

# Copolymerization of cyclohexene oxide with CO<sub>2</sub> catalyzed by tridentate N-heterocyclic carbene titanium(IV) complexes†‡

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**A new class of complexes based on titanium(IV) bearing a bisanionic *mer*-tridentate N-heterocyclic carbene ligand were investigated for the copolymerization of cyclohexene oxide with CO<sub>2</sub>. Upon addition of [PPN]X' salts, all complexes were found to be active and highly selective toward the formation of poly(cyclohexene oxide-*alt*-carbon dioxide).**

N-heterocyclic carbene (NHC) ligands have become over the past few decades a major class of ancillary ligands for the development of late transition-metal catalysts.<sup>1</sup> With respect to early transition-metals, NHC ligands have received less attention due to their ease of dissociating from the metal center.<sup>2</sup> To overcome this limitation, multidentate NHC ligands with anionic tethers<sup>3</sup> have been designed to ensure an efficient NHC chelation onto early transition-metals.<sup>1e,g,h,4,5</sup> Hitherto few examples of tridentate bisanionic NHCs of group 4 have successfully been synthesized and investigated in catalysis.<sup>6</sup> Among the prominent examples, the Dagorne and Bellemine-Lapponnaz groups reported the use of tetravalent group 4 initiators supported by a *mer*-tridentate bis(phenolate)-NHC ([κ<sup>3</sup>-<sup>t</sup>BuOCO]-NHC) ligand exhibiting high activities and high control over the ring-opening polymerization (ROP) of *rac*-lactide.<sup>7</sup> Due to the properties of the [κ<sup>3</sup>-<sup>t</sup>BuOCO]-NHC pincer ligand, particularly its ability to bind a strong σ-donor (nucleophilic C<sub>carbene</sub>) in proximity to tetravalent metal centers in a planar constrained geometry, we were interested in assessing its usefulness for the copolymerization of epoxides with CO<sub>2</sub> which has never been explored before.

Indeed, since the seminal reports of Inoue in 1969 using a mixture of ZnEt<sub>2</sub>/H<sub>2</sub>O,<sup>8</sup> a plethora of catalysts based on divalent (Zn, Cd, Mg, Co) and trivalent (Al, Co, Cr, Fe, Mn, Ln) metal centers with a wide variety of ligands (mostly with

phenoxide, salen and β-diiminate type ligands) have been studied for various epoxides copolymerizing with CO<sub>2</sub>.<sup>9</sup> The only examples of active tetravalent metal (Ti, Zr, Ge and Sn) complexes, supported by a trisanionic tetradentate boxdipy ligand (boxdipy = 1,9-bis(2-oxido-phenyl)dipyrrinate) mimicking the salen-type ligands, were recently investigated by Nozaki and co-workers showing decent activities and high selectivities toward epoxides/CO<sub>2</sub> copolymerization especially for Ti(IV).<sup>10</sup> Thus, we report here for the first time the use of a bisanionic *mer*-tridentate NHC pincer ligand combined with a tetravalent titanium metal center ([κ<sup>3</sup>-<sup>t</sup>BuOCO]-NHC)Ti(X)<sub>2</sub>L (with X = Cl for **1**; X = OiPr for **2** and X = OiPr, Cl, L = THF for **3**) as catalysts for the copolymerization of cyclohexene oxide (CHO) with CO<sub>2</sub> (Chart 1).

Complexes **1–3** were initially evaluated, as CHO/CO<sub>2</sub> copolymerization catalysts, in neat CHO at 60 °C and under 10 bar of CO<sub>2</sub> for 24 h (Table 1). In the absence of a cocatalyst, the neutral complexes **1** and **3** showed only the formation of poly(cyclohexene oxide) (PCHO) rich in ether-linkage (≥99%) of relatively long-chain (*M*<sub>n</sub> = 83 and 56 kg mol<sup>−1</sup> for **1** and **3**, respectively) in low yield (Table 1, runs 1–3). The catalyst reactivity order, including the inactivity of complex **2**, are in accordance with the previous results arguing that poor *rac*-lactide ROP activity was observed due to the sterically congested complex **2**, impeding the formation of the putative active neutral 6-coordinate intermediate.<sup>7a</sup>

