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Highly Active Di- and Trimetallic Cobalt Catalysts for the Copolymerization of CHO and CO_2 at Atmospheric Pressure

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ABSTRACT: The synthesis and characterization of three new cobalt catalysts for the copolymerization of carbon dioxide and cyclohexene oxide are reported. All the complexes are extremely active at just 1 atm pressure of carbon dioxide, with very high selectivity for copolymerization and carbonate formation. The catalysts are dicobalt(II/II and II/III) and tricobalt(II/II/II) complexes coordinated by a macrocyclic, reduced "Robson" type ancillary ligand and by acetate groups. The complexes are significantly more active than their direct zinc analogues, which we attribute to the increased nucleophilicity of the cobalt−oxygen bond in the cobalt−carbonate propagating species. All three complexes are characterized using mass spectrometry, infrared and ultraviolet−visible spectroscopies, elemental analysis, and, for the tricobalt complex and mixed valence dicobalt species, single-crystal X-ray crystallography.

Introduction

Carbon dioxide is an attractive chemical feedstock: it is highly abundant, renewable, inexpensive, and of low toxicity. It is also the waste product of a myriad of industrial processes, including combustion and fermentation; chemistries that overcome its high thermodynamic stability and transform it into valuable products are, therefore, of significant interest.[1] The activation of CO_2 with metal complexes has been established for over 40 years, leading to the development of a number of potentially important catalytic and stoichiometric reactions.[1−5] The coupling or copolymerization of CO_2 with epoxides is one such reaction. The copolymerization of CO_2 and cyclohexene oxide (CHO) produces polycyclohexene carbonate, a tough and transparent material (Scheme 1).

The groundbreaking discovery by Inoue et al. in the late 1960s[6] established that diethylzinc/alcohol mixtures catalyzed the copolymerization of propylene oxide (PO) and CO_2. This inspired the development of more highly active and well-characterized catalysts as well as the use of other epoxides.[7−10] A variety of metal catalysts have been reported; of particular note are the zinc phenoxide,[11−13] zinc β-diiminate (BDI),[14−19] and chromium/cobalt(III) complexes, generally of salen ligands.[8,20−28] The most active of these for the copolymerization using CHO under mild conditions (50 °C, 7 atm CO_2) are the zinc BDI catalysts, although the salen catalysts show impressive activities under higher CO_2 pressures (typically 20−60 atm).[8] Coates et al. have proposed that the zinc BDI catalysts operate via a bimetallic mechanism,[19] and this has led to the preparation of a variety of bimetallic zinc catalysts.[29−33] Recently, we reported a series of reduced Robson-type[34−40] bimetallic and trimetallic zinc complexes (Figure 1) which displayed very impressive activity for the copolymerization of CHO and CO_2 at only 1 atm pressure. There are still only a few reports of catalysts effective at just 1 atm pressure of CO_2, the most active of which requires a cocatalyst and shows a maximum TOF of 100 h^{-1}.[19,32,33,41−44]

While most research, including ours, has focused on either chromium or zinc complexes, the use of catalysts containing cobalt has only started to be considered in the recent years. The first report came from Coates' group using a cobalt(III)−salcy complex[24] which was known to be active for the asymmetric ring-opening of epoxides[45] and has since been reported as an active catalyst for the coupling of PO and CO_2.[46] A number of different Co(III) catalysts based around the salcy/salen ligand system have since been reported to show good activity, particularly for the copolymerization of PO and CO_2, with a variety of initiating groups including Cl, Br, I, N_3, OAc, and NO_3 and the use of a cocatalyst.[25,26,47−49] More recently, a few substituted Co(III)−salcyl complexes bearing pendant arms containing either a base or a quaternary ammonium salt have been reported.[50−53] These are proposed to hinder cyclic carbonate production and/or hold the growing chain near the metal center and increase thermal stability of the catalyst. These catalysts are highly active and show good selectivity for polymerization over cyclic byproduct formation. A number of Co(III) catalysts are active under mild conditions, including low pressures, although only a few have been reported as active for the polymerization of CHO and CO_2. Sugimoto et al. recently reported a cobalt(III)−porphyrin catalyst system active at 1 atm CO_2 using CHO, although the activity was rather low.[42] More recently, Nozaki et al. reported a cobalt(III)−salalen complex that is highly active at low pressure.[44] It should be noted that all the salen, and other derivatives thereof, complexes are completely inactive as Co(II) complexes; indeed, thermal reduction of the active Co(III) site is a common catalyst degradation pathway.[52]

