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# Halide-Free and Bifunctional One-Component Catalysts for the Coupling of Carbon Dioxide and Epoxides

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### **Supporting Information**

**ABSTRACT:** In this paper, we first report a new class of halide-free and bifunctional one-component catalysts for the coupling of  $CO_2$  with epoxides. The catalysts do not need halide-based additives or tethered salts attached to the ligand when used for this coupling reaction. As the halide-free and bifunctional one-component catalysts, we chose nonionic and monomeric tetracarbonylchromium(0), tetracarbonylmolybdenum(0), and tetracarbonyltungsten(0) complexes chelated by modified ethylenediamines, namely N,N-dimethylethylenediamine, N,NN'-trimethylethylenediamine, N,NN'-trimethylethylenediamine, and N,N,N',N'-tetramethylethylenediamine.



A simple mixture of  $M(CO)_6$  (M = Cr, Mo, and W) with the modified ethylenediamines shows only one-third of the activity achieved with the tetracarbonyl metal complexes precoordinated to the corresponding modified ethylenediamines. Increasing the number of methyl substituents on the nitrogen atoms of the ethylenediamine derivatives as well as the chromium metal center in the metal carbonyl complex significantly enhanced the catalytic activity. Thus, among the 12 catalysts tested, tetracarbonyl(tetramethylethylenediamine)chromium(0) exhibited the best catalytic activity under the same reaction conditions. Various terminal and internal epoxides were easily converted into the corresponding cyclic carbonates using this chromium system. Calculations based on density functional theory were also carried out to elucidate the mechanism of the coupling reaction.

#### INTRODUCTION

The rapid increase in the carbon dioxide  $(CO_2)$  concentration in the atmosphere is of great concern globally, and this issue must be addressed. Extensive studies, including CO<sub>2</sub> emission reduction, carbon capture and sequestration, and carbon capture and utilization, are actively underway to reduce atmospheric  $CO_2$  levels.<sup>1</sup> From a synthetic chemist's point of view,  $CO_2$  is an attractive C1 source because of its safety, abundance, and renewability.<sup>2</sup> However, a considerable amount of energy is required for the chemical activation of highly oxidized and thermodynamically stable CO<sub>2</sub>. Nonetheless, various chemical substances, such as urea, methanol, cyclic carbonates, polycarbonates, and sodium 2-hydroxybenzoate, have been commercially produced from CO<sub>2</sub>.<sup>3</sup> Among the processes for synthesizing these compounds, the coupling of CO2 and epoxides to make cyclic carbonates is one of the most active research fields of  $CO_2$  conversion due to its atom economy (no side products) and broad applicability. Since aliphatic cyclic carbonates were first synthesized in the 1950s,<sup>4</sup> they have been used in many applications,<sup>3</sup> including as aprotic solvents, electrolytes for lithium-ion batteries, monomers for polymerizations, and pharmaceutical intermediates.

To date, numerous catalytic systems have been reported in the literature for the synthesis of cyclic carbonates.<sup>5-14</sup> As shown in Chart 1, catalytic systems can be roughly classified into three

Chart 1. Schematic Representation of Catalytic Systems for the Synthesis of Cyclic Carbonates



categories. The most effective catalytic systems are binary systems consisting of a metal-based catalyst in conjunction with a halide additive.<sup>5,6</sup> The metal complexes chelated by well-defined ligands can act as Lewis acids to activate the epoxides. Lewis basic halides serve as nucleophiles to open the epoxide ring in the catalytic cycle.<sup>7</sup> Unlike binary systems, the



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Chart 2. Logical Approach to Conceptionally Novel Halide-Free and Bifunctional One-Component Catalysts



Scheme 1. Synthetic Routes for  $L^nM(CO)_4$  (n = 1-4; M = Cr, Mo, W)



bifunctional one-component systems depicted in Chart 1b could definitely reduce the translational entropy cost by combining the Lewis acid and Lewis base in a single molecule, and consequently, the close proximity of the two functional groups could maximize the synergistic effect. Various kinds of bifunctional one-component catalytic systems equipped with both Lewis acid metallic regions and nucleophilic fragments in a single molecule for the synthesis of cyclic carbonates have been reported in the literature.<sup>8-12</sup> Recently, oxo-bridged dimeric aluminum(salen) complexes as catalysts in the absence of any additives or tethered salts have been reported for the synthesis of cyclic carbonates.<sup>13,14</sup> Unexpectedly, the  $\mu$ -oxo group in the oxobridged dimeric aluminum(salen) complexes was easily converted into a  $\mu$ -carbonato group in the first step of the coupling reaction, and epoxide insertion subsequently occurred. Because no halide-based additive was present and two aluminum centers in a single molecule were involved, this system belongs to the halide-free dimeric systems shown in Chart 1c. However, only two papers on aluminum-based dimers have been reported to date.<sup>13,14</sup>

