Supplementary Information

Copolymerization of cyclohexene oxide with CO_2 catalyzed by tridentate N-heterocyclic carbene titanium(IV) complexes†‡

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Experimental

General considerations

Experiments were carried out under inert atmosphere using Schlenk and glovebox techniques (MBraun MB200B-G; <1ppm O_2, <1 ppm H_2O). Dichloromethane, hexane, THF and toluene were purified using Grubbs columns (MB Braun Solvent Purification System 800). Pentane, benzene-*d*$_6$, chloroform-*d*$_3$ were purchased from Sigma-Aldrich, dried over sodium or CaH_2, vacuum transferred, degassed and filtered prior to use. All other chemicals, (*R*,*R*)-*N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride and tetrachlorotitanium(IV) (1M in toluene)/tetra-*iso*-propoxytitanium(IV) were obtained from Sigma-Aldrich and Strem Chemical Inc., respectively, and used as received. The bis-(phenolate)-*N*-heterocyclic carbene ligand and complexes **1-3** were prepared according to the literature procedures.[1, 2, 3] [PPN]Cl and [PPN]NO_2 were recrystallized prior to use.[4] PPh_3, [Bu_4N]Cl and DMAP were dried under heat in vacuo before to be transfer in the glovebox. Cyclohexene oxide and were purchased from Sigma-Aldrich and was distilled from CaH_2 under vacuum following three freeze-pump-thaw cycles and stored at -30°C in a glove box. CO_2 (from *Yara Praxair AS*, purity grade: 99.999%) was purified through a stainless steel cylinders (48.2 x 597 mm) filled with activated copper(II) oxide on alumina (14-20 mesh loading 13%) and 3Å molecular sieves (pellets 1.6 mm).

The NMR spectra of air and moisture sensitive compounds were recorded by using *J. Young* valve NMR tubes at 25±1 °C on a *Bruker*-AVANCE-DMX400 spectrometer (5 mm BB, ^1H: 400.13 MHz; ^{13}C: 100.62 MHz) and a *Bruker*-BIOSPIN-AV500 (5 mm BBO, ^1H: 500.13 MHz; ^{13}C: 125.77 MHz). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported in ppm relative to TMS.

The molecular weights (M_n and M_w) and PDIs were determined by GPC-SEC from Viscotek. Polystyrene PS-99K (M_w = 98 kg mol^{-1}, IV = 0.477) and PS-250K (M_w = 234 kg mol^{-1}, IV = 0.763) calibration standards for molecular weight calibration were obtained from ViscotekTM (PolyCAL TDS-PS standards). Sample solutions (≈1.0 mg mL^{-1} in THF) were filtered through a syringe filter Whatmann® (0.45 µm pore size) prior to injection. Chromatographic separation of polyisoprene samples was performed at a column temperature of 40 °C with a flow-rate of 1 mL min^{-1}. SEC was performed with a pump supplied by Viscotek (GPCmax), employing two ViscoGel^{TM} columns (GMHHR-H columns (300 (L) x 7.8 mm (I.D.), 10 µm particle size, 100Å pore size). Signals were detected by means of a triple detection array (TDA 302) and calibrated against polystyrene standards ($M_w/M_n < 1.15$, from 1-400 kg mol^{-1}). The microstructure of the polycarbonates was examined by means of ^{1}H and ^{13}C NMR experiments at ambient temperature, using $CDCl_3$ as solvent.

Representative Procedure for Copolymerization CHO/CO_2 (Table 1, run 7)

In a glovebox, an oven-dried scintillation vial equipped with a magnetic stir bar, a solution of the [PPN]Cl cocatalyst (8 µmol) in CH_2Cl_2 (1 mL) was added under vigorous stirring to a solution of complex **3** (8 µmol) in CH_2Cl_2 (1 mL). After 15 min, the solvent was removed and dried for 5 hours under vacuum. The remaining solid was then dissolved in 2 mL of CHO (20 mmol, 2 mL), and placed in an autoclave reactor. The mixture was stirred at the desired pressure and temperature adjusted with a heated oil bath. After 24 h, the pressure was released at room temperature and an aliquot of the solution was taken for the characterization of crude material by ^{1}H NMR spectroscopy in $CDCl_3$. Then the reaction mixture was quenched with 1 mL of acidic methanol, precipitated with MeOH and dried overnight at 80 °C. The yield was determined gravimetrically after washing the polymer with MeOH and dried until constant weight.

