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# Zwitterionic Design Principle of Ni(II) Catalysts for Carbonylative Polymerization of Cyclic Ethers

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Dedication: This paper is dedicated to Professor Richard A. Andersen on the occasion of his 75<sup>th</sup> birthday.

**Abstract:** Zwitterionic structure is necessary for Ni(II) complexes to catalyze carbonylative polymerization (COP) of cyclic ethers. The cationic charge at the Ni(II) center imparts sufficient electrophilicity to the Ni-acyl bond for it to react with cyclic ethers to give an acyl-cyclic ether oxonium intermediate, while the ligand-centered anionic charge ensures that the resultant oxonium cation is ion-paired with the Ni(0) nucleophile. The current catalysts give non-alternating copolymers of carbon monoxide and cyclic ethers and are the most effective when both ethylene oxide and tetrahydrofuran are present as the cyclic ether monomers.

Transition metal-catalyzed carbonylative polymerization (COP) utilizes CO as a comonomer to produce a variety of polymers, including polyketones, polyamides, and polyesters [1]. Since it can be easily obtained by  $CO_2$  reduction, CO is a raw materials with low carbon footprint. Among the products, polyketone is photodegradable, and polyesters are hydrolytically degradable. These features make COP an attractive platform for producing sustainable polymers for a variety of applications [2]. Among the COPs, CO-olefin copolymerization is well-studied [3-8], while the COPs of heteroatom-containing comonomers (for example, epoxides, aziridines, imines, *etc.*) only experienced a modest amount of research interest [9-16].

Cobalt was the metal of choice to catalyze the COPs of epoxides, aziridines, imines, etc [11-16]. Acyl-Co(CO)<sub>4</sub> is likely ubiquitously involved as the catalytically active species. The mechanisms for the enchainment of the polar co-monomers have much commonalities among themselves but are different from the coordinative-insertion mechanism of olefin enchainment. The electrophilic acyl group is the reactive site for the nucleophilic comonomers instead of the Co center. The COPs of cyclic amines and imines, which are good nucleophiles, are relatively fast, give polyamides in high yields, and often display living characters [11, 16]. Cyclic ethers, primarily epoxides, require the presence of a pyridine derivative as the co-catalyst to undergo COP [11d, 12-14]. The pyridine co-catalyst activates the acyl-Co bond just as in organic acyl-transfer reactions but unfortunately also cleaves the ester bonds in the polyester product [11d]. Continuous progress in this area has been hampered by the fact that acyl-Co(CO)<sub>4</sub> cannot be readily modified. Substitution of a CO ligand with

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Supporting information for this article is given via a link at the end of the document.

another ligand invariably (perhaps with the exception of PF<sub>3</sub>) retards the reactivity of the acyl group toward nucleophiles [11e]. The problem is particularly impairing for the epoxide COP since even acyl-Co(CO)<sub>4</sub> is barely reactive enough.

After testing an exhaustive list of organic acyl-transfer cocatalysts without any appreciable gain in either the productivity of the polymerization or the molecular weight of the product, we decided to explore other transition metals. What metal-acyl complexes are more electrophilic than acyl-Co(CO)<sub>4</sub>? One can arrive at a reasonable estimate by assuming a rough correlation between the electrophilicity of the metal-acyl bond and the acidity of the corresponding metal hydride. The documented acidities of a wide range of metal hydrides [17,18] suggest that acyl-Co(CO)<sub>4</sub> is likely the most electrophilic among neutral metal-acyl complexes and only cationic Ni(II) and Pd(II) acyl complexes are possibly more electrophilic than acyl-Co(CO)<sub>4</sub>.

However, we extensively screened cationic Ni(II) and Pd(II) complexes at the onset of our pursuit for the COP of cyclic ethers even before we turned our attention to cobalt. The results were disappointing without exception. Typically, when epoxides were subjected to the cationic Ni(II)- or Pd(II)-acetyl compounds under high-pressure CO, oligoethers with an acetate ester end group were obtained, but not poly- or oligoesters. The same type of reactivity was also observed for tetrahydrofuran (THF) by Arndtsen and cleverly taken advantage of for the synthesis of poly(norbornene-block-THF) using cationic Pd complexes [19]. Apparently, the initial attack by the cyclic ether on the acetyl-Ni(II)+ and acetyl-Pd(II)<sup>+</sup> bond indeed happens, but the resulting neutral Ni(0) and Pd(0) intermediate are separated from the acyloxonium cation in solution (Scheme 1). The acyloxonium cation then goes on by itself to initiate the cationic oligomerization of epoxide or polymerization of THF.



