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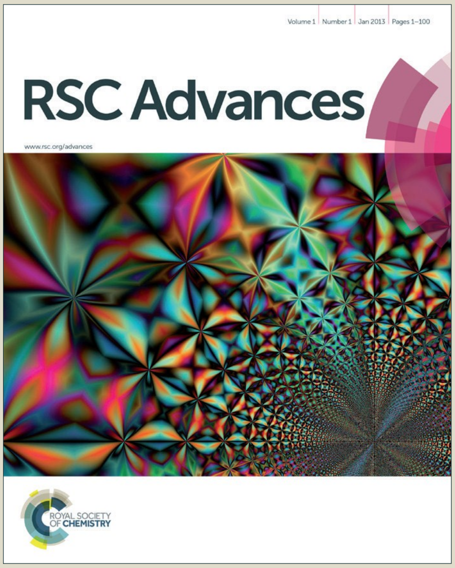

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PAPER

Facile Synthesis of Dimeric Titanium (IV) Complex with Terminal Ti=O Moiety and Its Application as a Catalyst for Cycloaddition Reaction of CO_2 to Epoxides†

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In this report, facile and exclusive synthesis of dimeric titanium (IV) complex with a terminal Ti=O moiety from the reaction between novel pyridine-based tridentate ligand (**LH_2**) and $Ti(O\text{-}i\text{-}Pr)_4$ under the bubbling of wet air is presented. Alternatively, the same dimeric Ti complex was obtained via wet air bubbling of monomeric $LTi(O\text{-}i\text{-}Pr)_2$ or addition of the same equiv of H_2O into $LTi(O\text{-}i\text{-}Pr)_2$. All compounds including **LH_2** and two titanium complexes were characterized by single crystal X-ray analyses. Newly synthesized terminal oxo-titanium compound is the first example of structurally characterized dimeric terminal oxo-titanium compound having no Ti=O→Ti bonds. Two titanium complexes were used as effective catalysts for the cycloaddition of CO_2 to propylene oxide in the presence of various kinds of cocatalysts such as $n\text{-}Bu_4PBr$, $n\text{-}Bu_4NI$, $n\text{-}Bu_4NBr$, $n\text{-}Bu_4NCl$, PPNCl, and DMAP.

Introduction

The efficient capture and utilization of carbon dioxide, a valuable C_1 building block, have been an important theme environmentally and chemically for a long time.[1] Thus, the development of chemical methods to activate and convert CO_2 into methanol, formic acid, urea, cyclic carbonate, and polycarbonates has drawn a significant attention in recent years. Among them, the cyclic carbonates from CO_2 and epoxide have been produced since 1950s and find their use as aprotic solvents,[2] electrolytes for secondary batteries,[3] and monomers for polymers[4] and pharmaceutical intermediate.[5]

A variety of metal-based catalytic systems, including those with Cr, Fe, Co, Ni, Cu, Al, and so on, have been developed to couple CO_2 and epoxide.[6-10] Titanium, the seventh most abundant metal in earth's crust (e.g., Al, Fe, Ca, Na, K, Mg, Ti in the order), could be an attractive metal candidate due to its low toxicity and high Lewis acidity.[10] Although Ti-based complexes have been widely used as catalysts for various organic transformation and polymer synthesis,[11-13] a few examples of Ti-based catalytic systems for the cycloaddition of CO_2 to epoxide have been reported in the literature.[14-20]

Due to high oxophilic property of titanium metal, many titanium compounds could easily react with oxygen-donating sources such as H_2O, O_2, and CO to form oxotitanium complexes. In general, oxotitanium compounds can be classified as two types of complexes depending on functional connectivity with: (1) quite common and bridging $[Ti\text{-}O\text{-}Ti]^{6+}$ unit and (2) very rare and terminal $[Ti{=}O]^{2+}$ moiety. Several structurally characterized titanium complexes with terminal Ti=O group were reported in the literature.[20-32] Interestingly, only titanium compounds chelated by sterically encumbering ligands such as tetradentate porphyrin-type ligands,[20-23] two bidentate ketiminate ligands,[24] two Cp* ligands,[25-27] tetradentate salen-type ligand,[28] tridentate Me_3tacn ligands (where Me_3tacn is 1,4,7-trimethyl-1,4,7-triazacyclononae),[29,30] two bidentate benzamidinate ligands,[31] and tridentate PNP scaffold ligand[32] could generate terminal oxo product. Their major coordination geometries around titanium are square pyramidal.[20-24] Others are trigonal planar,[25] tetrahedral,[26,27] trigonal bipyramidal,[28] and octahedral.[29-32] Interestingly, structurally characterized terminal oxo- titanium complexes are all monomeric though some dimeric Ti compounds with Ti=O→Ti bonds are reported in the literature.[33-36] In those cases, Ti-O bond distances are about 1.80 Å, which is much longer than pure Ti=O bond distances of 1.65 Å.[20-32] To our best knowledge, real dimeric terminal oxotitanium compound without Ti=O→Ti bonds has never been reported in the literature. In this regard, we focused on the development of new dimeric or polymeric terminal oxo-Ti compounds having no Ti=O→Ti bonds.

Whereas a lot of catalytic systems for CO_2 conversion into cyclic carbonates have been reported in the literature, the research of Ti-based complexes is an unexplored field.[14-17] Previous work in our group explored the importance of electronic effect at Ti center on catalytic activity for cycloaddition reaction.[16] During our continuous search for new Ti-based catalysts, we report here the synthesis and characterization of diisopropoxytitanium complex **1** containing the novel 2- tridentate aminopyridine-based ligand **LH_2** and its facile transformation to terminal oxo complex **2**, along with their catalytic behavior in the cycloaddition reaction of CO_2 to epoxides.

