLinO'Bu

Sodium hydride (28.0 mg, 1.16 mmol) was added, with continuous stirring, to a slurry of ligand Anv LH₂ (204 mg, 0.19 mmol), in THF (10 mL), at 25 °C. After 16 h, a cloudy solution was afforded, and the ³¹P(¹H) NMR spectrum, in C₆D₆, showed formation of the deprotonated species (singlet at 25.2 ppm). The insoluble sodium bromide salts were removed. InCl₃ (42.8 mg, 0.19 mmol) was then added and the solution was stirred for 16 h. The ³¹P(¹H) NMR spectrum, in C₆D₆, of the afforded cloudy solution confirmed the formation of an indium chloride complex (singlet at 41.4 ppm). Potassium tert-butoxide (21.7 mg, 0.19 mmol) was then added to the mixture, yielding a cloudy solution. Stirring was continued, for 24 h, and the product analysed by ³¹P(¹H) NMR spectroscopy. The ³¹P(¹H) NMR spectrum, in C₆D₆, showed formation of the indium alkoxide species (singlet at 40.0 ppm). Insoluble salts were filtered and the solvent removed from the filtrate under reduced pressure. The brown residue was then dissolved in a cyclohexane: hexane mixture (2.0 mL, 1:2) and the product was isolated as colourless crystals (140 mg, 0.126 mmol, 68 %).

¹H NMR (400 MHz, C₆D₆, 298 K) δ (ppm): 7.74 (m, 4H, P-Ph), 7.58 (d, ³J_H-H = 2.6 Hz, 2H, 1), 7.44 (m, 4H, P-Ph), 7.09 (m, 4H, P-Ph), 6.96 (m, 6H, P-Ph), 6.51 (dd, ³J_H-H = 17.3 Hz, ³J_H-p = 2.5 Hz, 2H, 2), 3.10 (m, 2H, N-CH(H)), 2.83 (m, 2H, N-CH(H)), 2.71 (m, 2H, o-CIV(CH₂CH₃)(CH₃)₂), 2.48 (m, 2H, p-CIV(CH₂CH₃)(CH₃)₂), 1.90 (s, 6H, o-CIV(CH₂CH₃)(CH₃)₂), 1.83 (s, 6H, o-CIV(CH₂CH₃)(CH₃)₂), 1.44 (s, 9H, O'Bu), 1.10 (s, 12H, p-CIV(CH₂CH₃)(CH₃)₂), 1.04 (t, ³J_H-H = 7.4 Hz, 6H, o-CIV(CH₂CH₃)(CH₃)₂), 0.64 (t, ³J_H-H = 7.4 Hz, 6H, o-CIV(CH₂CH₃)(CH₃)₂); ¹³C(¹H) NMR (100 MHz, C₆D₆, 298 K) δ (ppm): 170.9 (d, J_H-C = 4.3 Hz, CIV-O-In), 148.2 (s, o-PhCIV-o-²Bu), 146.5 (s, p-PhCIV-p-²Bu), 134.3 (d, J_H-C = 9.3 Hz, PPh), 133.5 (d, J_H-C = 9.0 Hz, PPh), 132.9 (d, J_H-C = 9.6 Hz, PPh), 132.2 (s, PPh), 131.4 (s, PPh), 131.3 (s, 1), 130.6 (s, PPh), 129.2 (s, PPh), 128.8 (d, J_H-C = 11.8 Hz, 2), 128.7 (s, PPh), 128.6 (d, J_H-C = 11.4 Hz, PPh), 127.6 (d, ²J_H-C =
A cloudy solution was yielded and the insoluble potassium bromide salt was removed. 

K[N(SiMe\textsubscript{3})\textsubscript{2}] (130 mg, 0.64 mmol) was added into a slurry of ligand \textsuperscript{cumyl}LI\textsubscript{2} (200 mg, 0.16 mmol), in THF (10 mL), at 25 °C. The deprotonation reaction was monitored by \textsuperscript{31}P\textsuperscript{1}H NMR spectroscopy, in C\textsubscript{6}D\textsubscript{6}. After 16 h, the deprotonated product was obtained and showed a characteristic resonance at 20.9 ppm. A cloudy solution was yielded and the insoluble potassium bromide salt was removed. 

\textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) δ (ppm): 7.52-7.46 (m, 4H, o-PPh), 7.45 (d, J\textsubscript{H-H} = 2.6 Hz, 2H, 1), 7.43 (s, 2H, PPh or C-Ph), 7.38-7.30 (m, 2H, PPh or C-Ph), 7.27-7.19 (m, 4H, o-PPh), 7.19-7.13 (m, 8H, PPh or C-Ph), 7.13-7.00 (m, 12H, PPh or C-Ph), 7.00-6.87 (m, 10 H, PPh or C-Ph), 6.35 (dd, J\textsubscript{H-H} = 17.3 Hz, J\textsubscript{P-P} = 2.5 Hz, 2H, 2), 2.96 (m, 2H, N-CHH), 2.68 (m, 2H, N-CHH), 2.37 (s, 6H, o-PhCH\textsubscript{2}CH\textsubscript{3}), 2.10 (s, 6H, o-PhCH\textsubscript{2}CH\textsubscript{3}), 1.48 (s, 9H, O\textsuperscript{Bu}), 1.39 (s, 12 H, p-Ph(CH\textsubscript{3})\textsubscript{3}), \textsuperscript{13}C\textsuperscript{1}H NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) δ (ppm): \textsuperscript{31}P\textsuperscript{1}H NMR (162 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) δ (ppm): 170.6 (d, J\textsubscript{P-P} = 4.3 Hz, C\textsuperscript{IV}-O-In), 152.2 (s, o-PhC\textsuperscript{IV}-o\textsuperscript{-1}Bu), 151.3 (s, p-PhC\textsuperscript{IV}-p\textsuperscript{-1}Bu), 142.6 (s, J\textsubscript{P-P} = 9.3 Hz, C\textsuperscript{IV}-PPh), 135.7 (d, 1, J\textsubscript{P-P} = 14.3 Hz), 134.2 (d, J\textsubscript{P-P} = 9.3 Hz, PPh or C-Ph), 132.8 (s, PPh or C-Ph), 132.7 (d, J\textsubscript{P-P} = 9.9 Hz, PPh or C-Ph), 132.2 (s, PPh or C-Ph), 131.2 (s, PPh or C-Ph), 131.8 (s, PPh or C-Ph), 128.8 (d, J\textsubscript{P-P} = 4.3 Hz, 2), 127.7 (s, PPh or C-Ph), 127.0 (s, PPh or C-Ph), 125.5 (s, PPh or C-Ph), 125.0 (s, PPh or C-Ph), 110.1 (s, i-Ph), 109.1 (s, i-Ph), 69.4 (s, OC\textsuperscript{IV}(Me\textsubscript{3})), 54.4 (s, o-C\textsuperscript{IV}Ph(CH\textsubscript{3})\textsubscript{3}), 46.7 (dd, J\textsubscript{P-P} = 4.6 Hz, d, J\textsubscript{P-P} = 11.3 Hz, N-CH\textsubscript{3}), 44.3 (s, p-C\textsuperscript{IV}Ph(CH\textsubscript{3})\textsubscript{3}), 42.4 (s, o-C\textsuperscript{IV}PhCH\textsubscript{3}CH\textsubscript{3}), 35.1 (s, O\textsuperscript{Bu}), 31.5 (s, o-C\textsuperscript{IV}Ph(CH\textsubscript{3})\textsubscript{3}), 28.4 (s, o-C\textsuperscript{IV}PhCH\textsubscript{3}CH\textsubscript{3}).
**LinCHD**

*LinCHD* was only produced under NMR scale reaction. *LinO' Bu* (20 mg, 0.02 mmol) was dissolved in d₈-THF (0.5 mL) and charged in a J-Young NMR tube. CHD (2.5 mg, 0.02 mmol, 1 equiv.) was directly added to the previously made solution. The reaction was monitored by ¹H and ³¹P NMR spectroscopy. *LinCHD* was formed in less than 5 min at 25 °C. The product can be crystallised from slow diffusion of a saturated THF solution of *LinCHD*.

¹H NMR (400 MHz, C₆D₆, 298 K) δ (ppm): 7.74 (m, 6H, 1+ α-PPh), 7.43 (m, 4H, α-PPh), 7.10 (m, 6H, m-Ph or p-Ph), 6.98 (m, 3H, m-Ph or p-Ph), 6.90 (m, 3H, m-Ph or p-Ph), 6.57 (dd, 2H, ³J₆-H = 16.8 Hz, ⁴J₆-H = 2.0 Hz, 2), 3.58 (m, 2H, In-CH₂), 3.12 (m, 2H, N-CH₂), 2.82 (m, 2H, N-CH₂), 2.04 (m, 2H, In-CH₂), 1.93 (s, 18H, o-tBu), 1.51 (m, 2H, In-CH₂), 1.35 (m, 2H, In-CH₂), 1.25 (m, 2H, In-CH₂), 1.14 (s, 18H, p-tBu).

¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K) δ (ppm): 170.4 (d, ³J₆,13C = 3.2 Hz, CIV-O-In), 142.5 (d, ³J₆,13C = 3.1 Hz, CIV-o-Ph), 133.7 (d, ³J₆,13C = 9.1 Hz, PPh), 133.4 (s, PPh), 133.3 (s, PPh), 129.5 (m, PPh+1), 127.1 (s, CIVPh), 126.5 (d, ³J₆,13C = 9.6 Hz, PPh), 108.3 (s, CIV₃PPh), 107.3 (s, CIV₃PPh), 78.5 (s, In-CH₂), 46.5 (s, N-CH₂), 36.2 (s, o-CIV₃Bu) 34.9 (s, In-CH₂), 31.6 (s, In-CH₂), 31.5 (s, In-CH₂), 31.2 (s, o-CIV₃Bu), 30.5 (s, o-CIV₃Bu), 25.4 (s, In-CH₂) 22.7 (s, In-CH₂); ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K) δ (ppm): 41.0 (s, P).

**LinO₂CO' Bu**

*LinO₂CO' Bu* was only produced under NMR scale reaction. *LinO' Bu* (20 mg, 0.02 mmol) was dissolved in d₈-THF (0.5 mL) and charged in a J-Young NMR tube. The solution was degassed with one cycle of freeze pump-thaw. CO₂ was added and the reaction was monitored by ¹H and ³¹P NMR spectroscopy. *LinO₂CO' Bu* was generated in less than 5 min at 25 °C.