Moreover upon addition of anionic cocatalysts such as bis-(triphenylphosphine)iminium chloride or nitrite salts ([PPN]-X', with X' = Cl, NO<sub>2</sub>) to 5- and 6-coordinate neutral complexes **1–3** produced active and highly selective catalysts for CHO/CO<sub>2</sub>

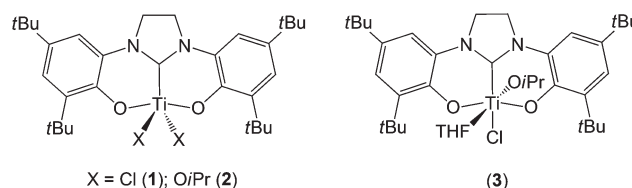


Chart 1

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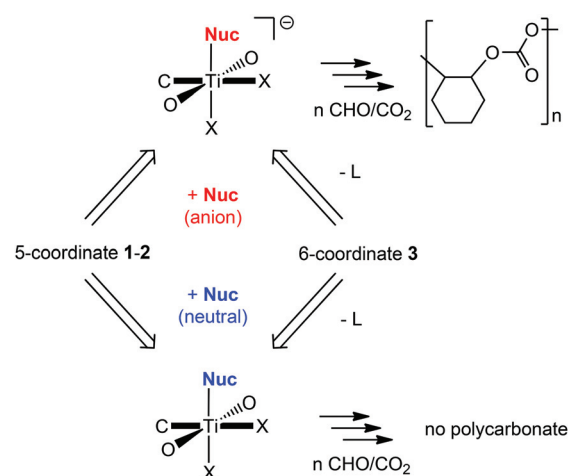
**Table 1** Cocatalysts effect on the CHO/CO<sub>2</sub> copolymerization catalyzed by complexes 1–3

Run <sup>a</sup>	Complex/cocat. <sup>b</sup> (equiv.)	Yield <sup>c</sup> (%)	Selectivity <sup>d</sup> (PCHO/PCHC%)	TOF <sup>e</sup> (h <sup>-1</sup> )	M <sub>n</sub> <sup>f</sup> (kg mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>f</sup>
1	1/None	15	≥99/0	16	83.2	3.04
2	2/None	0	—	—	—	—
3	3/None	5	≥99/0	5	56.3	2.29
4	1/[PPN]Cl (1)	38/27 <sup>g</sup>	0/≥99	40/29 <sup>g</sup>	12.5/5.7 <sup>g</sup>	1.28/1.30 <sup>g</sup>
5	1/[PPN]Cl (0.5)	9	0/≥99	10	3.2	1.25
6	2/[PPN]Cl (1)	27	0/≥99	28	8.0	1.37
7	3/[PPN]Cl (1)	44/32 <sup>g</sup>	0/≥99	46/20 <sup>g</sup>	13.8/6.2 <sup>g</sup>	1.38/1.46 <sup>g</sup>
8	3/[PPN]Cl (0.5)	16	0/≥99	17	4.2	1.32
9	3/[PPN]NO <sub>2</sub> (1)	12	0/≥99	12	n.d. <sup>h</sup>	n.d. <sup>h</sup>
11	(Boxdipy)TiCl/[PPN]Cl (1) <sup>i</sup>	45	0/≥99	76	13.0	1.27
12	(Salen)CrCl/[PPN]Cl (1) <sup>j</sup>	58	0/≥99	60	20.2	1.28

<sup>a</sup> Polymerization procedure: 8 μmol of precursor, 20 mmol of CHO (2 mL), P<sub>CO2</sub> = 10 bar at 60 °C for 24 h. <sup>b</sup> Catalyst pre-formation 15 min in CH<sub>2</sub>Cl<sub>2</sub> at 30 °C and dried for 5 h under vacuum. <sup>c</sup> Yield determined gravimetrically. <sup>d</sup> Measured by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> on the crude product. <sup>e</sup> Turnover frequency = mol<sub>CHO</sub> mol<sub>Ti</sub><sup>-1</sup> h<sup>-1</sup>. <sup>f</sup> Determined by GPC-SEC in THF at 30 °C against the polystyrene standard. <sup>g</sup> Adventitious presence of moisture (second run only). <sup>h</sup> n.d. = not determined. <sup>i</sup> See ref. 10 (time of reaction = 12 h). <sup>j</sup> Prepared according to ref. 11.