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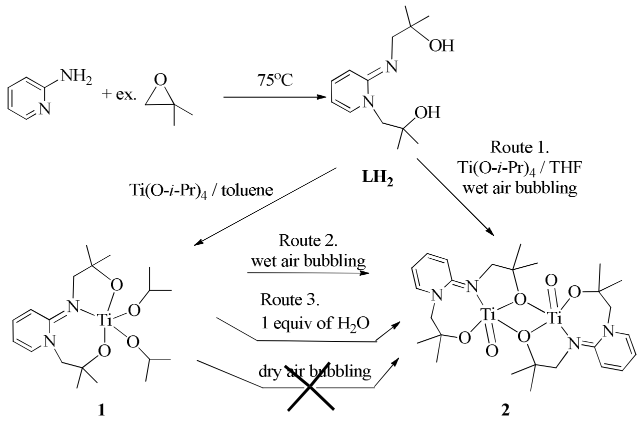


Scheme 1 Synthetic routes for complexes **1** and **2**.

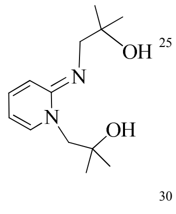
Experimental

Methods and Materials

All manipulations were carried out under an atmosphere of dinitrogen by using standard Schlenk-type glassware on a dual manifold Schlenk line in a glove box.[37] Dinitrogen was deoxygenated using activated Cu catalyst and dried with calcium sulfate.[38] All chemicals were purchased from Aldrich and used as supplied unless otherwise indicated. All solvents such as toluene, diethyl ether, and *n*-hexane, were dried by distillation from sodium diphenylketyl under dinitrogen and were stored over 3Å activated molecular sieves. $CDCl_3$ and CD_3OD were dried over 4Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

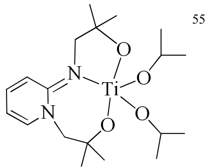
^1H and ^{13}C NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer using standard parameters. All chemical shifts are reported in δ units with reference to the peaks of residual $CDCl_3$ (δ 7.24, ^1H NMR; δ 77.0, ^{13}CNMR) or CD_3OD (δ 3.30, ^1H NMR; δ 49.0, ^{13}C NMR). Elemental analyses and mass data measurements were performed with EA 1110-FISONS analyser and VG Auto Spec., respectively.

Synthesis of $HOCMe_2CH_2NC_5H_4{=}NCH_2CMe_2OH$ (LH_2)



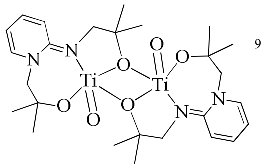
Isobutylene oxide (9.01 g, 125 mmol) and 2-aminopyridine (4.71 g, 50.0 mmol) were added to a 20 mL screw cap vial containing stirring bar. The vial was tightly sealed by Teflon tape and paraffin film. The mixture was maintained at room temperature for overnight and was then heated for 3 days at 75 °C. The removed of volatiles at reduced pressure gave the desired product LH_2 (11.8 g, 99.0 %) as a yellow powder. ^1H NMR ($CDCl_3$, 400.15 MHz): δ 7.76 (br, 1H, O*H*), 7.03 (t, *J* = 7.9Hz 1H, Ar–*H*), 6.97(d, 1H, *J* = 6.8Hz, Ar–*H*), 6.45(d, 1H, *J* = 9.4 Hz, Ar–*H*), 5.81(t, 1H, *J* = 6.6 Hz, Ar–*H*), 3.97 (s, 2H, Ar=NCH_2–), 2.99 (s, 2H, –NCH_2–), 2.44 (br, 1H, O*H*), 1.27 (s, 6H, –C*Me*$_2$OH), 1.23(s, 6H, –C*Me*$_2$OH). ^1H NMR (CD_3OD, 400.15 MHz): δ 7.28(dd, *J* = 6.8 and 1.2 Hz, 1H, Ar–*H*), 7.13(t, *J* = 7.9 Hz, 1H, Ar–*H*), 6.56(d, *J* = 9.5 Hz, 1H, Ar–*H*), 5.92(dt, *J* = 6.7 and 1.2 Hz, 1H, Ar–*H*), 4.04 (s, 2H, Ar=NCH_2–), 3.03 (s, 2H, –NCH_2–), 1.25 (s, 6H, –C*Me*$_2$OH), 1.19 (s, 6H, –C*Me*$_2$OH). ^{13}C NMR ($CDCl_3$, 100.63 MHz): δ 156.7, 139.8, 136.3, 113.2, 102.5 (Ar), 71.30 (Ar=N*C*H$_2$–), 70.56(–N*C*H$_2$–), 64.00 (–*C*Me$_2$OH), 58.80 (–*C*Me$_2$OH), 27.99 (–C*Me*$_2$OH), 27.61 (–C*Me*$_2$OH). ^{13}C NMR (CD_3OD, 100.63 MHz): δ 157.9, 141.8, 138.0, 113.6, 103.9(Ar), 72.64 (Ar=N*C*H$_2$–), 72.36(–N*C*H$_2$–), 64.76 (–*C*Me$_2$OH), 59.92 (–*C*Me$_2$OH), 27.95 (–C*Me*$_2$OH), 27.86 (–C*Me*$_2$OH). HRMS m/z calcd for $C_{13}H_{22}N_2O_2$ 239.1760, found 239.1754.