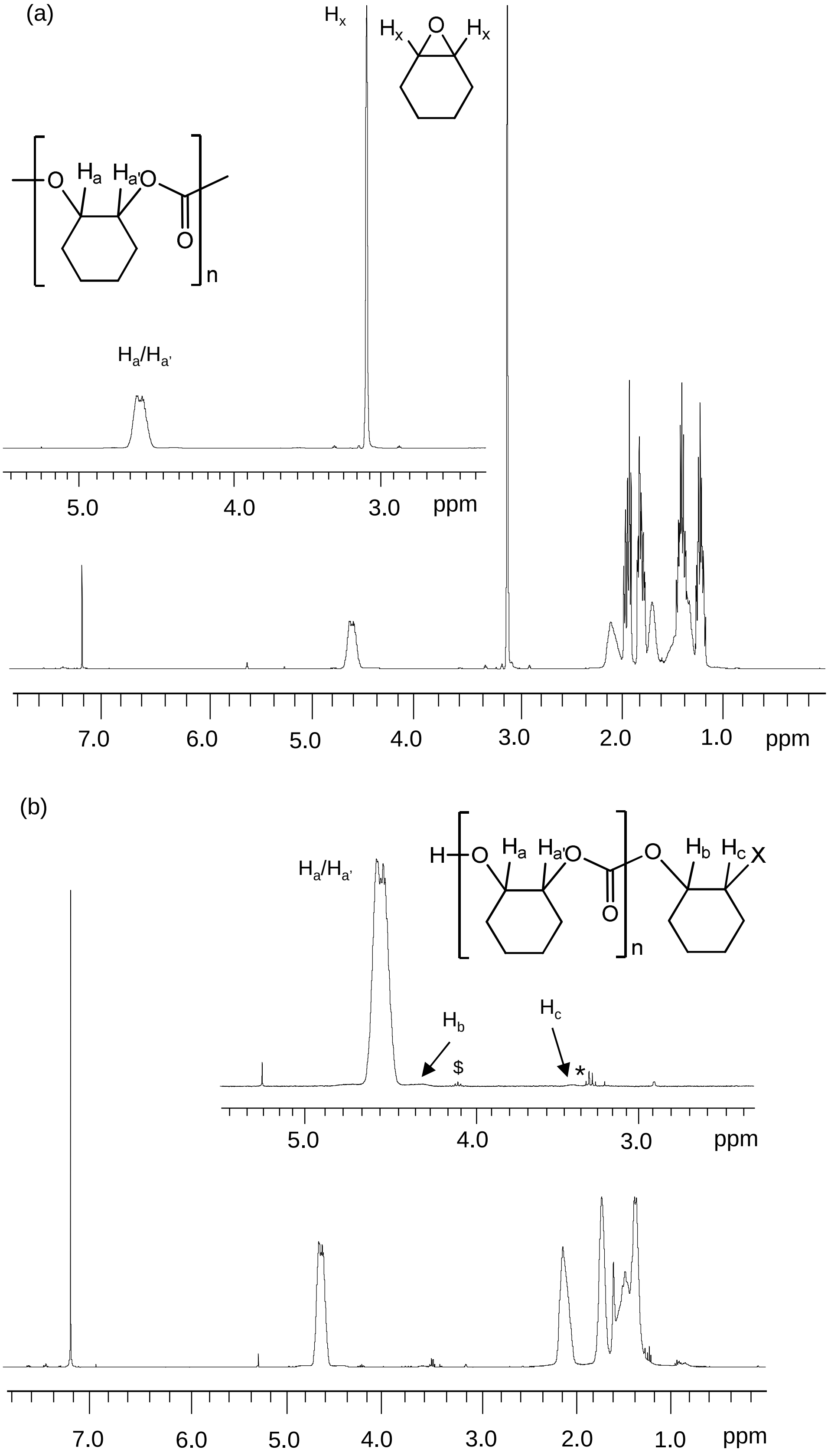


Figure S1. ^{1}H NMR spectra: (a) crude reaction mixture and (b) PCHC after extraction (Table 1, run 7). Traces of cyclohexene carbonate (CHC) at 4.10 ppm ($) and poly(cyclohexene oxide) (PCHO) at 3.55 ppm (*): ≤1%.

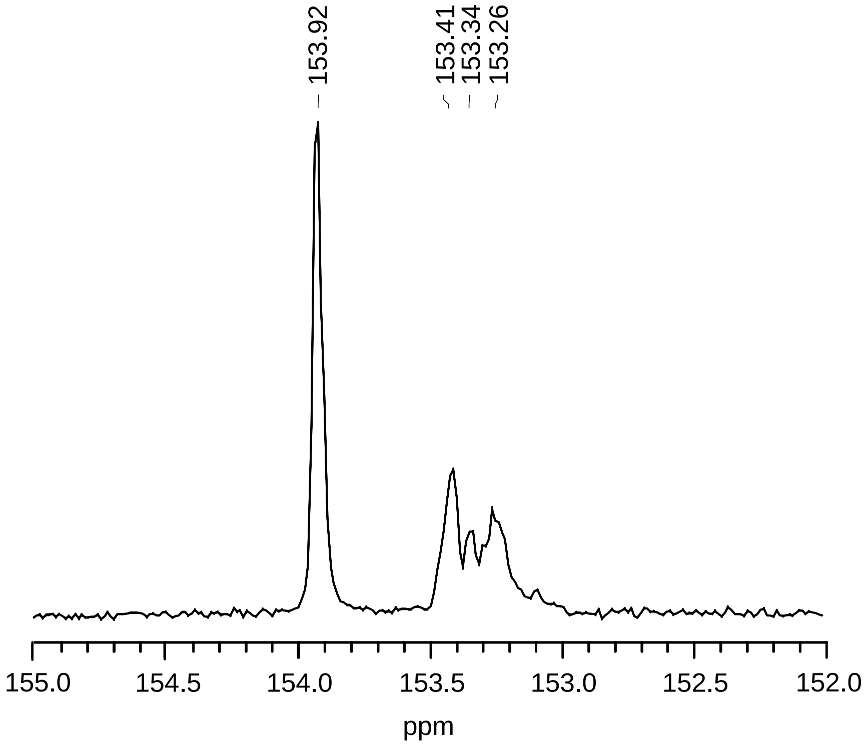


Figure S2. ^{13}C NMR of PCHC (Table 1, run 7).