Apart from the three systems shown in Chart 1, another promising catalytic system is halide-free and bifunctional onecomponent catalysts. As shown in Chart 2a, we hypothesized that catalysts of this new concept could be achieved if the ligand molecule has both a binding site and a Lewis basic site, and at the same time, the Lewis acidic metal center remains coordinatively unsaturated to allow epoxide coordination. Thus, we chose  $L^nM(CO)_4$  (M = Cr, Mo, and W;  $L^n$  = bidentate diamine ligands) as model catalysts for the halide-free and bifunctional one-component systems. The  $L^nM(CO)_4$  compounds were selected as model catalysts for the following reasons. (1) Bidentate diamine ligands could bind to the metal center and still have a free Lewis basic site because in solution, bidentate diamines of these metal complexes are hemilabile, and this lability results in a vacant site for epoxide coordination as depicted in Chart 2b. The kinetics of the reaction between (N,N,N',N')-tetramethylethylenediamine $)M(CO)_4$  (M = Cr and W) and phosphite were reported in the literature.<sup>15,16</sup> (2) The Lewis basicities<sup>17</sup> of diamine ligands  $L^n$  and chromium complexes<sup>18-20</sup> for cyclic carbonate synthesis are well-known. Thus, we chose  $L^n M(CO)_4$  as a halide-free and bifunctional onecomponent system. (3) The presence of strong-field CO ligands permits the generation of  $L^{n}M(CO)_{4}$  as the sole product without contamination by any side products from the reaction between commercially available  $M(CO)_6$  and bidentate ligand L.<sup>21–27</sup> Unlike other chromium-based catalysts with oxidation states of +3 to +5,  $^{18-20}$  the oxidation state of  $L^{n}M(CO)_{4}$  is zero, which means that  $L^{n}M(CO)_{4}$  is diamagnetic and its purity could be determined by NMR experiments.

In this context, we report here group VI metal (0) tetracarbonyls containing four different kinds of diamines as a new class of halide-free and bifunctional one-component monomeric catalysts for the coupling of CO<sub>2</sub> with terminal or internal epoxides. The detailed mechanism for this reaction was also confirmed by density function theory calculations.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of Halide-Free and Bifunctional One-Component Catalysts. As outlined in Scheme 1, 12 target products, group VI metal tetracarbonyls chelated by bidentate ligands, namely, N,N-dimethylethylenediamine ( $L^{1}$ ), N,N'-dimethylethylenediamine ( $L^{2}$ ), N,N,N'-

trimethylethylenediamine ( $L^3$ ), and *N,N,N',N'*-tetramethylethylenediamine ( $L^4$ ), as halide-free and bifunctional onecomponent catalysts, were prepared in one step directly from commercially available  $M(CO)_6$  (M = Cr, Mo, and W) and bidentate ligands  $L^1-L^4$ . To synthesize  $L^nM(CO)_4$ , a mixture of polar solvents di-*n*-butyl ether and THF (20:3 v/v) was applied. The synthesis of the Cr and Mo compounds required a relatively short reaction time of 2 h, while the W compounds need an extended reaction time of 7 h. After appropriate workup, high purity products  $L^nCr(CO)_4$ ,  $L^nMo(CO)_4$ , and  $L^nW(CO)_4$  were obtained as yellow solids in yields of 49–64%, 78–92%, and 83–90%, respectively. As the metal center becomes heavier and the number of methyl groups attached to the N atom increases, the yield of the final product increases.

All  $L^{n}M(CO)_{4}$  compounds were freely soluble in polar organic solvents such as THF, acetone, MeOH, and DMSO but insoluble in toluene and nonpolar solvents such as hexane. These compounds were relatively stable in air and even in polar solvents for a few days. The solubility of  $L^{n}M(OC)_{4}$  compounds increases as the increased number of methyl substituents on the nitrogen atoms increases. All compounds were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR and IR spectroscopy (see the Supporting Information). Newly synthesized  $L^{2}Cr(CO)_{4}$ ,  $L^{3}Cr(CO)_{4}$ , and  $L^{3}W(CO)_{4}$  species were also characterized by elemental analysis.