We were motivated to compare the activity of cobalt and zinc catalysts using our macrocyclic ligand system. We were particularly interested to study Co(II) catalysts, which have received very little attention; indeed, reports are restricted to the homoleptic complex, $Co(OAc)_2$, with acetic acid as a cocatalyst.[54] This is somewhat surprising as Co(II) and Zn(II) have similar sizes and charge densities[55,56] and, furthermore, cobalt(II) acetate is readily available. To this end, we herein report the synthesis, characterization, and polymerization studies of bi- and trimetallic cobalt complexes $[L^1Co_2(OAc)_2]$ (**1**) and $[L^1Co_3(OAc)_4]$ (**2**) and of a mixed valence bimetallic Co(II)/Co(III) complex (**3**). These new complexes show very impressive activity and excellent polymerization control for the copolymerization of carbon dioxide, at only 1 atm pressure, and cyclohexene oxide.

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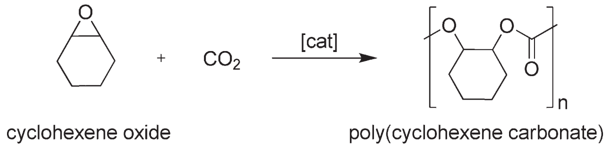
Results and Discussion

Synthesis and Characterization. Although most other cobalt and chromium catalysts for this copolymerization use chloride or azide coligands, these species are relatively inactive without the presence of a cocatalyst, and such species can interfere with and complicate the catalytic cycle.[8] We chose to prepare cobalt acetate complexes instead as they can initiate the copolymerization efficiently without the need for any cocatalyst, and they can be directly compared with our previously reported zinc acetate catalysts. The macrocyclic pro-ligand H_2L^1 was prepared according to literature methods[41] and reacted with anhydrous $Co(OAc)_2$ in toluene at room temperature. Reaction of H_2L^1 with 2 equiv of $Co(OAc)_2$ yielded the pink dicobalt(II) complex **1**, while the use of 3 equiv gave the purple tricobalt(II) complex **2** (Scheme 2). Both of these complexes were synthesized in good yields (~80%, unoptimized), and the complex stoichiometries were confirmed by elemental analysis, which were in close agreement with the theoretical values. FAB mass spectrometry gave peaks corresponding to $[L^1Co_2(OAc)]^+$ for both the di- and tricobalt complexes. The zinc analogues of these complexes gave complicated ^1H NMR spectra due to the fluxionality of the molecules, particularly $[L^1Zn_2(OAc)_2]$, requiring high temperatures to resolve discernible spectra. This combined with the paramagnetism of the cobalt(II) centers rendered NMR spectroscopy ineffective for the characterization of these complexes. The coordination of $Co(OAc)_2$ was also confirmed by infrared spectroscopy, the acetate groups showing symmetric and asymmetric stretches at 1575 and 1418 cm^{-1} for **1** and 1581 and 1425 cm^{-1} for **2**. These values are typical for bridged acetate groups.[57]

The reaction of H_2L^1 with 2 equiv of $Co(OAc)_2$, followed by oxidation in air, gave the olive green complex **3**, containing a mixed valence Co(II)/Co(III) metal core (Scheme 2). As with the cobalt(II) complexes, NMR spectroscopy was unsuitable for characterization of this complex due to the paramagnetism of the Co(II) center and the fluxionality of the complex. The complex stoichiometry was confirmed by elemental analysis.