Scheme 1. Difference between Cationic and Zwitterionic M-acyl Species (M = Ni/Pd) in Reaction with Cyclic Ether.

In retrospect, the existence of the anionic metal nucleophile and the cationic chain end as an ion pair apparently is a key to the success of the charge-neutral acyl-Co(CO)<sub>4</sub> catalyst. Zwitterionic Ni(II)-acyl complexes possess the critical features of both their cationic analogs and acyl-Co(CO)<sub>4</sub>, namely, the high electrophilicity at the acyl site and the overall charge neutrality. One can expect that after nucleophilic displacement by a cyclic ether from the acyl site (Scheme 1), the Ni(0) species carrying an

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anionic phosphine ligand [20] would remain ion-paired with the acyl-oxonium. The probability for addition of the anionic Ni(0) nucleophile to the activated cyclic ether should be vastly improved in comparison to a neutral Ni(0) nucleophile.

Our group has explored the above concept in the last several years [21]. The previous zwitterionic Ni(II) catalysts suffered from insufficient stability under CO and were inactive for the COP of cyclic ethers. With our newly developed ligands that feature *ortho*-methoxy auxiliaries to stabilize the coordination, we demonstrate here the validity of the zwitterionic design principle of Ni(II) catalysts for the COP of cyclic ethers.

Zwitterionic Ni(II) acetyls, **1a** and **1b**, are synthesized by reaction of the lithium salt of the corresponding Ni(0) anion with  $Me_3O^+BF_4^-$  under CO (eq 1). Both **1a** and **1b** are stable in aromatic

$$Li^{+}(DME)_{x} \xrightarrow{Ar^{OMe}_{2}} P_{R_{2}}^{OMe} \xrightarrow{CH_{2}Cl_{2}, -30 \ ^{\circ}C} (1 \text{ atm}) \xrightarrow{Ar^{OMe}_{2}} P_{R_{2}}^{OO} (1 \text{ atm}) \xrightarrow{CO(1 \text{ atm})} P_{R_{2}}^{OO} (1 \text{ atm}) \xrightarrow{Ar^{f}_{3}B} P_{R_{2}}^{OO} (1 \text{ atm}) \xrightarrow{P_{R_{2}}^{OO}} (1 \text{ atm}) \xrightarrow{P_{R_{$$

Ar<sup>f</sup> = 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and Ar<sup>OMe</sup> = 2-(MeO)C<sub>6</sub>H<sub>4</sub> **1a**, R = Ph; **1b**, R = <sup>i</sup>Pr. solvents at room temperature and are isolated and completely characterized (see Supporting Information). They are the only detectable species under CO (1 atm) in solution by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy but are in equilibrium presumably with the methyl complexes, **1a-CO** and **1b-CO**, under nitrogen. Since **1a-CO** and **1b-CO** are absent under CO, the relatively broad linewidths of the *o*-methoxy <sup>1</sup>H NMR signal in **1a** and **1b** (9.6 an 8.4 Hz at half height, respectively) under CO are likely attributable to weak dynamic interactions between the *o*-methoxy groups and Ni. Also worth noting is that we were unable to isolate or observe the methyl or acetyl compounds with the previous generations of anionic *o*, *o*'-diphosphinobenzene ligands devoid of the *o*-methoxy auxiliaries.

X-ray crystallographic study confirms that **1a** adopts square planar conformation (Figure 1). The distances between Ni and the O atoms in the *o*-methoxy groups (O(3)-Ni(1) = 3.021(8) and O(4)-Ni(1) = 3.531(8) Å) are substantially greater than the sum of the Ni and O atomic radii. However, one of the *o*-methoxy groups appears to point toward the Ni center, suggesting some weak interaction. Single crystals of **1b-CO** were obtained by diffusion of pentane into the solution of **1b** under N<sub>2</sub>. The crystal structure of **1b-CO** reveals a similar bonding situation (Figure 1). The O-Ni distances (O(2)-Ni(1) = 2.977(3) and O(3)-Ni(1) = 3.593(3) Å) are out of the bonding range, but one of the *o*-methoxy groups points toward the Ni center.