In comparison with free ligands  $L^1-L^4$ , all signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra are shifted downfield, which is a result of complexation with the metal. The magnitude of the downfield shifts in the <sup>1</sup>H NMR spectra roughly decreased in the order Cr to Mo to W under the fixed ligand system. In addition, in the <sup>1</sup>H NMR spectra, the magnitude of the downfield shift is greater for N-H resonances than for N-CH<sub>3</sub>. The N-H and N-CH<sub>3</sub> resonances shifted downfield by approximately 1.55 and 0.53 ppm, respectively, relative to those of the corresponding free ligand.

**Coupling of CO<sub>2</sub> with Epoxides.** To determine if  $L^{n}M(CO)_{4}$  could act as halide-free and bifunctional onecomponent catalysts in the coupling reaction, the coupling of CO<sub>2</sub> with epichlorohydrin (EH) was performed using a fixed [EH]/[catalyst] molar ratio of 1000 and a CO<sub>2</sub> pressure of 10 bar at 100 °C for 3.5 h. The results are summarized in Table 1.

As expected,  $M(CO)_6$  (M = Cr, Mo, and W) did not show any catalytic activity (Table 1, entries 1-3). Our recent report<sup>17</sup> on  $L^1-L^4$  as organocatalysts by themselves for the synthesis of cyclic carbonates showed that the greater number of methyl substituents on the N atoms of the ethylenediamine ligand provided the higher catalytic activity (entries 4-7). Under the same conditions,  $M(CO)_6$  in conjunction with L<sup>4</sup> showed activities similar to that achieved with  $L^4$  alone (entries 8–10). These results indicate that simple mixtures of  $M(CO)_6$  with L<sup>4</sup> did not show any cooperative effect in their activity. Then, we explored tetracarbonyl group VI metal complexes chelated by  $L^1-L^4$ . Surprisingly, all complexes could act as halide-free and bifunctional one-component catalysts (entries 11-22). Interestingly, the catalytic activities of the metal complexes with more methyl substituents are greater than those of complexes with fewer methyl groups (entries 11, 14, 17, and 20; entries 12, 15, 18, and 21; entries 13, 16, 19, and 22). In addition, the activity decreased going down the group from Cr to Mo to W with the same ligand (entries 11-13, 14-16, 17-19, and 20-22).

Among the 12 tetracarbonyl complexes,  $L^4Cr(CO)_4$  showed the highest TON (872) and TOF (249.1) (entry 20). Many kinds of chromium-based complexes have been reported as Table 1. Catalyst Screening for the Coupling Reaction of Epichlorohydrin and CO<sub>2</sub>

	OCI + CC 10 mmol 10 k	0.1 mol% Catalyst 100°C, 3.5 par	in O	p ∕—cı
$\sum_{N}$	NH <sub>2</sub> N N H H	N H	N N	I N
	$L^1$ $L^2$	L <sup>3</sup>		L <sup>4</sup>
entry	catalyst	yield [%] <sup>a</sup>	TON <sup>b</sup>	TOF $[h^{-1}]^c$
1	$Cr(CO)_6$	0	0	0
2	$Mo(CO)_6$	0	0	0
3	$W(CO)_6$	0	0	0
4	$L^1$	0	0	0
5	$L^2$	0	0	0
6	$L^3$	19.4	194	55.4
7	$L^4$	23.4	234	66.9
8	$Cr(CO)_6 + L^4$	27.8	278	79.4
9	$Mo(CO)_6 + L^4$	28.1	281	80.3
10	$W(CO)_6 + L^4$	28.4	284	81.1
11	$L^1Cr(CO)_4$	27.4	374	107
12	$L^1Mo(CO)_4$	19.0	190	54.3
13	$L^1W(CO)_4$	8.8	88	25.1
14	$L^2Cr(CO)_4$	47.8	478	137
15	L <sup>2</sup> Mo(CO) <sub>4</sub>	28.6	286	81.7
16	$L^2W(CO)_4$	25.6	256	73.1
17	$L^{3}Cr(CO)_{4}$	65.9	659	188
18	L <sup>3</sup> Mo(CO) <sub>4</sub>	46.9	469	134
19	$L^{3}W(CO)_{4}$	28.6	286	81.7
20	$L^4Cr(CO)_4$	87.2	872	249
21	L <sup>4</sup> Mo(CO) <sub>4</sub>	56.3	563	161
22	$L^4W(CO)_4$	47.6	476	136