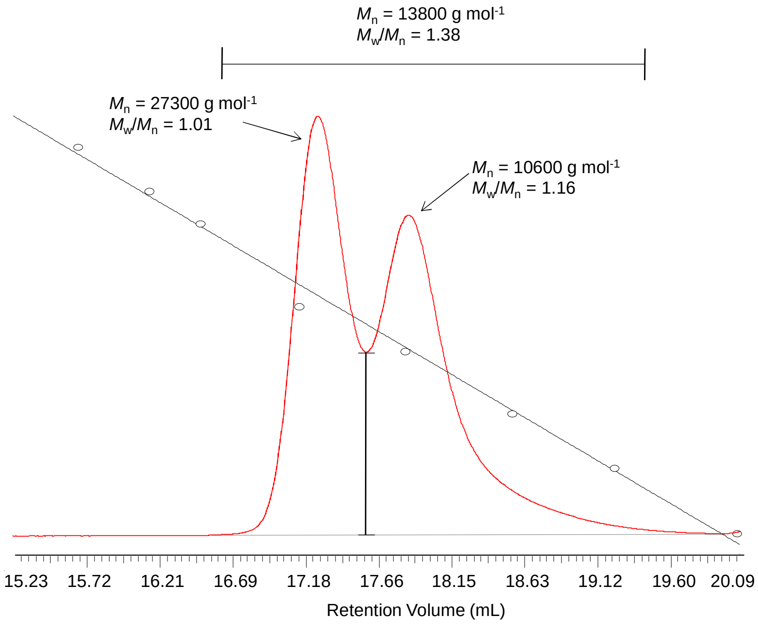


Figure S3. GPC-SEC profile of PCHC (Table 1, run 7, yield: 44%).

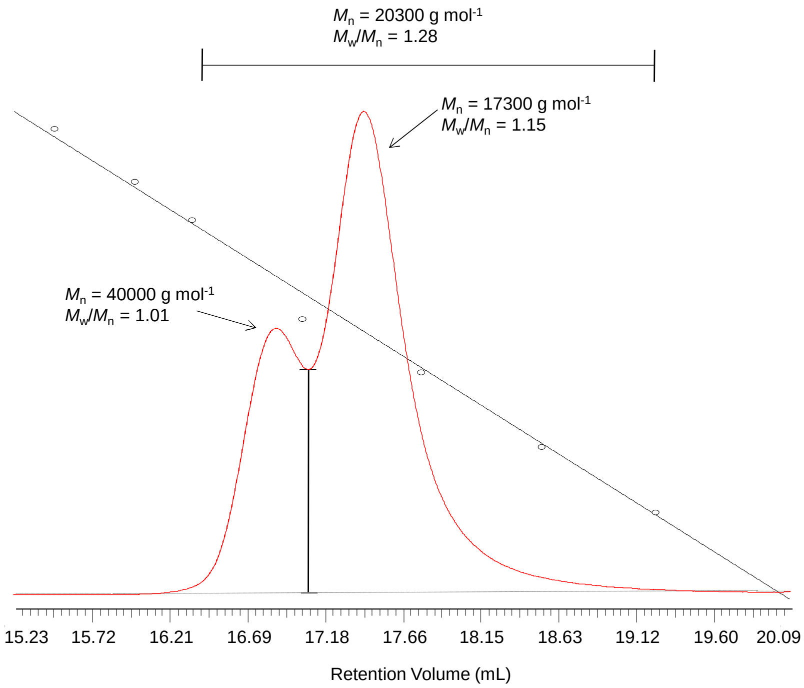


Figure S4. GPC-SEC profile of PCHC (Table 1, run 12, yield: 58%).