¹H NMR (400 MHz, d₈-THF, 298 K) δ (ppm): 7.78-7.66 (b m, 4 H, PPh₂), 7.66-7.45 (b.m, 12 H, PPh₂), 7.45-7.37 (b. m, 4H, PPh), 7.36 (d, ³J₆-H = 2.5 Hz, 2H, 1), 6.39 (dd, ³J₆-H = 17.2 Hz, ⁴J₆-H = 2.4 Hz, 2H, 2), 2.99 (m, 2H, N-CH₂H), 2.81 (m, 2H, N-CH₂H), 1.42 (s, 18H, o-tBu), 1.13 (s, 9H, In-O₂C₃Bu), 1.02 (s, 18H, p-tBu); ¹³C{¹H} NMR (126 MHz, d₈-THF, 298 K) δ (ppm): 171.3 (d, ³J₆,13C = 3.1 Hz, CIV-O-In), 164.9 (s, In-O₂CR), 142.7 (d, ³J₆,13C = 9.6 Hz, CIV-o-Ph), 136.2 (d, ³J₆,13C = 15.2 Hz, CIV₃-p-Ph), 135.1 (d, ³J₆,13C = 9.1 Hz, PPh), 133.7 (d, ³J₆,13C = 9.4 Hz, PPh), 133.7 (s, PPh), 133.4 (s, PPh), 129.5 (m, PPh+1), 119.11 (d, ³J₆,13C = 2.0 Hz, PhCIV₃PPh), 127.5 (d, ³J₆,13C = 13.5 Hz, 2), 110.7 (s, i-PPh), 109.8 (s, i-PPh), 79.0 (s, In-O₂C-O(CH₃)₃), 47.3 (s, N-CH₂), 34.7 (s, o-CIV₃Ph), 32.7 (s, p-CIV₃Ph), 31.9 (s, o-CIV₃Bu), 30.8 (s, p-CIV₃Bu), 28.6 (s, In-O₂C-O(CH₃)₃); ³¹P{¹H} NMR (162 MHz, d₈-THF, 298 K) δ (ppm): 38.7 (s, P).
Figure S3. $^1$H and $^{31}$P($^1$H) NMR spectra of LH$_2$ (CDCl$_3$, 298 K).

Figure S4. $^{13}$C($^1$H) NMR spectrum of LH$_2$ (CDCl$_3$, 298 K).
Figure S5. $^1$H and $^{31}$P($^1$H) NMR spectra of AmylLH$_2$ (CDCl$_3$, 298 K).

Figure S6. $^{13}$C($^1$H) NMR spectrum of AmylLH$_2$ (CDCl$_3$, 298 K).
Figure S7. $^1$H and $^{31}$P($^1$H) NMR spectra of $\text{CumylLH}_2$ (CDCl$_3$, 298 K), * correspond to remaining traces of petroleum ether.

Figure S8. $^{13}$C($^1$H) NMR spectrum of $\text{CumylLH}_2$ (CDCl$_3$, 298); * correspond to remaining traces of petroleum ether.
Figure S9. $^1$H NMR spectrum of L’H$_2$ (CDCl$_3$, 298 K).

Figure S10. $^{13}$C($^1$H) NMR spectrum of L’H$_2$ (CDCl$_3$, 298 K).
Figure S11. Molecular structure of $\text{L'InCl}$ with thermal ellipsoids at the 50% probability level, hydrogen atoms and a hexane molecule omitted for clarity.

Figure S12. $^1$H NMR spectrum of $\text{L'InCl}$ (CDCl$_3$, 298 K). * Traces of toluene
Figure S13. $^{13}$C($^1$H) spectrum of L’InCl (CDCl$_3$, 298 K). *Traces of toluene.

Figure S14. DOSY NMR analysis of L’InCl in d$_8$-THF (298 K).
Figure S15. $^1$H NMR and $^{31}$P($^1$H) NMR spectra of $\text{LLiCl}$ in CDCl$_3$ (298 K).

Figure S16. $^{13}$C($^1$H) NMR spectrum of $\text{LLiCl}$ (CDCl$_3$, 298 K).

Figure S17. DOSY NMR analysis of LInCl in d₈-THF (298 K).

Table S2. Polymerization results for LInCl and L’InCl with and without co-catalyst.

| Catalyst | Co-catalyst | Conversion (%) | % Carbonate linkages | % Polymer selectivity | % cis/trans CHC | $M_n$ | $Đ$ |
|----------|-------------|----------------|----------------------|-----------------------|----------------|------|-----|
| LInCl    | -           | 14             | 66                   | 94                    | 0/100          | 197000 | 2.0 |
|          |             |                |                      |                       |                | 7500   |     |
| L’InCl   | -           | 21             | <1                   | >99                   | -              | 416000 | 1.2 |
|          |             |                |                      |                       |                | 104000 |     |
| LInCl    | PPN-Cl      | 8              | >99                  | 0                     | 73/27          | -     | -   |
| L’InCl   | PPN-Cl      | 26             | >99                  | 43                    | 79/21          | 4300   | 1.2 |
| LInCl    | DMAP        | 10             | >99                  | 72                    | 0/100          | 600    | 1.2 |
| L’InCl   | DMAP        | trace          | -                    | -                     | -              | -     | -   |

Copolymerization conditions: [cat] = 0.1 mol%, 60 °C, 48 h, [cat]/[co-cat] = 1. a Determined by comparison of the integrals of signals arising from the methylene protons in the $^1$H NMR spectra due to copolymer carbonate linkages ($δ = 4.65$ ppm) and copolymer ether linkages (only for % polymer selectivity, $δ = 3.45$ ppm), and the signals due to the trans-cyclic carbonate ($δ = 4.00$ ppm), and cis-cyclic carbonate ($δ = 4.67$ ppm). b Determined by SEC, in THF, at 40 °C, calibrated using polystyrene standards.
Figure S18. $^1$H NMR spectra of the products obtained using LiInCl and L’InCl as catalysts at 60 °C and 1 bar of CO$_2$ after 48 h of reaction.