Synthesis of LTi(O-*i*-Pr)$_2$ (1)



To a stirred colorless solution of **LH$_2$** (0.596 g, 2.50 mmol) in 30 mL of toluene was added Ti(O–*i*–Pr)$_4$ (0.711 g, 2.50 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. The residue, obtained by removing the solvent under vacuum, was recrystallized in toluene. The desired product **1** was isolated as yellow crystals after the solution remained at -15 °C in a refrigerator for a few days (94.7%, 0.953 g). ^1H NMR ($CDCl_3$, 400.13 MHz): δ 7.18 (m, 1H, Ar–*H*), 7.15 (dt, *J* = 1.2 and 5.6 Hz, 1H, Ar–*H*), 6.61 (d, *J* = 9 Hz, 1H, Ar–*H*), 6.10 (td, *J* = 6.6 and 1.3 Hz, 1H, Ar–*H*), 4.63 (m, 2H, –OC*H*Me$_2$), 4.04 (br, 2H, Ar=NC*H*$_2$–), 3.28 (br, 2H, –NC*H*$_2$–), 1.29 (s, 6H, -C*Me*$_2$O–), 1.23 (s, 6H, –C*Me*$_2$O–), 1.15 (d, *J* = 6.1 Hz, 6H, –OCH*Me*$_2$), 1.11 (d, *J* = 6.1 Hz, 6H, –OCH*Me*$_2$). ^1H NMR (CD_3OD, 400.15 MHz): δ 7.58 (s, 1H, Ar–*H*), 7.49 (d, *J* =4.9 Hz, 1H, Ar–*H*), 6.90 (d, *J* = 5.4 Hz, 1H, Ar–*H*), 6.35 (d, *J* = 3.8 Hz, 1H, Ar–*H*), 4.15 (s, 2H, Ar=NC*H*$_2$–), 3.91 (m, 2H, –OC*H*Me$_2$), 3.18 (s, 2H, –NC*H*$_2$–), 1.27 (d, *J* = 7.4 Hz, 12H, –C*Me*$_2$O–), 1.15 (d, *J* = 6.1 Hz, 12H, –C*Me*$_2$O–) ^{13}C NMR ($CDCl_3$, 100.63 MHz): δ 159.2, 140.2, 136.7, 115.1, 105.2 (Ar), 79.97 (Ar=N*C*H$_2$–), 77.13 (–N*C*H$_2$–), 75.90 (–O*C*Me$_2$), 66.01 (–O*C*Me$_2$), 64.06 (–O*C*Me$_2$), 28.81(–OC*Me*$_2$), 26.06 (–OC*Me*$_2$), 25.95 (–OC*Me*$_2$). ^{13}C NMR (CD_3OD, 100.63 MHz): δ 157.4, 142.5, 140.4, 113.8, 107.8 (Ar), 72.55 (Ar=N*C*H$_2$–), 71.82 (–N*C*H$_2$–), 65.34 (–O*C*Me$_2$), 64.74 (–O*C*Me$_2$), 57.94 (–O*C*Me$_2$), 27.67 (–OC*Me*$_2$), 27.65 (–OC*Me*$_2$), 25.25 (–OC*Me*$_2$). Anal. Calcd. for $C_{19}H_{34}N_2O_4Ti$: C, 56.72; H, 8.52; N, 6.96. Found: C, 56.84; H, 8.28; N, 7.12.

Synthesis of [LTi(=O)]$_2$ (2)



(Route 1) To a stirred colorless solution of **LH$_2$** (0.596 g, 2.50 mmol) in 30 mL of toluene was added Ti(O-*i*-Pr)$_4$ (0.711 g, 2.50 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. After 12 h, an air using air pump was bubbled into the reaction vessel for more than

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6 h. The residue, obtained by removing the solvent under vacuum, was recrystallized in toluene. The desired product **2** was isolated as yellow crystals after the solution remained at -15 ^{o}C in a refrigerator for a few days (94.5%, 1.42 g).

(Route 2) To a solution of **1** (1.00 g, 2.50 mmol) in 30 mL toluene was bubbled an air using air pump for more than 4 h. The removal of volatiles at reduced pressure gave the desired product **2** (91.8%, 1.38 g) as a yellow powder.

(Route 3) To a solution of **1** (1.00 g, 2.50 mmol) in 30 mL toluene was added H_2O (0.045 g, 2.5 mmol), which was degassed prior to adding with dinitrogen for 5 min. After 4 h, the removal of volatiles at reduced pressure gave the desired product **2** (94.0%, 1.41 g) as a yellow powder. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 7.02 (t, *J* = 7.8 Hz, 1H, Ar–*H*), 6.97 (d, *J* = 6.8 Hz, 1H, Ar–*H*), 6.44 (d, *J* = 9.4 Hz, 1H, Ar–*H*), 5.80 (t, *J* = 6.6 Hz, 1H, Ar–*H*), 3.96 (s, 2H, Ar=NCH_2–), 2.98 (s, 2H, –NCH_2–), 1.26 (s, 6H, –CMe_2O–), 1.23 (s, 6H, –CMe_2O–). ^{1}H NMR (CD_3OD, 400.15 MHz): *δ* 7.36 (d, *J* = 7.8Hz, 1H, Ar–*H*), 7.23 (m, 1H, Ar–*H*), 6.64 (d, *J* = 9.4Hz, 1H, Ar–*H*), 6.01 (t, *J* = 6.7Hz, 1H, Ar–*H*), 4.07 (s, 2H, Ar=NCH_2–), 3.07 (s, 2H, –NCH_2–), 1.25 (s, 6H, –CMe_2O–), 1.21 (s, 6H, – CMe_2O–). ^{13}C NMR ($CDCl_3$, 100.63 MHz): δ 156.8, 139.9, 136.3, 113.3, 102.6 (Ar), 71.37 (Ar=N*C*H_2–), 70.63 (–N*C*H_2–), 64.07 (–O*C*Me_2), 58.90 (–O*C*Me_2), 28.07 (–OCMe_2), 27.69 (–OCMe_2). ^{13}C NMR (CD_3OD, 100.63 MHz): *δ* 158.2, 142.0 138.7, 113.5, 105.2 (Ar), 72.63 (Ar=N*C*H_2–), 72.24 (–N*C*H_2–), 68.86 (–O*C*Me_2), 59.47 (–O*C*Me_2), 27.87 (–OCMe_2), 26.49 (–OCMe_2). Anal. Calcd. for $C_{26}H_{41}N_4O_6Ti_2$: C, 51.93; H, 6.87; N, 9.32. Found: C, 52.19; H, 7.04; N, 9.11.