"Yield of pure isolated cyclic carbonate. <sup>b</sup>TON (turnover number) = (mol of epichlorohydrin consumed)/(mol of catalyst). <sup>c</sup>TOF (Turnover frequency) = (mol of epichlorohydrin consumed)/(mol of catalyst  $\times$  time (h)).

catalysts in conjunction with a cocatalyst for the synthesis of cyclic carbonates.<sup>18–20</sup> Surprisingly, bidentate and tridentate ligands chelated to chromium have never been used in this reaction. Although the metal sources have been extended to molybdenum and tungsten, to the best of our knowledge, group VI complexes in zero oxidation states chelated by bidentate ligands have never been used as catalysts for the synthesis of cyclic carbonate.

The influences of the concentration of  $L^4Cr(CO)_4$  catalyst, CO<sub>2</sub> pressure, and temperature on the coupling reaction between CO<sub>2</sub> and epichlorohydrin were investigated, and the results are summarized in Table 2. Using a fixed catalyst concentration and temperature, the catalytic activity was found to be proportional to the CO<sub>2</sub> pressure (Table 2, entries 1–4; entries 5–8; entries 9–12; entries 19–22). The highest TOF (2010) was obtained using 0.01 mol % catalyst loading and 30 bar of CO<sub>2</sub> pressure at 100 °C in 1 h (entry 4). As expected, higher catalyst concentrations resulted in higher activities (entries 1, 5, 9, and 19; entries 2, 6, 10, and 20; entries 3, 7, 11, and 21; entries 4, 8, 12, and 22). The TOF increased rapidly from 42 to 541 as the reaction temperature was gradually increased from 25 to 125 °C (entries 14–18).

To demonstrate the important discovery that  $L^4Cr(CO)_4$  acting as a halide-free and bifunctional one-component catalyst

Table 2. Screening of Coupling Reaction Conditions Using  $L^4 \mbox{Cr}(\mbox{CO})_4$ 



<sup>*a*</sup>Yield of pure isolated cyclic carbonate. <sup>*b*</sup>TON (turnover number) = (mol of epichlorohydrin consumed)/(mol of catalyst). <sup>*c*</sup>TOF (turnover frequency) = (mol of epichlorohydrin consumed)/(mol of  $L^4Cr(CO)_4 \times time (h)$ ).

is not restricted to epichlorihydrin, the synthesis of a variety of cyclic carbonates from the corresponding terminal and internal epoxides as substrates was carried out (Figure 1). Substrates include seven terminal epoxides, propylene oxide (1a), 1,2epoxybutane (1b), 1,2-epoxyhexane (1c), epichlorohydrin (1d), glycidyl methyl ether (1e), 1,2-epoxy-3-phenoxypropane (1f), and tert-butyl glycidyl ether (1g), and four internal epoxides, 1,2-epoxy-2-methylpropane (1h), 2,3-epoxybutane (1i), cis-cyclohexene oxide (1j), and cis-cyclopentene oxide (1k). The reactions of epoxides 1a-1c with simple alkanes (R = Me, Et, and n-Bu) showed a substantial dependence on chain length. Interestingly, epoxides with short chains gave higher conversions. Among the tested substrates, 1d was the most active epoxide in the coupling reaction, and it showed a TON of 938 and TOF of 312.7 within only 3 h. 1e with a -CH<sub>2</sub>OMe substituent and 1f with a -CH2OPh substituent showed excellent TONs of 893 and 971, respectively; however, 1g with a sterically hindered -CH2OBut group exhibited a relatively slow conversion. Interestingly, oxo-bridged dimeric aluminum(salen) complexes, a typical halide-free dimeric system (shown in Chart 1c), could not catalyze the reaction of internal epoxides for the synthesis of the corresponding cyclic carbonates even under harsh conditions of 2.5 mol % catalyst loading and 50 bar of CO<sub>2</sub> pressure at 50 °C for 60 h.<sup>13</sup> Our system  $L^4Cr(CO)_4$  could catalyze the reaction of internal epoxides 1h-1k using 0.1 mol % catalyst loading and 10 bar of CO2 pressure at 120 °C in 48 h. In addition, halide-free bifunctional one-component catalyst  $L^4Cr(CO)_4$  showed serval times better higher TOF-based catalytic activities than halidefree dimeric system in the synthesis of terminal epoxides.<sup>13</sup> As shown in Figures S67–S70, cis-hexahydrobenzo[d][1,3]dioxol-2-one  $(2j)^{28}$  and *cis*-tetrahydro-4*H*-cyclopenta[*d*][1,3]dioxol-2one  $(2k)^{29}$  with the retained original configuration of the corresponding epoxides were obtained. This means that the cyclic carbonate obtained in the coupling reaction is made by the nucleophilic ring-opening  $(S_N 2)$  of epoxide, followed by the  $S_N 2$ ring-closing pathway, rather than the S<sub>N</sub>1 ring-closing pathway.