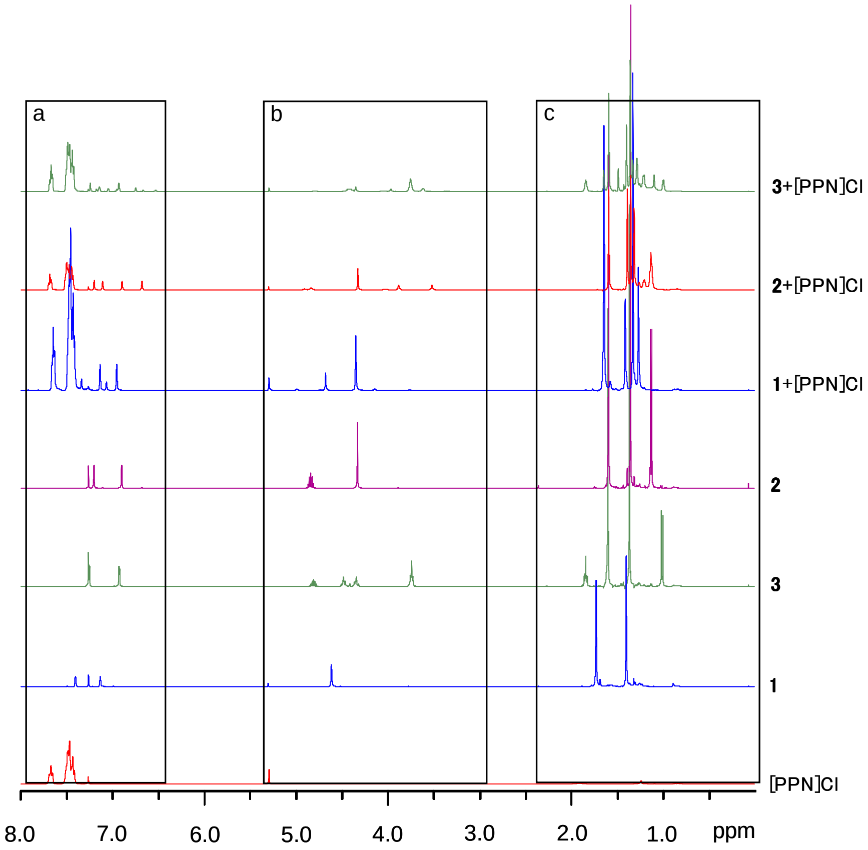


Figure S5. ^{1}H NMR spectra of complexes **1-3**, [PPN]Cl and complexes **1-3** after activation with 1 equiv. of [PPN]Cl in $CDCl_3$.

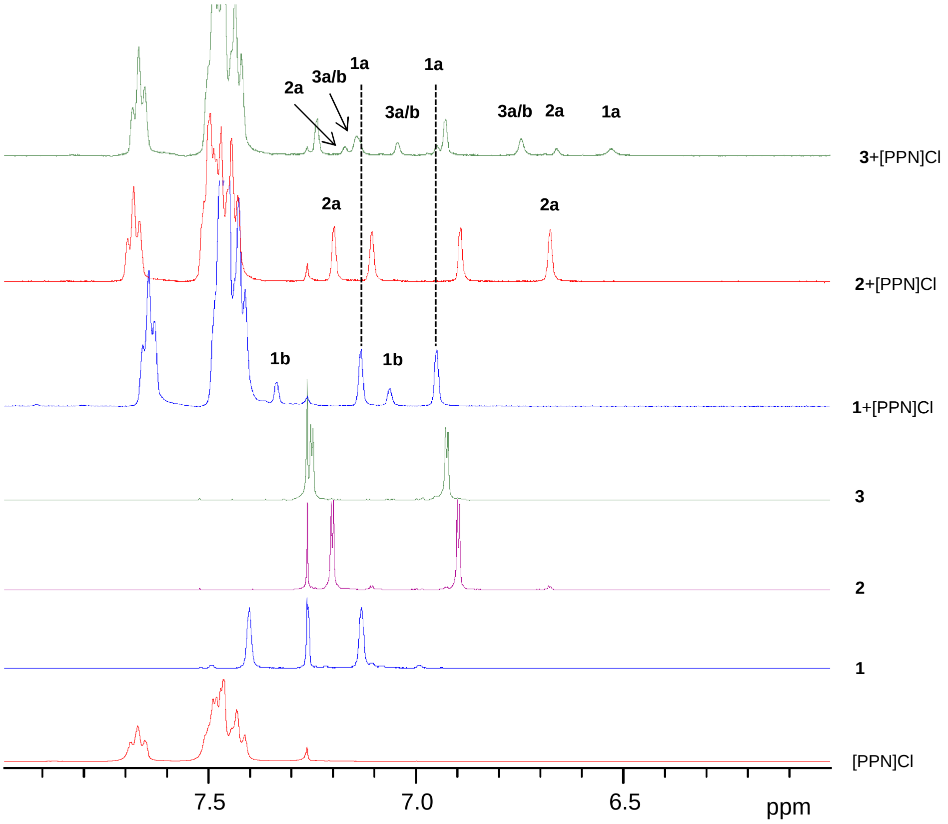


Figure S6. Magnified section (a) of Figure S5. Complex **1a** (<10%) chemical resonances are overlapping with major complexes **3** and **3a/b** peaks in **3**+[PPN]Cl spectrum.