Figure S19. SEC traces obtained for PCHC catalysed by LiInCl (left), L’InCl (middle) and L’InCl+DMAP (right) at 60 °C and 1 bar of CO$_2$ after 48 h of reaction.
Figure S20. Molecular structure of LinBr with thermal ellipsoids at the 50% probability level, hydrogen atoms omitted for clarity.

Figure S21. $^1$H and $^{31}$P($^1$H) NMR spectra of LinBr in C$_6$D$_6$ (298 K) after the addition of a slight excess of THF. It can clearly be seen that the THF resonances stayed unchanged compared to "free" THF, indicating that the THF is not coordinated to indium in solution.
Figure S22. DOSY NMR analysis of LinBr in d$_8$-THF (298 K). As it can be seen from the DOSY, there is no mixing of the d$_8$-THF and LinBr resonances indicating that THF is not coordinating to indium in solution.

Figure S23. $^1$H NMR and $^{31}$P($^1$H) NMR spectra of LinBr in CDCl$_3$ (298 K).
Figure S24. $^{13}$C$^1$H NMR spectrum of LiInBr in CDCl$_3$ (298 K).

Figure S25. Molecular Structure of LiInO$^t$Bu with thermal ellipsoids at the 50% probability level, hydrogen atoms omitted for clarity.
Figure S26. DOSY NMR analysis of Li\textsubscript{In}O\textsubscript{t}Bu\textsubscript{i}n d\textsubscript{8}-THF (298 K).

Figure S27. \textsuperscript{1}H and \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectra of Li\textsubscript{In}O\textsubscript{t}Bu\textsubscript{i}n C\textsubscript{6}D\textsubscript{6} (298 K).
Figure S28. $^{13}$C$\left(^1\text{H}\right)$ NMR spectrum of Li$\text{N}^\text{Bu}_\text{O}$ ($\text{C}_6\text{D}_6$, 298 K).

Figure S29 Molecular Structure of Li$\text{N}^\text{OAc}$, with thermal ellipsoids at the 50% probability level, hydrogen atoms and a hexane molecule omitted for clarity.
Figure S30. Molecular Structure of $\text{LiInNO}_3$ with thermal ellipsoids at the 50% probability level, hydrogen atoms and a hexane molecule omitted for clarity.

Figure S31. DOSY NMR analysis of $\text{LiInOAc}$ in $d_8$-THF (298 K).
Figure S32. DOSY NMR analysis of LiInNO$_3$ in d$_8$-THF (298 K).

Figure S33. $^1$H and $^{31}$P($^1$H) NMR spectra of LiInOAc (C$_6$D$_{14}$, 298 K).
Figure S34. $^{13}$C(1H) NMR spectra of LiInOAc (C$_6$D$_6$, 298 K).

Figure S35. $^1$H NMR and $^{31}$P(1H) NMR spectra (C$_6$D$_6$, 298 K) of LiInNO$_3$. 
Figure S36. $^{13}$C($^1$H) NMR spectrum of $\text{LiInNO}_3$ ($\text{C}_6\text{D}_6$, 298 K).

Figure S37. Comparison of $^1$H NMR spectra of $\text{LiInBr}$ and $\text{LiInOAc}$ ($\text{C}_6\text{D}_6$, 298 K). For pentacoordinate $\text{LiInBr}$, 2 sharp multiplets, at 7.72 ppm and 7.41 ppm, are observed for the ortho-phenyl protons. For octahedral $\text{LiInOAc}$, a single broad signal at 7.60 is observed for the same protons. Similarly, the $m$- and $p$-phenyl protons differ between $\text{LiInBr}$ and $\text{LiInOAc}$. 
Figure S38. Variable temperature $^1$H NMR spectra of LiOAc in d$_8$-THF from 173 K to 333 K expanded in the phenyl region showing that the equilibrium between the two cis-β conformers can be frozen under 273 K.

Scheme S5. The proposed equilibrium between the two cis-β conformers observed for both LiOAc and LiNO$_3$.
Figure S39. $^1$H NMR spectra (CDCl$_3$, 298 K) of the products obtained using LiInX (X = Cl, Br, O'Bu, OAc, NO$_3$) at 60 °C and 1 bar of CO$_2$ after 48 h of reaction.

Figure S40. SEC traces obtained for PCHC catalysed by LiInCl (left), LiInO'Bu (middle) and LiInNO$_3$ (right) at 60 °C and 1 bar of CO$_2$ after 48 h of reaction.

Scheme S6. The proposed formation of cis-cyclohexene carbonate and trans-cyclohexene carbonate.
Figure S41. MALDI-ToF spectrum of PCHC, catalysed by cumylLInO\textsuperscript{Bu}.

Figure S42. \textsuperscript{1}H NMR spectra (d\textsubscript{8}-THF 298 K) of LInOAc before the addition of CHO (higher spectrum), after CHO addition (second spectrum from the top), after heating the mixture at 60 °C for 24 h (third spectrum from the top) and after heating the mixture at 60 °C for 48 h (lower spectrum).
Figure S43. Molecular structure of $\text{Amyl}_2\text{InO}_2\text{Bu}$ with thermal ellipsoids at the 50% probability level, hydrogen atoms and a THF molecule omitted for clarity.

Figure S44. $^1$H and $^{31}$P($^1$H) NMR spectra of $\text{Amyl}_2\text{InO}_2\text{Bu}$ ($C_6D_6$, 298 K).
Figure S45. $^{13}$C\([^{1}H\)] NMR spectrum of $^{*}$Amy$\text{Li}$OnBu ($C_6D_6$, 298 K).