Figure 1. Scope of epoxides using  $L^4Cr(CO)_4$ .



Figure 2. Variable temperature NMR spectra for  $L^1W(CO)_4$ .



Figure 3. Plausible mechanism for coupling the reaction of  $CO_2$  with propylene oxide using  $L^4Cr(CO)_4$ . For clarity, the four carbonyl groups attached to the chromium center in  $L^4Cr(CO)_4$  are omitted.



Figure 4. Computed energy profile of cyclic propylene carbonate formation with catalyst  $L^4Cr(CO)_4$  at 373.15 K and 10 bar. For clarity, the four carbonyl groups attached to the chromium center in  $L^4Cr(CO)_4$  are omitted.



Figure 5. Two possible mechanistic pathways from intermediate D.

Mechanism for the Coupling Reaction of CO<sub>2</sub> with Epoxides. Figure 2 shows the chemical shifts for  $-NMe_2$  and  $-NH_2$  arm protons in the variable temperature NMR spectra of  $L^1W(CO)_4$  in DMSO- $d_6$ . Interestingly,  $-NMe_2$  protons of  $L^1W(CO)_4$  appear as a two singlets (or a doublet) at room temperature. Similar observation for 5-membered ring compounds with W-NMe<sub>2</sub> bond was reported in the literature.<sup>30-32</sup> This peak splitting is probably due to the coordination of ring nitrogen of  $L^1$  with tungsten (I = 1/2). A clear upfield shift in the  $-NH_2$  arm of  $L^1W(CO)_4$  as a broad singlet from 5.34 ppm at 25 °C to 5.13 ppm at 100 °C was observed. As the temperature goes up, the methyl protons of the  $-NMe_2$  arm shifted downfield and new two singlets (or a doublet) appear at the downfield region. The upfield shift of  $-NH_2$  protons and the peak splitting of  $NMe_2$  protons in complex  $L^1W(CO)_4$  indicated that the  $-NH_2$ arm of the bound diamine in  $L^1W(CO)_4$  dissociates reversibly at high temperature and other  $-NMe_2$  arm is firmly attached to metal center even at high temperature of 100 °C. This result supports the existence of hemilability for our catalytic systems (see Figures S71–S75 in the Supporting Information).

Figures 3 and 4 summarize the computational mechanistic investigations of the coupling reaction of carbon dioxide and



Figure 6. Comparison of the energy barriers in the reactions catalyzed by  $L^4M(CO)_4$ . For clarity, the four carbonyl groups attached to the metal center in  $L^4M(CO)_4$  are omitted.

propylene oxide using our halide-free and bifunctional onecomponent catalyst  $L^4Cr(CO)_4$ , and the proposed mechanism takes into account all our experimental observations and theoretical calculation studies.

In order to help understand catalytic cycle in our work, we adopted the energetic span model which systematically expresses TOF in terms of the energies of all states in catalytic cycle.<sup>33,34</sup> The model quantitatively identifies TOF-determining intermediate (TDI) and TOF-determining transition state (TDTS) in a single catalytic cycle based on the degree of TOF control of each state, which measures how much influential the state is on the TOF value. The TDTS – TDI energy difference  $\Delta G^{\ddagger}$ , called the energetic span, can serve as the apparent activation energy, expressing approximately TOF  $\approx \frac{k_{\rm B}T}{h} e^{-\Delta G^{\ddagger}/RT}$ . Thus, the  $\Delta G^{\ddagger}$  values characterizing catalytic cycles allow us to compare the plausibility of proposed mechanisms and the efficiency of various catalysts.