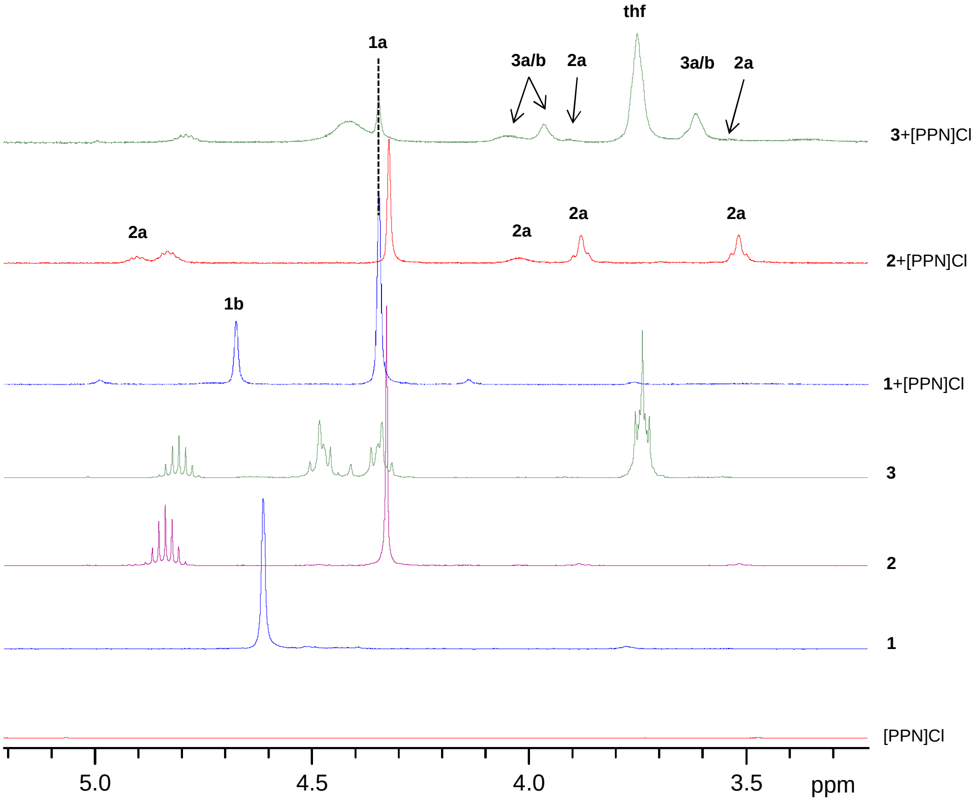


Figure S7. Magnified section (b) of Figure S5. Complex **2a** (<10%) chemical resonances are barely observable in **3**+[PPN]Cl spectrum.