(Trial to synthesis of **2** using dry air bubbling method) To a solution of **1** (1.00 g, 2.50 mmol) in 30 mL toluene was bubbled an air, which was passed through the drierite column, for more than 4 h. The removal of volatiles at reduced pressure gave only unreacted **1**.

Single crystal X-ray diffraction

Single crystals suitable for X-ray diffraction analysis were obtained from NMR cells containing **LH_2**, **1**, and **2** dissolved in $CDCl_3$. The crystallographic measurements were performed at 296(2) K for all compounds **LH_2**, **1**, and **2** using a Bruker APEX II diffractometer with Mo K_α (λ= 0.71073 Å) radiation. Specimens of suitable quality and size were selected, coated with Paratone® oil, mounted onto a glass capillary, and centred in the X-ray beam by using a video camera. The structures were solved by the direct method and refined by full matrix least-squares methods using the SHELXTL[39] program package with anisotropic thermal parameters for all non-hydrogen atoms. Final refinement based on the reflections ($I > 2\sigma(I)$) converged at R_1 = 0.0373, wR_2 = 0.0872, and GOF = 1.009 for **LH_2**, and at R_1 = 0.0322, wR_2 = 0.0876, and GOF = 1.021 for **1**, and at R_1 = 0.0396, wR_2 = 0.1022, and GOF = 1.030 for **2**. Further details are listed in Table 1. X-ray crystal structures were drawn by the Diamond Program ver. 2.1e.[40] Details for crystallographic data and parameters are listed in Table 1.

Table 1 Crystallographic data for **LH2**, **1** and **2**

Sample	**LH_2**	**1**	**2**
Chemical formula	$C_{13}H_{22}N_2O_2$	$C_{19}H_{34}N_2O_4Ti$	$C_{28}H_{42}Cl_6N_4O_6Ti_2$
Formula mass	238.33	402.38	839.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	12.9760(3)	10.145(2)	9.5970(3)
b (Å)	9.0107(2)	14.8386(3)	19.6755(6)
c (Å)	12.2487(3)	14.7511(3)	9.9008(3)
α (^{o})	90	90	90
β (^{o})	102.498(2)	103.9490(10)	105.588(2)
γ (^{o})	90	90	90
Z	4	4	2
V (Å^3)	1398.22(6)	2146.51(8)	1800.76(10)
Temperature (K)	100(2)	100(2)	100(2)
Density (g cm^{-3})	1.132	1.245	1.548
μ (mm^{-1})	0.077	0.423	0.934
F(000)	520	864	864
θ range (^{o})	2.77 – 25.00	1.977 – 30.689	2.070 – 26.573
Index ranges	$-15 \leq h \leq 15$ $-10 \leq k \leq 10$ $-14 \leq l \leq 13$	$-10 \leq h \leq 14$ $-21 \leq k \leq 16$ $-21 \leq l \leq 19$	$-12 \leq h \leq 12$ $-24 \leq k \leq 24$ $-12 \leq l \leq 12$
Reflections collected	7785	25010	31380
# of Independent reflections	2464	6620	3738
# of Parameters	161	272	212
GOF($I > 2\sigma(I)$)	1.009	1.021	1.030
$R_1(I > 2\sigma(I))$ [a]	0.0373	0.0322	0.0396
$wR_2(I > 2\sigma(I))$ [a]	0.0872	0.0816	0.0955

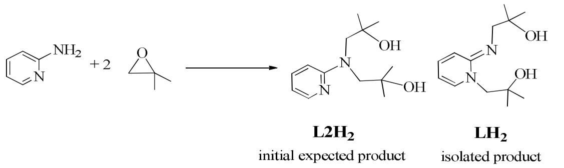
[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Representative procedures for the cycloaddition reaction of epoxide and CO_2

The cycloaddition reaction of CO_2 to epoxide was carried out by charging a stirring bar, epoxide (10 mmol), catalyst (20 μmol), and cocatalyst (20 μmol), into a stainless steel pressure reactor (10 mL inner volume). Then, CO_2 was charged in the reactor and the pressure was adjusted to desired pressure at appropriate temperature. The reactor was maintained for the desired time. After then, the pressure reactor was cooled to ambient temperature, and the excess CO_2 was vented. A small sample of mixture was taken for ^{1}H NMR analysis.

