SYNTHESIS AND ALTERNATING COPOLYMERIZATIONS OF CARBON DIOXIDE WITH CYCLOHEXENE OXIDE OVER (6-Me-pyCAr$_2$O)Zn(OAc) COMPLEXES CONTAINING BIDENTATE PYRIDINE-ALKOXIDE LIGANDS

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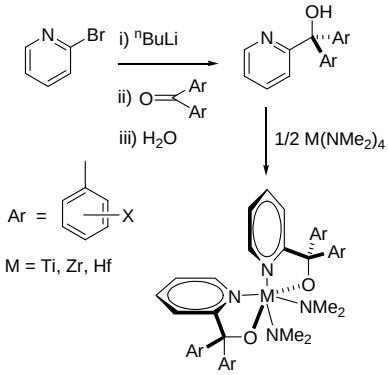
Abstract

The reaction of 2-lithio-6-methylpyridine or 2-lithiopyridine and the appropriated diarylketone followed by hydrolysis yields 6-Me-pyCAr$_2$OH pyridine alcohols (**1a**, Ar = -C$_6$H$_5$; **1b** = 4-Me-C$_6$H$_4$; **1c** = 4-Cl-C$_6$H$_4$; **1d** = 4-Me$_2$N-C$_6$H$_4$) or pyCAr$_2$OH pyridine alcohols (**2a**, Ar = -C$_6$H$_5$; **2b** = 4-Me-C$_6$H$_4$; **2c** = 4-Cl-C$_6$H$_4$; **2d** = 4-Me$_2$N-C$_6$H$_4$). The reactions of zinc acetate with 1 equiv of lithiated products of **1a-d** and **2a-d** proceed rapidly to afford LiOAc salt and mono(ligand) complexes (6-Me-pyCAr$_2$O)Zn(OAc) (**3a-d**) and (pyCAr$_2$O)Zn(OAc) (**4a-d**), respectively, in high yield. The copolymerizations of carbon dioxide with cyclohexene oxide using 3**a-d** complexes were investigated. The (6-Me-pyCAr$_2$O)Zn(OAc) showed comparable yield and CO$_2$ incorporation with the β-diiminate zinc complexes. **3c** complex gave high polymers with high carbonate linkage (> 60%) and narrow polydispersity (< 2.0), indicating single active sites.

Introduction

Jordan and coworkers[1] described the synthesis of new group 4 metal alkyl complexes of the general form (Ox)$_2$MR$_2$ and (pyCR$_2$O)$_2$MR$_2$ which contain quinolato or pyridine-alkoxide ancillary ligands. The reaction of 2-lithiopyridine and the appropriated diarylketone followed by hydrolysis yields pyCAr$_2$OH pyridine alcohols. The reaction of M(NMe$_2$)$_4$ (M = Ti, Zr, Hf) with 2 equiv of pyCAr$_2$OH yielded (pyCAr$_2$O)$_2$M(NMe$_2$)$_2$ complexes (**Chart 1**) which adopt distorted octahedral structure with *trans*-O, *cis*-py, *cis*-amide arrangement of ligands and are active for the ethylene polymerizations.[1]

Chart 1



Coates developed β-diiminate zinc complexes for preparation of aliphatic polycarbonate (PC).[2] The β-diiminate zinc complex showed significantly higher activity than previous catalysts and produced aliphatic PC with very narrow polydispersity. These homogeneous single-site zinc complexes can give different activity and structure of the resulting copolymer according to β-diimine ligand structure. The specific objectives of this study were to develop efficient synthetic routes to (pyCAr$_2$O)Zn(OAc) complexes for the preparation aliphatic polycarbonate. Initial efforts to activate these complexes for the alternating copolymerization of carbon dioxide with cyclohexene oxide (CHO) are also described.

Experimental

General procedure. All reactions with air and/or moisture sensitive compounds were carried out under dry nitrogen using standard Schlenk line techniques. ^{1}H NMR spectra were measured on a Varian Gemini 2000 & HP5P with CDCl$_3$ as a solvent. Gel permeation chromatography (GPC) analyses were carried out using a Waters-400 spectrometer using polystyrene as a standard and dimethyl formamide as a solvent. All materials such as zinc(II) acetate [Zn(OCOCH$_3$)$_2$] and n-butyl lithium were purchased from Aldrich and used without further purification. Cyclohexene oxide (CHO, Aldrich) was distilled for 6 hours over sodium metal and stored over Linde type 4Å molecular sieves. Tetrahydrofuran (THF) and methylene chloride were refluxed over sodium and stored over 4Å molecular sieves under dry nitrogen.