Figure S46. DOSY NMR analysis of Amy$\text{Li}$OnBu ($d_8$-THF, 298 K).
Figure S47. $^1$H and $^{31}$P($^1$H) NMR spectrum of [CumylLi]$_2$OBu (C$_6$D$_6$, 298 K).

Figure S48. $^{13}$C($^1$H) NMR spectrum of [CumylLi]$_2$OBU (C$_6$D$_6$, 298 K).
Figure S49. DOSY NMR analysis of Cumyl\textsubscript{Li}O\textsubscript{Bu}(d\textsubscript{8}-THF, 298 K).

Figure S50. \textsuperscript{1}H NMR spectrum (CDCl\textsubscript{3}, 298 K) of products obtained with \#LiO\textsubscript{Bu}(Y = \textsuperscript{t}Bu, Amyl, Cumyl) at 60 °C and 1 bar of CO\textsubscript{2} after 48 h of reaction.
Figure S51. SEC traces obtained for PCHC catalysed by Li\text{OTBu} (left), Am\text{OLiBu} (middle) and Cum\text{OLiBu} (right) at 60 °C and 1 bar of CO\textsubscript{2} after 48 h of reaction.

Figure S52. 13C{\text{^1}H} NMR spectrum (CDCl\textsubscript{3}, 298 K) of PCHC catalysed by Li\text{OTBu}. The spectrum shows only the carbonyl region (CDCl\textsubscript{3}, 298 K). Peaks were assigned based on previously reported literature values.\textsuperscript{6,7}

Figure S53. 13C{\text{^1}H} NMR spectra of PCHC (298 K, CDCl\textsubscript{3}) catalysed by Am\text{OLiBu} expended in the carbonyl region.
Polymerization Stereochemistry and Mechanism for Stereocontrol:

- Bernoullian Statistical Analysis:

  Statistical analysis of tetrad distributions observed in the $^{13}$C{[$^1$H]} NMR spectra in the carbonyl region was used to determine the stereocontrol of the polymerization. The probability of racemic ($P_r$) or meso ($P_m$) enchainment was determined by solving the following equations. The predicted tetrads sequences are governed by:

  \[
  [mmmm] = P_m^4 + (1-P_m)^4 \quad [S1]
  \]
  \[
  [mmr] = P_m[(1-P_m)(1-2P_m+2P_m^2)] \quad [S2]
  \]
  \[
  [rmm] = P_m[(1-P_m)(1-2P_m+2P_m^2)] \quad [S3]
  \]
  \[
  [mrr] = P_m[(1-P_m)(1-2P_m+2P_m^2)] \quad [S4]
  \]
  \[
  [rrm] = P_m[(1-P_m)(1-2P_m+2P_m^2)] \quad [S5]
  \]
  \[
  [mmr] = 2P_m^2(1-P_m)^2 \quad [S6]
  \]
  \[
  [rmm] = 2P_m^2(1-P_m)^2 \quad [S7]
  \]
  \[
  [rrr] = 2P_m^2(1-P_m)^2 \quad [S8]
  \]

  $P_m$ was determined from the [mmm] and [mmr] peak (at 153.8 ppm) by solving the following equation (x being the [mmm] and [mmr] normalized integral):

  \[
  P_m^4 + (1-P_m)^4 + P_m[(1-P_m)(1-2P_m+2P_m^2)] = x \quad [S9]
  \]

  After rearrangement the equation is simplified to:

  \[
  3P_m^2 - 3P_m + 1 = x \quad [S10]
  \]

  The Bernoullian test B described by the equation below was used to assess the accuracy of the model. A value equal to 1 is indicative of a chain-end control mechanism:

  \[
  B = \frac{4P_m^2(1-P_m)^2}{[2P_m(1-P_m)]^2} \quad [S11]
  \]

Figure S54. $^{13}$C{[$^1$H]} NMR spectrum of PCHC (298 K, CDCl$_3$) catalysed by $\text{cumyl LiO}_2\text{Bu}$ expended in the carbonyl region.
Table S3. Comparison of observed tetrad concentrations to corresponding calculated statistical occurrences in iso-enriched PCHC catalysed by $^{t}$LiO$t$Bu (y = $^{t}$Bu, Amyl, Cumyl).

| Catalyst    | $P_m$ | $[mmm]+[mmr]$ | $[mrm]+[rrm]$ | $[rrr]$ | $B$  |
|-------------|-------|---------------|---------------|---------|------|
| $^{t}$LiO$t$Bu | 0.85  | 0.76          | 0.62          | 0.13    | 0.19 | 0.03 | 0.05 | 1.00 |
| Amyl$^{t}$LiO$t$Bu | 0.88  | 0.78          | 0.66          | 0.13    | 0.18 | 0.04 | 0.04 | 1.00 |
| Cumyl$^{t}$LiO$t$Bu | 0.92  | 0.86          | 0.80          | 0.14    | 0.14 | 0.03 | 0.02 | 1.00 |

Table S4. Polymerization data using $^{t}$LiO$t$Bu at different temperature (1 bar, 60 °C-100 °C) and pressures (80 °C, 1-40 bar).