Results and Discussion

The tridentate ligand $HOCMe_2CH_2NC_5H_4{=}NCH_2CMe_2OH$ (**LH_2**) was synthesized by the reaction of 2-aminopyridine with 2 equivalents of isobutylene oxide in almost quantitative yield. As depicted in Scheme 2, **$L2H_2$** was an initial expected product; however, the isolated product from this reaction was **LH_2**, whose the resonance in 6-membered pyridine ring was collapsed. This structure was confirmed by single crystal X-ray analysis (vide infra).



Scheme 2 The result of the reaction between 2-aminopyridine and 2 equiv of isobutylene oxide

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As outlined in Scheme 1, a new monomeric diisopropoxytitanium complex **1** was prepared *via* simple exchange reaction by adding a solution of Ti(O-*i*-Pr)$_4$ dropwise to an equimolar solution of **LH$_2$** in toluene. Analytically pure samples were obtained as yellow crystalline solids after the removal of the volatiles. Terminal oxo titanium complex **2** can be made by three different synthetic routes as shown in Scheme 1. For Route 1, compound **2** was prepared *in situ* by treating mixed solution of Ti(O-*i*-Pr)$_4$ and **LH$_2$** with wet air bubbling (Figures 11 and 12). Wet air bubbling of compound **1** (Figure S16) and the direct addition of water into compound **1** (Figure S17) were applied for Route 2 and Route 3, respectively. Interestingly, dry air bubbling of compound **1** did not work for the synthesis of compound **2** (Figure S18). Thus, oxygen of Ti=O in compound **2** definitely comes from water. Route 1 is better than Routes 2 and 3 in regards to yield and time efficiency. Unlike compound **1**, compound **2** was stable in air. All compounds **LH$_2$**, **1**, and **2** were characterized by ^{1}H and ^{13}C NMR spectroscopies, HR mass spectrometry for **LH$_2$** and elemental analysis for **1** and **2** and by single crystal X-ray crystallographic method.

The ^{1}H and ^{13}C NMR spectra were in accord with the suggested structures, and all chemical shifts of the protons and carbons for **LH$_2$**, **1**, and **2** were in the expected range. ^{1}H NMR spectra of **1** and **2** show the absence of signals for alcoholic protons, corroborating successful formation of Ti complexes chelated by **L^{2-}** ligand. Their molecular structures were determined by single-crystal X-ray diffraction analysis. X-ray quality crystals were obtained by fractional recrystallization at -15 °C in a refrigerator for a few days. Figures 1 – 3 display the molecular structures of **LH$_2$**, **1**, and **2**, respectively.

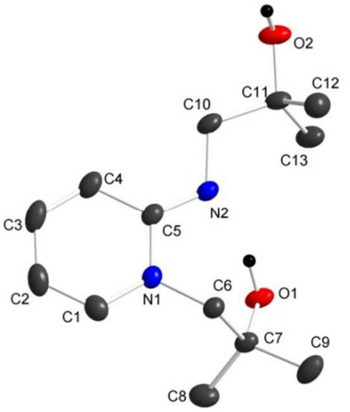

Fig. 1 X-ray structure of **LH$_2$** with thermal ellipsoids drawn at the 50% probability level. All hydrogens except for alcoholic protons are omitted for clarity. Selected bond lengths (Å): N1–C1 1.366(2); C1–C2 1.352(2); C2–C3 1.411(2); C3–C4 1.351(2); C4–C5 1.442(2); C5–N1 1.402(2); C5–N2 1.296(2); N1–C6 1.474(2); N2–C10 1.455(2). Selected angles (deg): N1–C5–N2 117.10(12); C5–N1–C1 122.00(12); C5–N1–C6 118.57(11); N1–C1–C2 122.17(14); C1–C2–C3 118.33(14); C2–C3–C4 120.57(15); C3–C4–C5 121.79(14); C4–C5–N1 115.03(12); C4–C5–N2 127.87(13); C5–N2–C10 117.56(12).

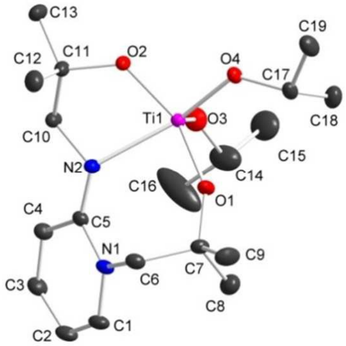

Fig. 2 X-ray structure of **1** with thermal ellipsoids drawn at the 50% probability level. All hydrogens are omitted for clarity. Selected bond lengths (Å): Ti1–N2 2.2685(9); Ti1–O1 1.8119(8); Ti1–O2 1.8663(8); Ti1–O3 1.8074(9); Ti1–O4 1.8586(8); N1–C1 1.3719(14); C1–C2 1.3520(17); C2–C3 1.4076(18); C3–C4 1.3582(16); C4–C5 1.4358(15); C5–N1 1.3871(14); C5–N2 1.3215(13); C6–N1 1.4685(14); N2–C10 1.4701(14). Selected angles (deg): O1–Ti1–O2 140.83(4); O1–Ti1–O3 106.71(4); O1–Ti1–O4 93.98(4); O2–Ti1–O3 109.73(4); O2–Ti1–O4 89.70(4); O3–Ti1–O4 105.73(4); N2–Ti1–O1 87.29(4); N2–Ti1–O2 76.01(3); N2–Ti1–O3 94.63(4); N2–Ti1–O4 158.25(4); Ti1–O1–C7 152.41(8); Ti1–O2–C11 125.90(7); Ti1–O3–C14 135.37(10); Ti1–O4–C17 130.52(7).