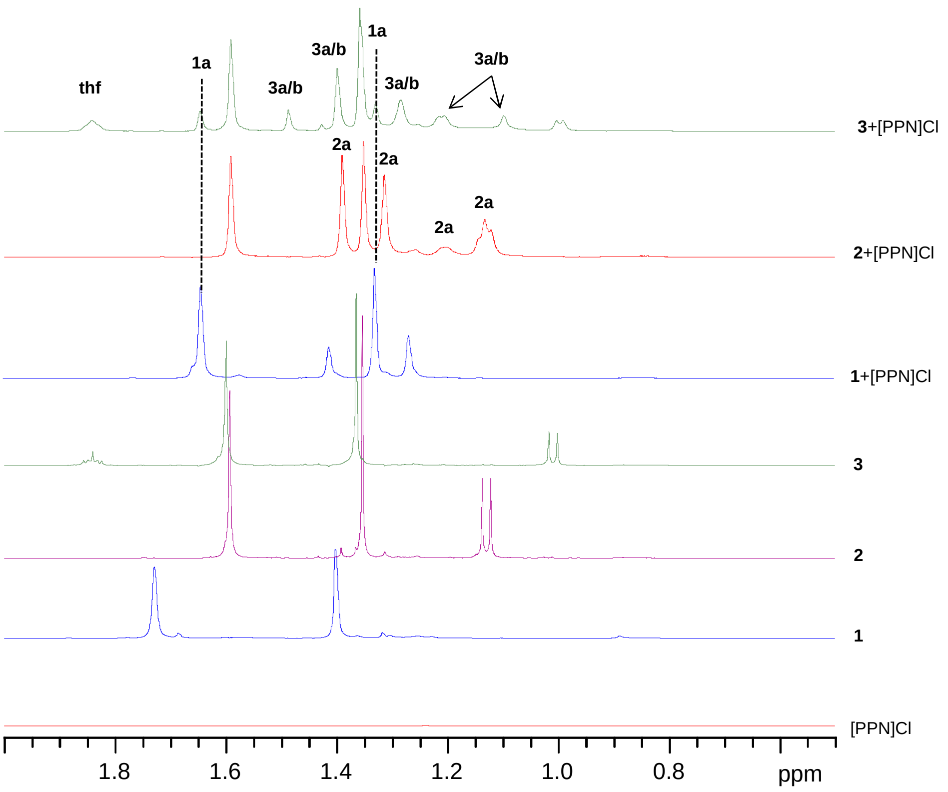
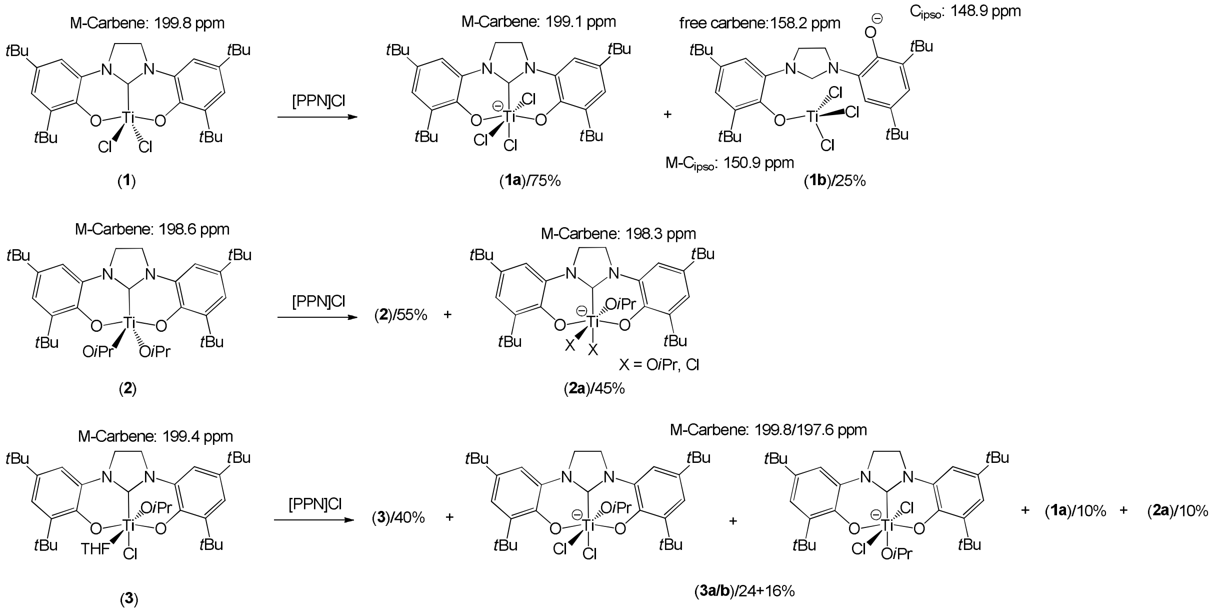


Figure S8. Magnified section (c) of Figure S5. Complex **2a** (<10%) chemical resonances are barely observable and overlapping with major complexes **3a/b** peaks in **3**+[PPN]Cl spectrum.