| Catalyst | $P_{CO_2}$ (bar) | $T$ (°C) | Conversion (%) | TOF (h$^{-1}$) | % Carbonate linkages | % Polymer selectivity | $M_n$ (g/mol) | $D$ |
|----------|-----------------|----------|---------------|----------------|---------------------|----------------------|---------------|-----|
| $^{t}$LiO$t$Bu | 1               | 60       | 14            | 2.5            | >99                 | 83                   | 1400          | 1.23 |
| $^{t}$LiO$t$Bu | 1               | 80       | 31            | 6.5            | >99                 | 84                   | 2600          | 1.55 |
| $^{t}$LiO$t$Bu | 1               | 100      | 34            | 7              | >99                 | 86                   | 600           | 1.20 |
| $^{t}$LiO$t$Bu | 10              | 80       | 13            | 5.5            | >99                 | 87                   | 12 600        | 1.94 |
| $^{t}$LiO$t$Bu | 20              | 80       | 12            | 5              | >99                 | 71                   | 4 000         | 1.15 |
| $^{t}$LiO$t$Bu | 30              | 80       | 11            | 4.5            | >99                 | 72                   | 6 500         | 2.21 |
| $^{t}$LiO$t$Bu | 40              | 80       | 9             | 4              | >99                 | 75                   | 10 600        | 1.89 |

Copolymerization conditions: [cat] = 0.1 mol%, polymerizations at 1 bar of CO$_2$ were run for 48 h; polymerization at higher CO$_2$ pressure (10 bar, 20 bar, 30 bar and 40 bar of CO$_2$) were run for 24 h. *Determined by comparison of the integrals of signals arising from the methylene protons in the $^1$H NMR spectra due to copolymer carbonate linkages ($\delta = 4.65$ ppm), copolymer ether linkages ($\delta = 3.45$ ppm), and the signals due to the cyclic carbonate byproduct ($\delta = 4.00$ ppm). **Determined by SEC in THF calibrated using polystyrene standards.

Figure S55. $^1$H NMR spectra (298 K, CDCl$_3$) of the products formed with $^{t}$LiO$t$Bu at 1 bar of CO$_2$ and different temperatures (60-100 °C), after 48 h of reaction.
Figure S56. SEC traces obtained for PCHC, catalysed by LinO'Bu, at 80 °C (right spectrum) and 100 °C (left spectrum), for 48 h reaction at 1 bar of CO₂ pressure.

Figure S57. ¹H NMR spectrum (298 K, CDCl₃) and SEC trace of PCHC, obtained using cumyl LinO'Bu (0.1 mol %), at 80 °C, at 1 bar of CO₂.
Figure S58. $^1$H NMR spectra (298 K, CDCl$_3$) of products formed, with LinO$^\text{Bu}$, at 80 °C, at different pressures of CO$_2$ (1-40 bar), after 24 h of reaction.

Figure S59. SEC traces obtained for PCHC, catalysed by LinO$^\text{Bu}$, at 10 bar (top left), 20 bar (top right), 30 bar (bottom left) and 40 bar (bottom right) at 80 °C for 24 h.
Figure S60. CO$_2$/CHO ROCOP reaction performed in diethylcarbonate (1.5 mL) with LiN$\text{InO}_t$Bu (0.2 mol%), at 80 $^\circ$C.

Figure S61. Overlay of plots of the formation of [PCHC] vs. time for the copolymerization of CHO/CO$_2$ initiated from LiN$\text{InO}_t$Bu obtained at two different specific IR bands assigned to PCHC: C=O stretch at 1787-1731 cm$^{-1}$ (left) and a polymer mode at 1014 cm$^{-1}$ (right) at four catalyst concentration: ■: [In] = 20.24 mM, ●: [In] = 13.3 mM, ▲: [In] = 10 mM ▲: [In] = 8.4 mM. Initial rates are determined from the slope of the linear fitting of each band and correspond to 0-10 % conversion.
Figure 62. Plots of $k_{\text{obs}}$ against the concentration of catalyst ([In]) with various fits applied. Dashed lines represent data fits with variable orders: ♣: second order in catalyst, ▼: 1.5 order in catalyst, ▲: first order in catalyst, ●: 0.5 order in catalyst). The solid line represents the experimental data (■) obtained for the C=O stretch at 1787-1731 cm$^{-1}$.

Figure 63. Plot of the ln($k_{\text{obs}}$) vs. ln([In]) for the data obtained at the two different specific IR bands of PCHC [at 1787-1731 (▲), 1014 cm$^{-1}$ (■)].
Figure S64. $^1$H NMR spectrum obtained from the reaction of $\text{LiInO}^\text{tBu}$ and cyclohexene diol (CHD) after 5 min at 298 K which shows the formation of $\text{LiInCHD}$ and $^\text{tBuOH}$, ($C_6D_6$, 298 K).

Figure 65. $^{13}$C NMR spectrum obtained from the reaction of $\text{LiInO}^\text{tBu}$ and cyclohexene diol (CHD) after 5 min at 298 K which shows the formation of $\text{LiInCHD}$ and $^\text{tBuOH}$, ($C_6D_6$, 298 K).
Figure S66. Overlay of $^1$H NMR spectra with expansion from 0-4 ppm. $\text{LinO}^\text{Bu}$ (top spectrum), $\text{LinCHD}$ (middle spectrum) and CHD (bottom spectrum) showing the successful coordination of CHD to the metal centre ($\text{C}_6\text{D}_6$, 298 K). *Residual THF and hexane.

Figure S67. DOSY NMR spectrum of the reaction of $\text{LinO}^\text{Bu}$ and CHD ($\text{C}_6\text{D}_6$, 298 K). All the resonances corresponding to the Lin are aligned, while the resonances corresponding to the coordinated CHD are lower than expected. There is also some mixing between the resonances of the butanol (at 1.06 ppm) and CHD.
Figure S68. Ellipsoid representation at 50 % probability of the molecular structure of LiHCD. The CHD coordinated to indium and a molecule of uncoordinated CHD are present in two orientations in the crystal lattice (upper structure and lower structure). Hydrogen atoms, a hexane molecule and a THF molecule were removed for clarity.