copolymerization into poly(cyclohexene-*alt*-carbonate) (PCHC) (Table 1, runs 4–9). The best activity was obtained for 6-coordinate complex 3 activated by [PPN]Cl with a TOF (turnover frequency) reaching 46 h<sup>-1</sup> which is very close to the benchmark catalysts (boxdipy)TiCl/[PPN]Cl<sup>10</sup> and (salen)CrCl/[PPN]Cl<sup>11</sup> under similar reaction conditions (TOFs = 76 and 60 h<sup>-1</sup>, respectively, Table 1, runs 11–12). Based on the <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy, all copolymers present a high degree of carbonate-linkage (≥99%) without other products derived from side reactions, *i.e.* cyclohexene carbonate (CHC), and show atactic configurations (ESI, Fig. S1–2<sup>†</sup>).<sup>12</sup> All PCHCs synthesized by [PPN]X'-activated complexes 1–3 and the benchmark (salen)-CrCl/[PPN]Cl system gave narrow, but bimodal, polydispersities (M<sub>w</sub>/M<sub>n</sub> ranging from 1.25 to 1.46) indicative of controlled polymerization (ESI, Fig. S3–4<sup>†</sup>). The molecular weights measured for these PCHCs catalyzed by 1–3/[PPN]X' or (salen)CrCl/[PPN]Cl are lower than the expected theoretical values (*e.g.* M<sub>calcd</sub> = 156 kg mol<sup>-1</sup>; Table 1, run 7). The low M<sub>n</sub> values are tentatively attributed to chain transfer due to the adventitious presence of moisture (Table 1, runs 4 and 7, second run) and/or possible monomer enchainment on both *trans* and *cis* sides to the Ti–C<sub>carbene</sub> bond.<sup>13,14</sup>

The addition of 1 equiv. of a neutral base such as DMAP (4-dimethylaminopyridine) or PPh<sub>3</sub> to 5- and 6-coordinate complexes 1 and 3, respectively, did not lead to the production of polycarbonates. The activation by anionic [PPN]X' cocatalysts on either the 5- or 6-coordinate ([κ<sup>3</sup>-*t*BuOCO]-NHC)Ti(X)<sub>2</sub>L complexes seems to have a predominant role toward the formation of active anionic 6-coordinate intermediates compared to their neutral 6-coordinate analogues (Scheme 1). Corroborating the influence of the anionic cocatalyst [PPN]Cl over the formation of active anionic ([κ<sup>3</sup>-*t*BuOCO]-NHC)Ti species from complexes 1–3, a larger amount did not lead to the formation of PCHC. Interestingly, the coordination of [PPN]Cl (including an excess) to the Lewis acid metal centers is often described as a reversible exchange, which is able to increase the electron density on the metal centers favoring the formation of the anionic 6-coordinate *trans*-(salen)MX<sub>2</sub> and labilizing the *trans* ligand to it.<sup>9c,15</sup> In our case, an excess of ion chloride on complexes 1–3 has a

**Scheme 1** Proposed activation pathway upon addition of anionic ([PPN]X') or neutral (DMAP, PPh<sub>3</sub>) cocatalysts to 5- and 6-coordinate 1–2/3 complexes (L = THF, Nuc = nucleophile).

detrimental effect on the catalysis as already observed with (salen)CrCl complexes for instance.<sup>13f</sup> In contrast, a substoichiometric amount of [PPN]Cl on complexes 1 and 3 show a reduced activity (Table 1, runs 5 and 8) indicating a decrease in the concentration of anionic 6-coordinate intermediates diminishing the overall yield in PCHCs.<sup>10,13d,f,16</sup> Additionally, the less interacting and sterically encumbered [PPN]<sup>+</sup> cation appears to greatly affect the formation of the active putative anionic 6-coordinate Ti-based intermediate.<sup>13f,17</sup> Indeed the use of 1 equiv. of [nBu<sub>4</sub>N]Cl salt (tetrabutylammonium chloride) as an anionic cocatalyst with complex 3, with a more interacting [nBu<sub>4</sub>N]<sup>+</sup> cation, did not afford the formation of polycarbonate.