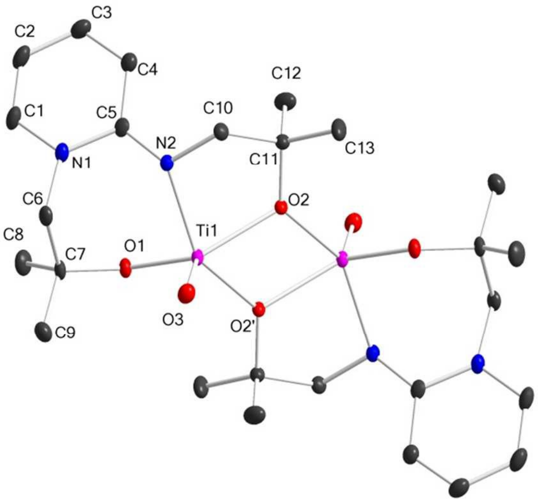

Fig. 3 X-ray structure of **2** with thermal ellipsoids drawn at the 50% probability level. All hydrogens and CDCl$_3$ are omitted for clarity. Selected bond lengths (Å): Ti1–N2 2.153(2); Ti1–O2 2.0549(16); Ti1–O2' 2.0147(16); Ti1–O1 1.8459(17); Ti1–O3 1.6638(17); N1–C1 1.375(3); C1–C2 1.351(4); C2–C3 1.399(4); C3–C4 1.360(4); C4–C5 1.430(3); C5–N1 1.385(3); C5–N2 1.329(3); N1–C6 1.478(3); N2–C10 1.470(3). Selected angles (deg): O2–Ti1–O2' 73.50(7); O2–Ti1–O1 139.32(7); O2–Ti1–O3 111.88(8); O2'–Ti1–O1 99.43(7); O2'–Ti1–O3 108.45(8); O1–Ti1–O3 108.35(8); N2–Ti1–O2 77.71(7); N2–Ti1–O2' 144.99(7); N2–Ti1–O1 89.54(7); N2–Ti1–O3 100.45(8); Ti1–O1–C7 133.55(15).

There are only four π-electrons, not six, in six-membered pyridine ring for tridentate ligand **LH$_2$**, **1**, and **2**. As shown in Figure 4, two different types of carbon-carbon bond lengths certainly exist. A single crystal X-ray diffraction analysis of **1** and **2** confirmed the compounds to be monomeric and dimeric, respectively (Figures 2 and 3). Complexes **1** and **2** have five-coordinate titanium centers. The titanium atom in **1** is ligated to two O-*i*-Pr and one tridentate **L^{2-}**. In addition to anionic oxygens and neutral nitrogen in tridentate **L^{2-}**, each titanium metal in dimeric **2** has one =O ligand and a bridging oxygen from another

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tridentate $\mathbf{L}^{2-}$, which is the less encumbered tridentate ligand than other tridentate alkoxy/phenoxy pincer ligands bridging two Ti centers.[20,42] Two Ti–O_{bridge} bond distances in **2** [2.0549(16) and 2.0147(16) Å] are within the range found in previously reported dimeric Ti complexes having Ti–O_{bridge} bond at 2.0122(16) – 2.2332(16) Å.[20,42] Interestingly, Ti–O1(terminal) bond length [1.8459(17) Å] is extremely shorter than the two other Ti–O_{bridge} bonds [2.0549(16) and 2.0147(16) Å] in **2**. In addition to the short Ti–O1(terminal) bond length, a wide Ti1–O1–C7 bond angle of 133.55(15)^o indicates the existence of strong Ti–O π-donation. Thus, O1 atom of $\mathbf{L}^{2-}$ chelated to dimeric **2** is somewhat *sp*^{2} hybridized and **2** has two weak Ti–O_{bridge} bonds and a strong Ti–O1(terminal) bond. This provides some idea on how the encumbered five coordinate complex **2** could potentially free an open coordination site allowing consequently the epoxide and/or cocatalyst coordination. Complex **2** has an inversion center (*i*) at the centroid of the Ti_2O_2 ring plane. There is no direct Ti–Ti interaction for **2**.

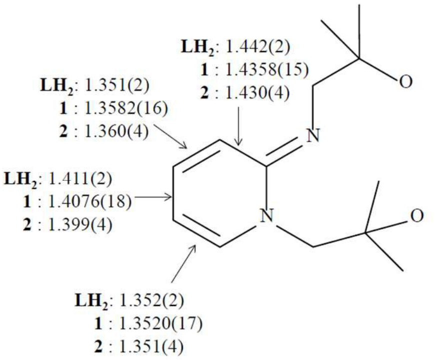


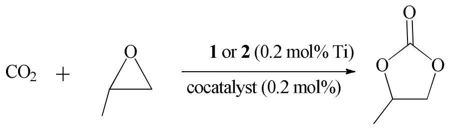
Fig. 4 Comparison of carbon-carbon bond lengths in 6-membered pyridine ring for $\mathbf{LH_2}$, **1**, and **2**.

The coordination geometry around metal center in the 5-coordinate systems (*e.g.*, trigonal bipyramidal or square pyramidal) could be determined by the trigonality parameter τ ($\tau = [\alpha - \beta]/60$, where α and β are the largest and next-largest interligand bond angles).[43,44] The largest and next-largest interligand bond angles for **1** are ∠O4–Ti1–N2 (158.25(5)^o) and ∠O1–Ti1–O2 (140.83(5)^o), respectively. Those values for **2** are ∠N2–Ti1–O2' (145.00(7)^o) and ∠O1–Ti1–O2 (139.31(7)^o), respectively. Thus, the τ values are 0.29 for **1** and 0.09 for **2**. The trigonality parameter τ for the regular trigonal bipyramidal (tbp) complexes is 1.0 and τ for square pyramidal (sqp) complexes is zero. The titanium center in **2** is almost regular square pyramidal geometry; however, **1** could be reasonably defined as having less square pyramidal geometry than **2**.