Figure 69. $^{13}$C($^1$H) NMR spectrum ($d_8$-THF) of LiHCD$^{13}$Bu.
Figure S70. $^1$H NMR spectrum of the product of the CO$_2$ inserted product into LiInO$^t$Bu (d$_8$-THF, 298 K); * side product attributed to partial hydrolysis of LiInO$^t$Bu due to residual water in CO$_2$; * residual hexane.
Figure 71. $^1$H NMR spectrum of $\text{Li} \text{InO}_2\text{CO}_2\text{Bu}$ ($\text{C}_6\text{D}_6, 298$ K); *side product attributed to partial hydrolysis of $\text{Li} \text{InO}_2\text{Bu}$ due to residual water in CO$_2$.

Figure S72. Graph representing the initial rate of the CO$_2$ dissolution into THF (R.H.S) and the initial rate of the CO$_2$ insertion into indium alkoxide bond (L.H.S).
Figure S73. LHS: Ellipsoid representation at 50 % probability of the molecular structure of the white crystalline powder obtained from the reaction of PO/CO$_2$ catalysed by LInO'Bu. Hydrogen atoms, the disorder around the propylene bridge and one PO molecule have been removed for clarity. RHS: Schematic representation of the molecular structure.

Figure S74. Ellipsoid representation at 50 % probability of half of the molecular structure of the white crystalline powder obtained from the reaction of PO/CO$_2$ catalysed by LInO'Bu showing the coordination around indium. Hydrogen atoms and one PO molecule have been removed for clarity.
Figure S75. $^1$H NMR of the white crystalline precipitate collected from the reaction of $\text{Li} \cdot \text{InO} \cdot \text{Bu}$ with PO/CO$_2$ ($\text{C}_6\text{D}_6$, 298 K).

Figure 76. Solid state IR of [(LiInCO$_2$)$_2$POD].
Figure 77. $^1$H NMR spectra (d$_8$-THF) of [LInCO$_2$O$^\text{Bu}$] (298 K) before the addition of DMAP (lower spectrum), after the addition of DMAP (middle spectrum, 298 K) and at 190 K (top spectrum). * Residual THF.

Figure 78. DOSY NMR spectrum (d$_8$-THF, 298 K) of [LInCO$_2$O$^\text{Bu}$] in presence of DMAP. The red circles highlight the mixing observed between the resonances corresponding to DMAP and [LInCO$_2$O$^\text{Bu}$].
Table 5. Selected crystallographic details.