The reactions of neat cyclic ethers with CO (300 - 900 psi) were screened in the presence of **1a** as the catalyst. For ethylene oxide (EO), no catalytic reaction occurred. For oxetane (OT) and THF, a very small amount of oligomer was obtained in each case. The product primarily consisted of ether repeat units but also ester linkages as the result of CO incorporation (eqs 2 and 3). In both cases, an acetyl end group, which apparently originates from **1a**, was observable in the <sup>1</sup>H NMR spectra of the product (see Supporting Information).

$$CO (900 \text{ psi}) + O \xrightarrow{1a}_{RT} H_{3C} \xrightarrow{O}_{6n} M_{n} = 3,300 \text{ PDI} = 1.21$$
(2)  

$$CO (300 \text{ psi}) + O \xrightarrow{1a}_{RT} H_{3C} \xrightarrow{O}_{6n} M_{n} = 2,600 \text{ PDI} = 1.40$$
(3)

Interestingly, when the polymerization was performed in the presence of both EO and THF (entry 1 in Table 1), a substantial amount of viscous product was obtained. 1- and 2-Dimensional NMR spectroscopic studies and GPC analysis were carried out to characterize the product (see Supporting Information). <sup>1</sup>H NMR shows that the product is composed of ester and ether units with



**Figure 1.** X-Ray structures of **1a** (top) and **1b-CO** (bottom) with 35% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths in **1a**: C(1)-Ni(1) = 1.785(7), C(2)-Ni(1) = 1.926(8), C(1)-O(1) = 1.120(10), C(2)-O(2) = 1.236(13), P(1)-Ni(1) = 2.2252(19), P(2)-Ni(1) = 2.2039(16) Å. Selected bond lengths in **1b-CO**: C(1)-Ni(1) = 1.771(3), C(2)-Ni(1) = 1.780(3), C(2)-O(1) = 1.119(3), P(1)-Ni(1) = 2.1817(7), P(2)-Ni(1) = 2.1994(7) Å.



Figure 2. <sup>1</sup>H NMR spectra of the products of the COP of EO and THF (top) and the COP of EO and THF-d<sub>8</sub> (bottom) in CDCl<sub>3</sub>. The peak assignments are made on the basis of chemical shifts and <sup>1</sup>H-<sup>1</sup>H COSY (see Supporting Information).

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Table 1. Summary of EO-THF COP catalyzed by 1a and 1b.<sup>[a]</sup>

CO +	0 + 03	J → H <sub>3</sub> C	$\{ \overset{o}{\models} (\circ, \cdot)_{x} (\circ, \cdot) $						
Entry	Catalyst	Temperature (°C)	CO Pressure (Atmosphere)	Reaction Time (h)	EO (mL)	CO : EO : THF ratio <sup>[b]</sup> in the product $(1 : x : y)$	M <sub>w</sub> <sup>[c,d]</sup> (g/mol)	PDI <sup>[d]</sup>	Yield (g)
1	1a	25	20	16	0.5	1:2.3:6.7	21,200	2.01	0.84
2	1a	25	20	16	1	1 : 5.2 : 7.4	16,500	1.97	1.09
3	1a	25	60	16	1	1 : 5.2 : 8.0	15,800	2.00	0.93
4	1a	25	20	3	1	1:3.1:6.9	13,500	2.01	0.32
5	1a	25	20	6	1	1 : 2.6 : 4.5	16,600	2.08	0.69
6	1a	0	20	16	1	1 : 4.5 : 14.2	34,500	2.35	0.28
7	1b	25	20	16	0.5	1 : 3.2 : 8.0	11,800	1.85	1.08
8	1b	25	20	16	1	1:4.9:7.2	12,600	1.85	1.21

[a] Reaction conditions: 15 mg of catalyst in 1 mL of THF. [b] Determined by <sup>1</sup>H NMR integration. [c] Weight-average molecular weight. [d] Determined by GPC relative to polystyrene standards.