Six-coordinated precatalyst  $L^4Cr(CO)_4$ , denoted as  $A_0$ , was activated to hemilabile species A with a vacant site, resulting from one  $-NMe_2$  group detaching from the chromium center of  $A_0$ . The actual catalytic species A was first optimized, and the Gibbs free energies,  $\Delta G(sol)$ , of all other structures are shown relative to that of A. The catalytic cycle starts with the occupation of the vacant site by propylene oxide to afford intermediate **B** with a solution-phase binding free energy of only 1.65 kcal/mol. Then, the sterically less hindered carbon of the propylene oxide is attacked by the basic  $-NMe_2$  group in a nucleophilic fashion to give eight-membered metallacycle **C** via transition state **B**–**TS**. This step features the highest activation barrier (36.18 kcal/mol) in the catalytic cycle from **A** to **C** although there is another comparable, but lower barrier in the later part. Intermediate **C** can attack  $CO_2$  in a nucleophilic manner leading to five-coordinated intermediate **E** with a vacant site via **D**. As shown in Figure 5, it is also possible that intermediate **E**' with six-coordinated Cr center through other pathway. However, this mechanistic pathway was removed from consideration due to its high activation energy of 54.70 kcal/mol to give the final products (see Supporting Information).

Intriguingly, the activation energy from **E** to **E**–**TS** is only 4.57 kcal/mol, which implies the formation of the C–O bond and cleavage of the C–N bond are facile. It is also interesting that the energy barrier of 35.36 kcal/mol from **C** to **E**–**TS** in the second half of the cycle is comparable to the highest one, 36.18 kcal/mol from **A** to **B**–**TS**. We found that the most important TDI and TDTS in Figure 4 are **A** (0.60) and **B**-**TS** (0.80) with the energetic span  $\Delta G^{\ddagger} = 36.18$  kcal/mol. The TDI and TDTS in alternative mechanistic pathway are **E**' (0.64) and **E**'–**TS** (1.00) with  $\Delta G^{\ddagger} = 54.70$  kcal/mol, where the numbers 0.64 and



Figure 7. Schematic computed energy profiles of cyclic propylene carbonate formation with catalyst  $L^{n}Cr(CO)_{4}$  (n = 1-4) at 373.15 K and 10 bar.



Figure 8. Schematic computed energy profiles of cyclic propylene carbonate formation with catalyst L<sup>4</sup>Cr(CO)<sub>4</sub> at 373.15 K and 1, 5, 10, and 30 bar.

1.00 in parentheses represent the degree of TOF control of the state. Therefore, the barrier of 36.18 kcal/mol from **A** to **C** can be considered an apparent rate-determining step of the overall

catalytic cycle. On the other hand, we also checked the possibility that the reaction proceeds by intermolecular attack of free diamine (such as entry 8 in Table 1,  $Cr(CO)_6 + L^4$ ) on the

metal-bound epoxide. However, we found the barrier of 43.0 kcal/mol for such attack, and so such catalysts proved to be less efficient than  $L^4Cr(CO)_4$  (see Supporting Information).

As shown in Table 1, the activities decrease going down the group from Cr to Mo to W with the same ligand. For DFT calculations, we consistently used ligand L<sup>4</sup>, which showed the highest activity among the four bidentate ligands. Figure 6 shows the computed energy profiles of cyclic propylene carbonate formation using  $L^4M(CO)_4$  (M = Cr, Mo, and W). It is noteworthy that the rate-determining step for  $L^4Cr(CO)_4$  is primarily in the first half of catalytic cycle with a comparable barrier in the second half; however, for the two other metals,  $L^4Mo(CO)_4$  and  $L^4W(CO)_4$ , the second half steps are solely rate-determining. Although the overall shapes of profiles look similar, the first half cycle tends to be stabilized while the other half is destabilized as the central metal becomes heavier. This trend shifts the TOF-determining spotlight to the second half, making C (1.00) and E-TS (1.00) be TDI and TDTS, respectively, for the heavier catalysts. Note that the degree of TOF control in this single set of TDI and TDTS is 1.00, which implies that TDI and TDTS are unambiguously defined in the case of heavier metal catalysts. According to the energetic span model shown in Figure 6, the apparent activation energies are found to be  $\Delta G^{\ddagger} = 36.18 \text{ kcal/mol for } L^4 Cr(CO)_4$ , 42.66 kcal/ mol for  $L^4Mo(CO)_4$ , and 50.11 kcal/mol for  $L^4W(CO)_4$ , which matches with experimental trends.