| Compound                  | (LInCO₂)₂POD          | LInBr          | LInCHD         | AmylLInO'Bu          |
|---------------------------|------------------------|----------------|----------------|----------------------|
| Chemical formula          | C₁₁₉H₁₄₆In₂N₄O₁₂P₄     | C₅₈H₂₂BrInN₂O₅P₂ | C₆₆H₈₂InN₂O₅P₂ | C₆₂H₈₁N₂O₃P₂In₄C₄H₈O |
| Formula weight            | 2177.91                | 1101.84        | 1181.13        | 1151.15              |
| Temp (K)                  | 150(2)                 | 150(2)         | 150(2)         | 173(2)               |
| Space group               | Orthorhombic, Pbcn     | Triclinic, P-1 | Triclinic, P-1 | Triclinic, P-1       |
| a (Å)                     | 17.5120(2)             | 12.0970(2)     | 12.7684(4)     | 12.8461(4)           |
| b (Å)                     | 18.3743(2)             | 13.7584(2)     | 15.1118(5)     | 16.1610(7)           |
| c (Å)                     | 35.2302(5)             | 17.4723(3)     | 19.4416(8)     | 16.2133(6)           |
| α (°)                     | 93.243(1)              | 89.598(3)      | 81.366(3)      | 81.366(3)            |
| β (°)                     | 93.243(1)              | 78.609(3)      | 69.926(3)      | 69.926(3)            |
| γ (°)                     | 98.039(2)              | 83.967(3)      | 82.584(3)      | 82.584(3)            |
| V (Å³)                    | 11336.0(2)             | 2866.11(8)     | 3656.7(2)      | 3114.8(2)            |
| Z                         | 4                      | 2              | 2              | 2                    |
| Dcalc (Mg/m³)             | 1.276                  | 1.277          | 1.073          | 1.227                |
| Crystal size (mm)         | 0.18 X 0.15 X 0.08     | 0.25 X 0.25 X 0.10 | 0.10 X 0.10 X 0.05 | 0.67 X 0.22 X 0.13 |
| Theta range for data collection (°) | 3.706 to 76.268 | 3.701 to 76.091 | 2.318 to 76.534 | 2.488 to 28.228 |
| μ (mm⁻¹)                  | 4.257 (Cu, Kα)         | 4.960 (Cu, Kα)| 3.323 (Cu, Kα)| 0.477 (Mo, Kα)       |
| Reflections collected     | 71487                  | 45256          | 40637          | 17977                |
| Unique reflections        | 11793 [Rint = 0.0488]  | 11832 [Rint = 0.0306] | 15110 [Rint = 0.0652] | 12228 [R(int) = 0.0211] |
| Data Completeness to [θ₀] | 100.0% [67.684]        | 100.0% [67.684] | 100.0% [67.684] | 98.3% [25.242]       |
| Data/restraints/parameters| 11793 / 34 / 670       | 11832 / 42 / 657 | 15110 / 598 / 893 | 12228 / 635 / 760   |
| R1 [I>2σ(I)] (all data)  | 0.0561 (0.0641)        | 0.0329 (0.0348) | 0.0528 (0.0616) | 0.0397 (0.0516)      |
| wR2 [I>2σ(I)] (all data) | 0.1316 (0.1350)        | 0.0807 (0.0844) | 0.1346 (0.1461) | 0.0922 (0.0989)      |
| Goodness-of-fit on F²     | 1.266                  | 1.049          | 1.024          | 1.043                |
| Largest diff. peak and hole (e Å⁻³) | 1.134 and -0.701 | 2.423 and -0.652 | 1.655 and -0.741 | 0.677 and -0.393 |
| Compound       | L'InCl                              | LiNO₃                                | LiNOAc                              |
|----------------|-------------------------------------|--------------------------------------|-------------------------------------|
| Chemical formula | C₃₂H₴₆ClInN₂O₂                      | C₆₆H₇₈InN₃O₅P₂                      | C₆₂H₸₁InN₂O₄P₂                      |
| Formula weight  | 640.98                              | 1098.01                              | 1095.04                              |
| Temp (K)        | 150(2)                              | 150(2)                               | 150(2)                              |
| Space group     | Orthorhombic, Pbca                  | Monoclinic, P2₁/c                    | Monoclinic, P2₁/c                    |
| a (Å)           | 19.8736(5)                          | 19.3561(3)                           | 19.3450(2)                          |
| b (Å)           | 9.6676(3)                           | 11.2195(2)                           | 11.1601(1)                          |
| c (Å)           | 34.8047(11)                         | 28.6971(6)                           | 28.8507(3)                          |
| α (°)           |                                    | 107.254(2)                           | 105.923(1)                          |
| β (°)           |                                    |                                     |                                     |
| γ (°)           |                                    |                                     |                                     |
| V (Å³)          | 6687.0(3)                           | 5951.6(2)                            | 5989.65(11)                         |
| Z               | 8                                   | 4                                    | 4                                   |
| Dcalcd (Mg/m³)  | 1.273                               | 1.225                                | 1.214                               |
| Crystal size (mm)| 0.22 X 0.050 X 0.001               | 0.20 X 0.10 X 0.05                   | 0.25 X 0.25 X 0.10                  |
| Theta range for data collection (°) | 4.450 to 76.280                  | 4.258 to 76.257                      | 4.270 to 76.274                     |
| μ (mm⁻¹)        | 6.592 (Cu, Kα)                      | 4.049 (Cu, Kα)                       | 4.003 (Cu, Kα)                      |
| Reflections collected | 32073                        | 41635                                | 62590                               |
| Unique reflections | 6923 [Rint = 0.0652]              | 12290 [Rint = 0.0500]                | 12458 [Rint = 0.0367]               |
| Data Completeness to [ θ ] | 100.0% [ 67.684 ]                | 100.0% [ 67.684 ]                    | 100.0% [ 67.684 ]                   |
| Data/restraints/parameters | 6923 / 0 / 343                | 12290 / 88 / 662                     | 12458 / 55 / 645                    |
| R1a (%) (all data) | 0.0739 (0.0997)                  | 0.0416 (0.0553)                      | 0.0382 (0.0432)                     |
| wR2b (%) (all data) | 0.1589 (0.1682)                  | 0.1057 (0.1144)                      | 0.1038 (0.1089)                     |
| Goodness-of-fit on F² | 1.188                           | 1.042                                | 1.031                               |
| Largest diff. peak and hole (e Å⁻³)| 1.590 and -1.798        | 1.20 and -0.731                      | 1.062 and -0.693                    |
Structural Refinement Details

\( \text{LinNO}_3, \text{LinOAC}, \text{LinCHD}, \) and \( \text{LinBr} \) were found to have disordered \( \text{tBu} \) moieties. The two predominate positions were found in the difference map and their occupancies were refined with a free variable. In most cases bond distances and thermal parameters were restrained to allow for a stable refinement.

The C24- and C53-based \( i \)-pentyl groups, the O70-based \( t \)-butoxide ligand, and the O80-based included THF solvent molecule in the structure of \( \text{Amyl LinO} \text{tBu} \) were all found to be disordered, and in each case two orientations were identified, of ca. 92:8, 72:28, 59:41 and 74:26% occupancy respectively. The geometries of each pair of orientations were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

\( \text{LinCHD} \) showed severe disorder of the O-Cy-OH moiety attached to indium. This group could be modelled in two locations with a refined occupancy of nearly 50%. This disorder subsequently affected the cocrystallized CHD, which is involved in hydrogen bonding. This too was modelled in two locations with the same free variable. Bond distances and thermal parameters were restrained to allow for stable refinement. After modelling this disorder, additional electron density still remained elsewhere in the unit cell which was too severely disordered to be modelled as solvent, thus the SQUEEZE\textsuperscript{17} protocol of the PLATON\textsuperscript{18} suite of programs was utilized.

The bridging dicarbonate, \( \text{O}_3\text{C-propylene-CO}_3 \), in \( (\text{LinCO}_2)_2\text{POD} \) was disordered over an inversion center resulting in \( \frac{1}{2} \) of the propylene methyl present in the asymmetric unit. This methyl was further disordered over two positions resulting in the identification of two methyl groups within the asymmetric unit, each of \( \frac{1}{4} \) occupancy. Bond distances and thermal parameters were restrained to allow for stable refinement.

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