The combination of ([κ<sup>3</sup>-*t*BuOCO]-NHC)Ti(X)<sub>2</sub>L complexes 1–3 in conjunction with [PPN]X' cocatalysts efficiently enhances the catalytic activity of the alternating copolymerization of CO<sub>2</sub> and CHO. This effect could be attributed to the sp<sup>2</sup>-hybridized carbene (strong σ-donor) on the NHC ligand, reducing the Lewis acidity of the metal center and facilitating the reversible binding of epoxide/cocatalyst in the apical

position. Furthermore, the solid-state structure confirms that the 5-coordinate complex **1** can easily accommodate a THF molecule in the apical position and once coordinated, the Cl ligand in *trans* to the Ti–C<sub>carbene</sub> is more elongated than the one in *cis* (2.27 → 2.35 Å).<sup>7a</sup> When comparing solid-state structures of both 6-coordinate **1**-THF adduct and **3** complexes,<sup>7a</sup> the THF is closer to the metal center for the 6-coordinate **1**-THF adduct than the THF in complex **3** (2.12 → 2.27 Å) indicating that the steric hindrance and the *trans* effect from the co-ligands (Ti–Cl: 2.32 Å for **1**-THF and Ti–OiPr: 1.77 Å for **3**) could greatly affect the binding of the incoming THF donor molecule or by larger extent the epoxide and/or nucleophile.<sup>7a</sup>

A preliminary investigation by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies of complexes **1–3** activated by 1 equiv. of [PPN]Cl at room temperature in CDCl<sub>3</sub>, show that all chemical resonances of protons and the Ti–C<sub>carbene</sub> are shifted in the upfield region (ESI, Fig. S5–8 and Scheme S1†) indicating an increase in electron density on the Ti, which is consistent with the formation of the proposed anionic 6-coordinate intermediates in Scheme 1.<sup>18</sup> Nevertheless, there is some disparity toward the complexes activation due to the electronic/steric parameters induced by the co-ligands. The <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy of complex **1**/[PPN]Cl shows also the partial decooordination of the tridentate NHC ligands (25%), while only 45% of anionic 6-coordinate intermediates are observed when **2** is activated by [PPN]Cl. Upon addition of [PPN]Cl on complex **3**, the <sup>1</sup>H/<sup>13</sup>C NMR spectroscopies display the formation of 60% of the anionic 6-coordinate intermediates including the formation of similar anionic 6-coordinate intermediates observed for [PPN]-Cl-activated **1** and **2** (10% each), arising from the redistribution of Cl ↔ OiPr co-ligands (ESI, Scheme S1†). The overall catalytic results trend in combination with the NMR studies indicate that complex **3** has a superior catalytic performance over its congeners and could be tentatively attributed to: (a) the higher amount of active intermediates (in comparison with sterically congested complex **2**), (b) the important *trans* effect arising from the –OiPr co-ligand facilitating the (de-) coordination of the incoming epoxide/growing polymer chain and (c) less prone to decomposition (NHC decooordination) as observed for complex **1** once activated by [PPN]Cl.<sup>19</sup>

The variation of catalyst loading at fixed concentration of neat CHO (10 M) at the same aforementioned conditions and reaction time shows an improvement in the overall yield of PCHC at higher concentrations and a low yield for lower concentration of **3**/[PPN]Cl (Table 2, runs 1–4). The stagnation in catalytic performance at higher catalyst concentrations (Table 2, runs 3 and 4) has been already observed for other systems under similar conditions due to a mass transfer problem (the solidification of the reaction mixture hampers further conversion).<sup>13b,20</sup> To overcome the mass transfer problem, the reactions were performed with CHO and toluene as co-solvents in a 2 : 1 ratio (Table 2, run 5). The dilution of CHO to 6.6 M shows a great improvement in copolymer yield, reaching 77% for a concentration of 8 mM of **3**/[PPN]Cl. Further dilution of both **3**/[PPN]Cl and CHO in toluene (ratio 2 : 2) shows a decrease in the production of PCHC (Table 2,

**Table 2** Effect of the concentration of complex **3**/[PPN]Cl and CHO on the CHO/CO<sub>2</sub> copolymerization

Run <sup>a</sup>	[CHO] (M)	[ <b>3</b> /[PPN]Cl] <sup>b</sup> (mM)	Yield <sup>c</sup> (%)	TOF <sup>d</sup> (h <sup>−1</sup> )	M <sub>n</sub> <sup>e</sup> (kg mol <sup>−1</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>e</sup>
1	10	2	11	24	n.d. <sup>f</sup>	n.d. <sup>f</sup>
2	10	4	44	46	13.8	1.38
3	10	8	59	31	14.6	1.28
4	10	12	57	20	16.5	1.31
5	6.6	8	77	27	15.8	1.27
6	5	4	26	14	4.8	1.39