As shown in Figure 3, compound **2** possesses a square pyramidal geometry where three oxygens and one nitrogen from two $\mathbf{L}^{2-}$ ligands occupy the base and oxygen of Ti=O takes the apical position. The titanium metal is displaced by 0.59 Å toward the oxygen atom of Ti=O from the base, which is quite planar, the deviations from planarity ranging from -0.396 to 0.347 Å. The Ti=O bond length in **2** is 1.664(2) Å is within the normal range of structurally characterized terminal oxo-titanium complexes.[20-32] Until now, structurally characterized terminal oxo-titanium complexes reported in the literature are all monomeric. In addition, dimeric or polymeric terminal oxo-titanium complexes always use an oxygen atom of Ti=O as a bridge.[33-36] Thus, compound **2** is the first example of dimeric terminal oxo-titanium compound having no Ti=O→Ti bonds.

The cycloaddition of CO_2 to propylene oxide was performed without solvent using the titanium compounds **1** and **2** as catalysts in the presence of cocatalyst. The cycloaddition results are summarized in Table 2. We carried out the reaction at 75 ^oC under the condition of a fixed [Ti]/[cocatalyst] ratio of 1. Propylene oxide was easily converted into the cyclic carbonate with high selectivity (99%) without any polymerized products. To check the cocatalyst effect on the catalytic activity, we used six different kinds of cocatalysts, such as *n*-Bu_4PBr, *n*-Bu_4NI, *n*-Bu_4NBr, *n*-Bu_4NCl, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), and 4-dimethylaminopyridine (DMAP). The role of cocatalyst has been demonstrated for several epoxide/CO_2 coupling reactions.[14-20] It is known that Lewis basic cocatalysts can either 1) be reversibly coordinate to the metal center, increase the electron density on the metal, and labilize the trans ligand to it, acting in turn as nucleophile for the ring opening of epoxide, or 2) the counteranion X^- in cocatalyst act as a nucleophile and it proceeds directly to a nucleophilic attack to the coordinated Ti-epoxide. Anionic cocatalysts (*n*-Bu_4NX, *n*-Bu_4PBr, and PPNCl) and non-salt type cocatalyst (DMAP) showed the different catalytic behavior.

Table 2 Cocatalyst screening for the cycloaddition of CO_2 to epoxides using complexes **1** and **2**.



Entry	Cat.	Cocatalyst	Conv.(%)	TON^b	Selectivity(%)^c
1	**1**	*n*-Bu_4PBr	68	338	>99
2		*n*-Bu_4NI	95	470	>99
3		*n*-Bu_4NBr	78	392	>99
4		*n*-Bu_4NCl	83	416	>99
5		PPNCl	66	328	>99
6		DMAP	21	108	>99
7	**2**	*n*-Bu_4PBr	69	343	>99
8		*n*-Bu_4NI	51	255	>99
9		*n*-Bu_4NBr	86	432	>99
10		*n*-Bu_4NCl	49	245	>99
11		PPNCl	72	362	>99
12		DMAP	26	132	>99
13	**1**	none	20	98	>99
14	**2**		17	83	>99
15	none	*n*-Bu_4PBr	11	54	>99
16		*n*-Bu_4NI	13	64	>99
17		*n*-Bu_4NBr	12	59	>99
18		*n*-Bu_4NCl	10	49	>99
19		PPNCl	13	64	>99
20		DMAP	5	24	>99

[a] Cycloaddition conditions: [propylene oxide] = 10 mmol, [**1**] = 0.02 mmol, [**2**] = 0.01 mmol, [cocatalyst] = 0.02 mmol, [propylene oxide]/[Ti] = 500/1, CO_2 = 10 bar, Temperature = 75 ^oC, time = 24 h, [b] Turnover number (TON) = (mol of propylene oxide consumed)/(mol of catalyst), [c] Calculated by ^1H NMR spectral integration.

As expected, cocatalyst *n*-Bu_4NI for catalyst **1** is superior

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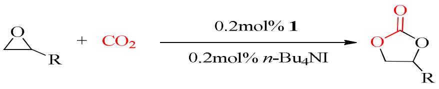
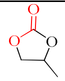
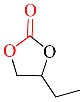
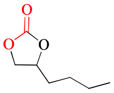
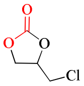
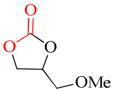
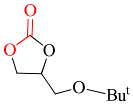
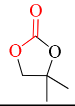
compared with the five others (entries 1–6) because the nucleophilicity for halide ions decreases on going up from I$^-$ to Cl$^-$. However, no similar trend for catalyst **2** was observed and the highest catalytic activity for **2** was obtained in the presence of *n*-Bu_4NBr (entry 9). Interestingly, amine-based cocatalyst such as *n*-Bu_4NBr showed the better activity than phosphine-based cocatalyst, *n*-Bu_4PBr in both **1** and **2** (entries 1 and 3 for **1** and entries 7 and 9 for **2**). The reason may be quaternary ammonium compounds could stabilize the carbonate intermediate. Compounds **1** and **2** showed marginal difference in catalytic activity (entries 1–12). Both **1** and **2** with non-salt-type cocatalyst DMAP showed very low activities (entries 6 and 12). Interestingly, compounds **1** and **2** without any cocatalyst showed the conversion of 20% and 17%, respectively, under the same cycloaddition condition (entries 13 and 14). In addition, six cocatalysts without **1** and **2** showed low conversion in the range of 5 – 13% (entries 15–20). Thus the coupling of catalyst and cocatalyst showed the synergistic activity for this cycloaddition reaction.