Scheme S1. Proposed activation pathway in presence of 1 equiv. of [PPN]Cl on **1-3** complexes (based on ^{1}H and ^{13}C NMR spectroscopy).

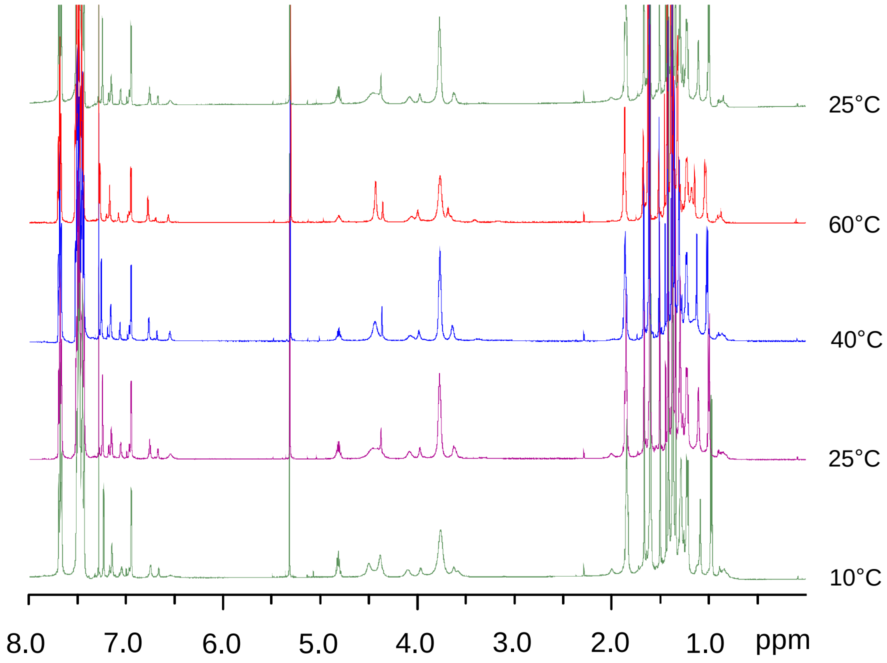


Figure S9. VT ^{1}H NMR spectra of complex **3** activated by 1 equiv of [PPN]Cl in the range of 10-60°C in $CDCl_3$.

Table S1 Pressure effect on the CHO/CO_2 copolymerization catalyzed by complex **3**/[PPN]Cl

Run[a]	P_{CO2} (bar)	Yield[b] (%)	Selectivity[c] (PCHC%)	TOF[d] (h^{-1})	M_n[e] (kg mol^{-1})	M_w/M_n[e]
1	2	34	≥99	35	7.4	1.45
2	20	36	≥99	37	7.8	1.42
3	25	34	≥99	35	6.8	1.41

[a] Polymerization procedure: 8 μmol of **3**, 8 μmol of [PPN]Cl, 20 mmol of CHO (2 mL), temp. = 60 °C for 24 h. [b] Yield determined gravimetrically. The lower yields observed (see Table 1, run 7) are attributed to the adventitious presence of moisture. [c] Measured by ^{1}H NMR spectroscopy in $CDCl_3$. [d] Turnover frequency = mol_{CHO} mol_{Ti}^{-1} h^{-1}. [e] Determined by GPC-SEC in THF at 30 °C against polystyrene standard.

References

1. K. S. Min, T. Weyhermüller, E. Bothe and K. Wieghardt, *Inorg. Chem.*, 2004, **43**, 2922-2931.
2. A. W. Waltman and R. H. Grubbs, *Organomettalics*, 2004, **23**, 3105-3107.
3. C. Romain, L. Brelot, S. Bellemin-Laponnaz and S. Dagorne, *Organomettallics*, 2010, **29**, 1191-1198.
4. A. Martinsen and J. Songstad, *Acta Chem. Scand.* , 1977, **31 A**, 645-650.