<sup>a</sup> Polymerization procedure: P<sub>CO2</sub> = 10 bar at 60 °C for 24 h. <sup>b</sup> Catalyst pre-formation 15 min in CH<sub>2</sub>Cl<sub>2</sub> at 30 °C and dried for 5 h under vacuum. <sup>c</sup> Yield determined gravimetrically. <sup>d</sup> Turnover frequency = mol<sub>CHO</sub> mol<sub>Ti</sub><sup>−1</sup> h<sup>−1</sup>. <sup>e</sup> Determined by GPC-SEC in THF at 30 °C against the polystyrene standard. <sup>f</sup> n.d. = not determined.

run 6). These results show a dependence on **3**/[PPN]Cl and CHO concentrations indicating that the activated ([κ<sup>3</sup>-*t*BuOCO]-NHC)Ti species proceed presumably *via* a cooperative intermolecular mechanism of the epoxide ring-opening similar to other [PPN]X'-activated salen-type Cr(III) complexes, for instance.<sup>13f,16d,20b,21</sup>

In order to optimize the catalytic performance, the copolymerization of CHO and CO<sub>2</sub> was investigated at different temperatures and CO<sub>2</sub> pressures (Table S1† and Table 3). The catalytic system **3**/[PPN]Cl shows no significant change in activity and selectivity both at low (2 bar) and high pressure of CO<sub>2</sub> up to 25 bar (ESI, Table S1†). This catalytic system is the first example of tetravalent Ti working almost at atmospheric pressure and these trends are in agreement with the previous study on (boxdipy)TiCl/[PPN]Cl, where higher pressure in CO<sub>2</sub> did not show any significant effect on the alternating epoxide/CO<sub>2</sub> copolymerization.<sup>10</sup> However, the decrease in polymerization temperature (<60 °C) diminishes the overall yields and TOFs while raising the temperature at 80 °C led to a more efficient catalytic system (TOF = 55 h<sup>−1</sup>) with similar selectivity in PCHC (≥99%) but with lower molecular weight and higher polydispersity (Table 3, run 4).<sup>22</sup> These data indicate that the enhanced activity is most likely due to a better homogeneity of the reaction mixture as well as the catalyst **3**/[PPN]Cl is thermally robust at high temperature.

**Table 3** Temperature effect on the CHO/CO<sub>2</sub> copolymerization catalyzed by complex **3**/[PPN]Cl

Run <sup>a</sup>	Temperature (°C)	Yield <sup>b</sup> (%)	TOF <sup>c</sup> (h <sup>−1</sup> )	M <sub>n</sub> <sup>d</sup> (kg mol <sup>−1</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
1	30	10	11	3.8	1.32
2	45	19	20	7.3	1.32
3	60	44	46	13.8	1.38
4	80	53	55	8.3	1.53

<sup>a</sup> Polymerization procedure: 8 μmol of **3**, 8 μmol of [PPN]Cl, 20 mmol of CHO (2 mL), P<sub>CO2</sub> = 10 bar for 24 h. <sup>b</sup> Yield determined gravimetrically. <sup>c</sup> Turnover frequency = mol<sub>CHO</sub> mol<sub>Ti</sub><sup>−1</sup> h<sup>−1</sup>. <sup>d</sup> Determined by GPC-SEC in THF at 30 °C against the polystyrene standard.



## Conclusions

In the present study, we reported the first tetravalent NHC titanium complexes which were examined as a new family of catalysts for the coupling of CHO with CO<sub>2</sub>. The present systems [PPN]X'-activated complexes are active, providing a high degree of CO<sub>2</sub> insertion producing completely alternating polycarbonates under low pressure of CO<sub>2</sub>. The present catalytic systems also offer attractive advantages for the future development of a sustainable process such as: (a) Ti is more environmentally benign than Cr/Co metals, and (b) NHC ligands are easily accessible with unique and readily tunable properties. Thus, this novel class of catalysts opens a new avenue for the copolymerization of epoxides with CO<sub>2</sub>.

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