Until now, four papers on Ti-based systems for the cycloaddition of CO_2 and epoxides to make cyclic carbonates were reported in the literature.[14-17] Harsh condition such as high catalyst loading of 1 mol%,[14,15,17] high temperature such as 100°C[17] and 150°C[14,15] and high CO_2 pressure such as 15 bar[17] and 22 bar[16] for the reported systems in needed. However, our system was applied under the condition of 0.2 mol% catalyst loading, 75°C, and 10 bar CO_2 pressure. Even though all systems conducted in different reaction condition, our systems are one of the mildest Ti-based systems. Interestingly, compounds **1** and **2** (0.2 mol%) showed complete conversion at 125°C within 1 hr. In addition, catalyst/cocatalyst ratio of 2 and CO_2 pressure change did not show any significant differences. Interestingly, in case of the synthesis of polymers via coupling reaction of propylene oxide and styrene oxide with CO_2 catalyzed by homogeneous Ti-based complexes under mild or similar conditions (1 – 35 bar of CO_2 pressure and 25 – 80°C).[18-20]

Table 3 The scope of epoxides on the cycloaddition reaction of epoxide and CO_2 using catalyst **1** [a]



Entry	Product	Time (h)	TON [b]	Selectivity(%)[c]
1		24	470	>99
2		48	344	>99
3		48	250	>99
4		14	403	>99
5		24	330	>99
6		46	406	>99
7		54	74	>99

[a] Cycloaddition conditions: [epoxide] = 10 mmol, [**1**] = 0.02 mmol, [*n*-Bu_4NI] = 0.02 mmol, [epoxide]/[**1**] = 500/1, CO_2 = 10 bar, Temperature = 75 °C. [b] Turnover number (TON) = (mol of epoxide consumed)/(mol of catalyst), [c] Calculated by ^1H NMR spectral integration.

We next moved to investigate the scope of substrates (Table 3) using **1** as a catalyst and *n*-Bu_4NI as a cocatalyst. Substrates include various kinds of epoxides such as propylene oxide (Table 2, entry 1), 1,2-epoxybutane (entry 2), 1,2-epoxyhexane (entry 3), epichlorohydrin (entry 4), 1,2-epoxy-3-methoxypropane (entry 5), *tert*-butyl glycidyl ether (entry 6), and 1,2-epoxy-2-methylpropane (entry 7). Epoxides with different alkyl substituents (R = Me, Et, and *n*-Bu) showed high dependence on chain length (entries 1–3). While propylene oxide gave an excellent conversion (entry 1), a quick loss of reactivity was observed from ethyl to butyl side chains (entries 2 and 3). Interestingly, when heteroatom was introduced at 3-position, epichlorohydrin (entry 4) showed the better activity than epoxides with –CH_2OMe (entry 5) and –CH_2OBu^t (entry 6) substituents. However, substrate with multi-substituents such as 1,2-epoxy-2-methylpropane (entry 7) exhibited low conversions. The observed dependency of the nature of the epoxide and the observed TONs may be related to the polarity of the reaction mixture and thus the solubility of the catalyst species could have been influenced.

Conclusions

The ligand $\mathbf{LH_2}$ from the reaction between 2-aminopyridine and 2 equiv of isobutylene oxide was synthesized and used to make monomeric LTi(O-*i*-Pr)$_2$ (**1**) and dimeric $[LTi(=O)]_2$ (**2**). Compound **2** has terminal oxo group and was bridged by the oxygen atom of L^{2-} ligand. Compound **2** is the first example of terminal oxo-titanium compound having no Ti=O→Ti bonds. New titanium complexes **1** and **2** could act as catalysts for the synthesis of cyclic carbonate via the cycloaddition of CO_2 to epoxides under somewhat mild condition of 0.2 mol% catalyst loading, 75°C, and CO_2 pressure of 10 bar compared with other reported Ti-based catalysts.

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Notes and references

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† Electronic Supplementary Information (ESI) available: crystallographic data in CIF and ^{1}H and ^{13}C NMR for **LH$_2$**, **1**, **2**, and cyclic carbonates synthesized see DOI: 10.1039/b000000x/

‡ The first and second authors contributed equally to the work.

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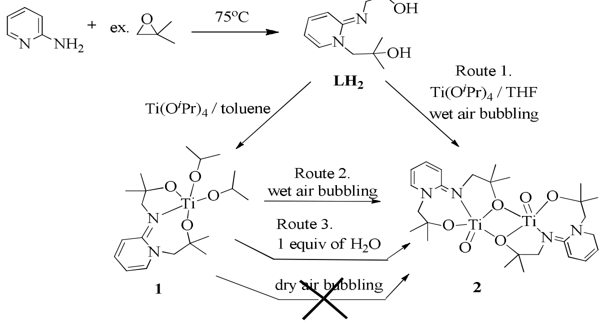

Dimeric terminal oxo-titanium complex **1** having no Ti=O→Ti bonds could be easily synthesized. The titanium complexes **1** and **2** could act as catalysts for cycloaddition between CO_2 and epoxides in the presence of cocatalysts.

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