Preparation of ligands and catalysts. Pyridine alcohol ligands were prepared according to literature procedures.[1] To a solution of ligand (1.28 mmol) in THF (10 mL), n-BuLi (1.6M in hexane, 0.88 mL, 1.41 mmol) was added dropwise at 0 ℃. Reacting the mixture for 5 min at 0 ℃, the solution was cannulated to a solution of zinc acetate (0.24 g, 1.41 mmol) dissolved in THF (10 mL). After stirring overnight at room temperature, the suspension was filtered and the clear solution was dried in vacuum. The resulting metal complexes were recrystallized in toluene and hexane and then characterized by ^{1}H NMR spectra.

(6-Me-pyCAr$_2$O)Zn(OAc) (**3a**, Ar = -C$_6$H$_5$); light yellow solid (57 % yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.58 – 6.62 (13H, m, ArH), 2.50 (3H, s, Py-Me), 1.49 (3H, s, OAc).

(6-Me-pyCAr$_2$O)Zn(OAc) (**3b**, Ar = 4-Me-C$_6$H$_4$); pale yellow solid (63 % yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.54 – 6.60 (11H, m, ArH), 2.59 (3H, s, Py-Me), 2.33 (3H, s, Ph-Me), 2.23 (3H, s, OAc).

(6-Me-pyCAr$_2$O)Zn(OAc) (**3c**, Ar = 4-Cl-C$_6$H$_4$); light yellow oil (21 % yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.52 – 6.79 (11H, m, ArH), 2.50 (3H, s, Py-Me), 1.19 (3H, s, OAc).

(6-Me-pyCAr$_2$O)Zn(OAc) (**3d**, Ar = 4-Me$_2$N-C$_6$H$_4$); yellow solid (49 % yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.43 – 6.57 (11H, m, ArH), 2.85 (12H, s, NMe), 2.48 (3H, s, Py-Me), 1.51 (3H, s, OAc).

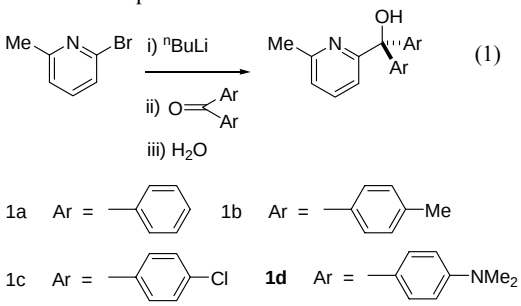
(pyCAr$_2$O)Zn(OAc) (**4b**, Ar = 4-Me-C$_6$H$_4$); pale yellow solid (52 % yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.57 – 6.77 (11H, m, ArH), 2.17 (3H, s, Ph-Me), 2.09 (3H, s, OAc).

Copolymerization of CO$_2$ with cyclohexene oxide. The copolymerizations were performed in a 10 mL high-pressure reactor equipped with a thermometer and a magnetic stirrer. The reactor was charged with catalyst (3.7×10^{-5} mol) and CHO (3.7×10^{-2} mol) in a dry box, and then transferred to a bath controlled at a desired temperature. The vessel was pressurized to 6.8 bar with CO$_2$ and allowed to stir. After 2 h of polymerization, the copolymer was dissolve in minimum amount of methylene chloride and precipitate from excess methanol. The product was then dried in vacuum.

Results and Discussion

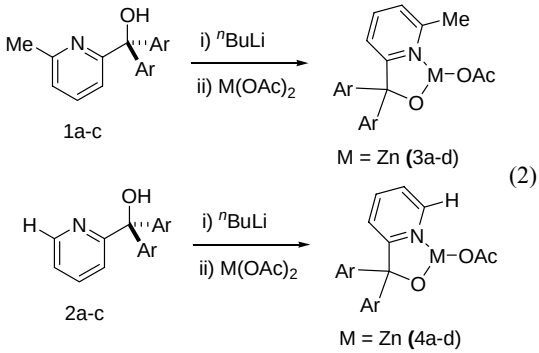
Ligand Synthesis. Pyridine-alcohols **1a-c** were prepared by addition of 2-lithio-6-methylpyridine to the appropriate ketone,

followed by aqueous workup (eq 1), using the approach developed originally by Holm.[3] These compounds are isolated as sharp-melting white to tan crystalline solids following recrystallization. The use of symmetric ketones yields symmetric 6-Me-pyCR$_2$OH alcohols, which in turn simplifies the stereochemical possibilities for metal complexes.[4]

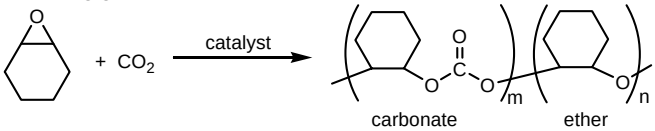


Similar ligands pyCAr$_2$OH pyridine alcohols (**2a**, Ar = -C$_6$H$_5$; **2b** = 4-Me-C$_6$H$_4$; **2c** = 4-Cl-C$_6$H$_4$; **2d** = 4-Me$_2$N-C$_6$H$_4$) without methyl substituent in 6-position of the pyridine ring were also successfully synthesized according to the similar procedures.