a CO : EO : THF stoichiometry of 1 : 2.3 : 6.7 (Figure 2). The number-average molecular weight ( $M_n$ ) is 10,600 g/mol relative to polystyrene standards, and the polydispersity index (PDI) is ~2.01. <sup>1</sup>H NMR DOSY analysis [22, 23] revealed that the diffusion coefficients individually determined using  $^{1}H$ resonances of the ester and ether units fall in a narrow range (D =  $0.88 \sim 1.17 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , see Supporting information), in agreement with notion that these structures belong to a single product. Ethanolysis of the product resulted in a substantial reduction in molecular weight (See Supporting Information). The experimentally determined  $M_n$  of the ethanolyzed product is consistent with the expected  $M_{\rm n}$  (730 vs 658 g/mol), which is the average molecular weight between two ester units plus the molecular weight of ethanol. The PDI of the ethanolyzed product is 3.24, indicating that the distribution of the ester groups is relatively uniform in the original product before ethanolysis. The expected ethyl ester end group after ethanolysis is identified by <sup>1</sup>H NMR (See Supporting Information). Thus, all spectroscopic and chemical evidence unequivocally confirms the structure of the poly(ether-co-ester) product.

When the aforementioned reactions were carried out under 1 atm of CO under otherwise identical conditions, no polymer or oligomer products were obtained. The requirement of high CO pressure suggests that 5-coordinate species 1a+CO is catalytically active, not 1a. The proposition is in agreement with the anticipated reactivities of 4- vs 5-coordinate Ni\*-acyl compounds, judging from the IR absorption wavenumber of the acyl C=O stretching vibration ( $\nu_{C=O}$ ). A high  $\nu_{C=O}$  value similar to that of an organic ester or acyl chlorides indicates high electrophilicity and high reactivity, and a low  $v_{C=O}$  value similar to that of organic amide indicates the opposite [24]. The reported  $v_{C=O}$  values of a pair of 4- and 5-coordinate cationic Ni-acetyl compounds are 1698 and 1733 cm<sup>-1</sup> [25], respectively, indicating that the acetyl group of the 5-coordinate compound is more electrophilic than that of the 4-coordinate compound. The  $v_{C=O}$ value is 1,691 cm<sup>-1</sup> for **1a**. This suggests that the acetyl group in 1a is guite unreactive similar to an organic amide.

The drastic difference in productivity between the COP of EO and THF together and the COPs of EO or THF alone can be satisfactorily accounted for by a mechanistic scenario (Scheme 2) fully compatible with the aforementioned working hypothesis (Scheme 1) for zwitterionic Ni(II)-acyl catalysts. A priori, EO is appreciably less nucleophilic than THF [26]. As such, EO cannot react with 1a+CO, but THF can to give b. The THF ring in b is not sufficiently activated by the acyl group to undergo rapid ringopening reaction but can rapidly exchange with EO to form c. The EO ring in c is highly reactive and undergoes rapid ringopening reaction with free THF (less likely with free EO or the least likely with the Ni(0) counter-anion) to give d. In essence, THF acts as a co-catalyst for promoting EO enchainment lil pyridine in the COP of epoxides catalyzed by acyl-Co(CO)<sub>4</sub>[11d]; while EO promotes THF enchainment the same way as it doce when a cationic initiator does not sufficiently activate THF to initiate THF polymerization [27]. The tertiary oxonium propagating chain end is sustained for several THF and EO enchainments ( $d \rightarrow e$ ) until nucleophilic addition of the Ni(0) counteranion to the THF oxonium re-establishes a Ni-C  $\sigma$  bond  $(e \rightarrow f)$ . Coordinative CO insertion ensues to regenerate the zwitterioinic Ni-acyl active species at the chain end.



Scheme 2. Proposed mechanism of mutually promoted THF and EO enchainments.

The above mechanistic scenario mandates a microstructural signature; that is, a CO enchainment is followed by an EO enchainment but rarely by a THF enchainment. To decipher this specific sequence, we carried out the COP of deuterated THF (THF-d<sub>8</sub>, 99.5 atom% D) and EO. The <sup>1</sup>H NMR spectrum of the product is compared to that of the product of regular THF and EO (Figure 2). The triplet of the methylene group vicinal to the ester bond remains intact in the <sup>1</sup>H NMR spectrum of the product from THF-d<sub>8</sub> and EO, but the triplet of the *α*-methylene next to the carbonyl group is no longer detectable. This observation confirms that the ester linkages arise primarily from EO. In other words, a CO enchainment is indeed followed by an EO enchainment but rarely by a THF enchainment. The specific sequence therefore provides convincing evidence for the mechanism depicted in Scheme 2.