According to Table 1, the catalytic activities of the metal complexes with more methyl substituents are higher than those of complexes with fewer methyl groups. Unlike  $L^4Cr(CO)_4$ , catalysts  $L^1Cr(CO)_4 - L^3Cr(CO)_4$  can have two or four  $\Delta G^{\ddagger}$ values depending on which nitrogen atom is detached from the chromium center. Figure 7 illustrates that the average apparent activation energies  $\Delta G^{\ddagger}$  obtained from the energetic span model are 36.18 kcal/mol for  $L^4Cr(CO)_4$ , 40.89 kcal/mol for  $L^{3}Cr(CO)_{4}$ , 44.93 kcal/mol for  $L^{2}Cr(CO)_{4}$ , and 45.23 kcal/ mol for  $L^1Cr(CO)_4$  (see Tables S3 and S4 in the Supporting Information). In other words, the coupling reaction of carbon dioxide and propylene oxide experiences 3.71-9.05 kcal/mol higher hindrance with  $L^{1}Cr(CO)_{4}-L^{3}Cr(CO)_{4}$  than with  $L^4Cr(CO)_4$ . Therefore, our calculations suggest that  $L^4Cr$ - $(CO)_4$  should exhibit a considerably higher activity than the other catalysts when taking the Arrhenius factor into account. In fact,  $L^4Cr(CO)_4$  (Table 1, entry 20) showed 1.3–3.2 fold higher activity than the three other catalysts (Table 1, entries 11, 14, and 17).

Finally, it is also noteworthy to mention pressure effects as the catalytic activities in experiment were found to be proportional to the pressure of CO<sub>2</sub>. Unfortunately, the energetic span model we adopted for activity analysis deals with only the temperature and the energetics of the intermediates and transition states, and the concentration or pressure effects are not taken into account in calculating TOF. However, we can consider changes in the pressure under which the whole reaction proceeds, not limiting the pressure effects just to that of  $CO_2$ . As illustrated in Figure 8, the two barriers in Gibbs energy profiles tend to decrease as the pressure increases, from 1 to 5, 10, and 30 bar. The entropy change for each step is negative except for the formation of final products. As the pressure increases, on the other hand, the translational entropy generally decreases while the number of reactants is greater than that of products (see Table S5 in the Supporting Information). It results in less negative entropy change and less positive Gibbs energy change, meaning less hindered catalytic reaction cycles. The decreases in energy

barriers are 1.2, 1.7, and 2.5 kcal/mol as the pressure increases from 1 bar to 5, 10, and 30 bar, respectively. Note also that the whole reaction Gibbs energy decreases from -2.03 to -3.22, -3.73, and -4.55, as the pressure increases from 1 to 5, 10, and 30 bar.

#### CONCLUSION

In conclusion, we hypothesized and synthesized a new class of halide-free and bifunctional one-component catalysts for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides. The catalysts were rationally and systematically designed, and we chose well-known classical group VI metal(0) tetracarbonyl complexes with bidentate diamine ligands as halide-free and bifunctional one-component catalysts. These kind of catalysts were selected because of the facile generation of a vacant site on the metal center for epoxide coordination due to the hemilability of bidentate diamines on group VI(0) carbonyls. In addition, in situ generated and neutral amine-centered nucleophiles, which are less likely to cause reactor corrosion than halide-based nucleophiles, can open the epoxide ring, and the translational entropy penalty was reduced by using an intramolecular reaction with nucleophile and epoxide in close proximity. Furthermore, the nucleophilicity of the diamine ligand can be easily controlled by the introduction of electron-donating alkyl groups into the N atoms. The optimized catalyst was highly effective in forming cyclic carbonates with a wide range of different substrates. These new catalysts can be readily synthesized and obtained in pure form with almost no contamination. Thorough evaluation of the catalytic activity using DFT theoretical mechanistic studies also supported the utility of these novel halide-free and bifunctional one-component catalysts.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00262.

Experimental procedures, analytical data, computational details, and Cartesian coordinates of all computed structures and copies of the <sup>1</sup>H and <sup>13</sup>C NMR spectra and IR spectra for all products (PDF)

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# Notes

The authors declare no competing financial interest.

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