Synthesis of (6-Me-pyCAr$_2$O)M(OAc) (M = Zn, Mn) complexes. The reactions of zinc acetate or manganese acetate with 1 equiv of lithiated products of **1a-c** proceed rapidly to afford LiOAc salt and mono(ligand) complexes (6-Me-pyCAr$_2$O)M(OAc) [M = Zn (**2a-c**), Mn (**3a-c**)] in high yield (eq 2).



Alternating copolymerization of CO$_2$ with cyclohexene oxide. Semi-batch copolymerizations of CHO and CO$_2$ using Zn complexes have been carried out at the temperature range between 30 and 70 ℃ at a constant pressure of CO$_2$ (6.8 bar). Copolymerization of CHO and CO$_2$ leads to the copolymers of the following general structure:



If the alternating copolymerization is perfect, only carbonate groups should be generated. However, homopolymerization of CHO results in ether linkage. The typical IR spectrum of the resultant copolymers obtained from 3b catalyst system is shown in **Figure 1**. It was found that the IR spectrum showed the strong absorption band at 1745 and 1238 cm^{-1} characteristic of stretching vibration of C=O bond and C-O-C bond of the carbonate group, respectively. The content of carbonate and ether linkages can be estimated exactly by assigning ^{1}H NMR spectrum of methine hydride (3.3 – 4.0 ppm) in cyclohexane backbone. Zinc complexes bearing ligands (**1a-c**) with 6-methyl substituted pyridyl produced aliphatic PCs which have high carbonate contents (≥ 60 %) as shown in Table 1. It is interesting to note that the **3d** catalyst bearing ligand with electron donating NMe$_2$ group on the aryl ring showed only negligible activity, while **3c** catalyst with electron withdrawing Cl group showed highest activities. Copolymers obtained by **3c** catalyst recorded highest molecular weight, demonstrating the electron withdraw group retards chain termination reaction. In addition the methyl group on the pyridyl ring influences both catalytic activity and CO$_2$ reactivity (compare **3b** and **4b** in Table 1). The Mn acetate complexes bearing **1b** and **2b** ligands were also prepared and utilized for the copolymerization of CO$_2$ and CHO, resulting in negligible activities. All Zn complexes bearing pyridine alcohol ligand can produce aliphatic PC with high molecular weight and narrow PDI at mild conditions.

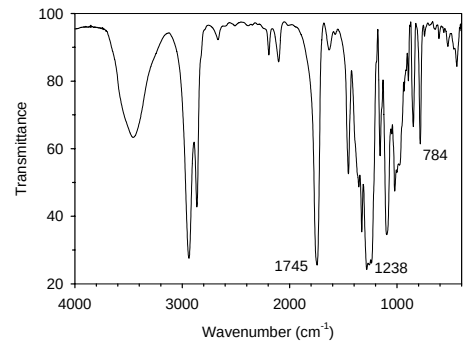


Figure 1. The typical IR spectra of CO$_2$/CHO copolymer obtained by 3b at 30 ^{o}C.

Table 1. Results of CO$_2$/CHO copolymerizations

No.	Cat.	Temp.	Yield (%)	M$_n$	MWD	Carbonate (%)
1	**3a**	30	22.8	4660	1.38	74.5
2		50	19.6	3830	1.10	72.2
3		70	19.2	3610	1.14	69.9
4	**3b**	30	15.4	4250	1.06	72.9
5		50	10.4	3890	1.04	56.4
6		70	11.6	3620	1.05	50.6
7	**3c**	30	26.8	6820	2.05	61.5
8		50	30.6	9540	2.55	62.6
9		70	26.0	5590	1.96	51.5
10	**3d**	30	nil	-	-	-
11		50	0.8	-	-	0.2
12		70	1.4	-	-	0.2
13	**4b**	30	13.6	3500	1.04	43.6
14		50	12.2	3560	1.03	47.3
15		70	11.2	3370	1.03	35.5

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