To assess the limits of the current catalysts and to further interrogate the mechanism, we carried out the polymerization under varied conditions (Table 1). For the reactions catalyzed by 1a, an increase in the EO amount in the feed resulted in a decrease in the molecular weight and an increase in the number of ether units (i.e., x + y) between two ester linkages in addition to the expected increase in EO incorporation in the product (entries 1 vs 2). Increasing the CO pressure from 300 psi to 900 psi did not result in any marked difference in the composition of the product (entries 2 vs 3). This is expected according to the mechanism depicted in Schemes 2 since coordinative CO insertion takes place at the metal center while EO and THF enchainments are initiated by the acyl group and proceed via the oxonium intermediate. They do not directly compete again each other. Shortening the reactions time decreased the yield (entries 2, 4, and 5). Lowering the reaction temperature from 25 °C to 0 °C doubled the molecular weight but also significantly lowered the yield. The amount of THF incorporated into the product markedly increased. When 1b was used as the catalyst, the yields increased modestly, but the molecular weights of the products decreased somewhat in comparison to the reactions catalyzed by 1a under identical conditions (entries 1 vs 3 and 2 vs 4). Overall, the differences between 1a and 1b are small. All poly(ether-co-ester)s produced by 1 a and 1b are viscous liquids.

Finally, a direct cationic analog of **1a** and **1b** with the same bis(phosphino)benzene lignad framework was synthesized and tested for the copolymerization of EO and THF under high-pressure CO (see Supporting Information). Only polyether was obtained. The amount of ester structure in the product is dubious at best. This unequivocally confirms that the zwitterionic structure is necessary.

In summary, we have provided the initial examples of zwitterionic Ni(II) compound-catalyzed COP of cyclic ethers and hence validated the zwitterionic design principle of Ni(II) catalysts. The polymerization catalyzed by **1a** and **1b** is nonalternating with respect to CO and cyclic ether enchainments. The COP of EO and THF together is far more effective than the COPs of EO, OT, or THF alone. The current poly(ester-co-ether) products are water-soluble and have glass transition temperatures well below room temperature. While potential applications can be envisioned based on these properties, for example, as the soft segment of thermoplastic elastomers and hydrogels, the value of the present work is that the zwitterionic catalyst design principle unlocks a new venue of catalyst development for COPs of heteroatom-containing monomers. With such novel catalysts, new polymerizations and useful polymer products will emerge.

#### **Experimental Section**

**Synthesis of 1a.** The overall synthetic route is outlined in Supporting Information (Scheme S1). The lithium salt of the corresponding Ni(0) anion (**6a**, 500 mg, 0.4 mmol) and trimethyloxonium tetrafluoroborate (200 mg, 1.35 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (8 mL). The mixture was stirred under CO at -30 °C for 6 h. Hexane (20 mL) was added to the orange solution. The mixture was stirred to give copious precipitate. The solvent mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> was removed by filtration. The solid was washed with hexane and extracted with toluene (20 mL) under CO. Hexane (50 mL) was layered on top of the toluene solution. The mixture was kept at -45 °C for several days to give a yellow crystalline precipitate accompanied by a small amount of orange oil. The solution was removed by filtration. The crude product was washed with benzene (7 mL) quickly to remove the orange oil. The yield of the resultant yellow crystalline product was 56% (216 mg).

**General Polymerization Procedure.** Catalyst **1a** or **1b** (15 mg) was added to an autoclave in the glove box under nitrogen. The nitrogen atmosphere in the autoclave was replaced with CO (1 atm) on a Schlenk line. The cyclic ether monomer(s) was cooled to -78 °C and injected to the autoclave via a syringe under a gentle flow of CO (1 atm). The pressure of CO was increased. The reaction was magnetically stirred for a period of time at a set temperature as specified in Table 1. The pressure was released. Caution! The autoclave was opened in a well-ventilated hood and allowed to sit in air for at least 1 h with continuing stir. This is to allow oxidative decomposition of any Ni(CO)<sub>4</sub> that might has adventitiously formed. The solution was then transferred into a vial, and the volatile fraction was removed under vacuum. The product was obtained as a viscous liquid.

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## COMMUNICATION

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# COMMUNICATION

#### Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

The necessity for the Ni(0) nucleophile and the cyclic ether oxonium to exists as an ion-pair requires the initial Ni(II) catalyst to be a zwitterion.



Yiwei Dai, Shiyu He, Bangan Peng, Laura A. Crandall, Briana R. Schrage, Christopher J. Ziegler, and Li Jia\*

Zwitterionic Design Principle of Ni(II) Catalysts for Carbonylative Polymerization of Cyclic Ethers

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