Electronic Spectra and Magnetism. The electronic spectra of the three complexes were determined in toluene solutions (Table 1). The spectra produced by **1** showed two d−d transitions at 489 nm (ε = 55 $dm^3\ mol^{-1}\ cm^{-1}$ per dimer) and 1042 nm (13 $dm^3\ mol^{-1}\ cm^{-1}$), which correspond respectively to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transitions of an octahedral, high-spin cobalt(II) center.[58] The mixed valence complex **3** shows two main d−d transitions. The $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition from the cobalt(II) center

Scheme 1. Alternating Copolymerization of Carbon Dioxide and Cyclohexene Oxide, Forming Poly(cyclohexene carbonate)



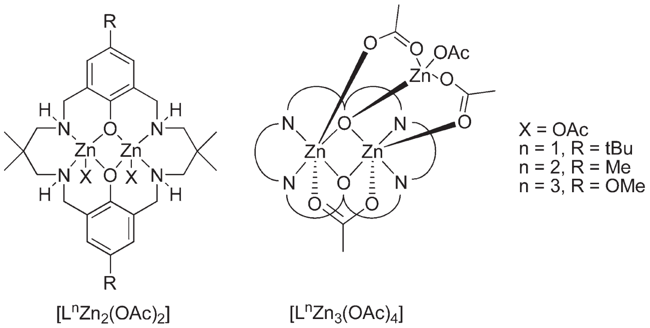
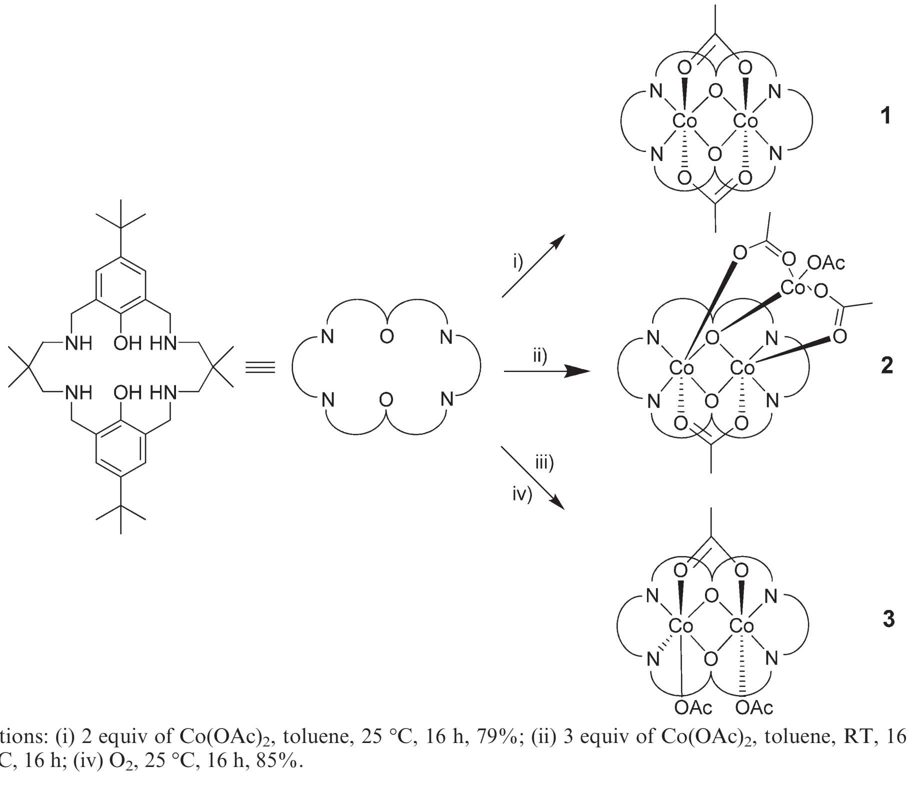


Figure 1. $[L^nZn_2(OAc)_2]$ and $[L^nZn_3(OAc)_4]$ highly active catalysts for the copolymerization of CHO and CO_2 at 1 atm pressure.

Scheme 2. Synthesis of 1, 2, and 3[a]



[a] Reagents and conditions: (i) 2 equiv of $Co(OAc)_2$, toluene, 25 °C, 16 h, 79%; (ii) 3 equiv of $Co(OAc)_2$, toluene, RT, 16 h, 83%; (iii) 2 equiv of $Co(OAc)_2$, toluene, 25 °C, 16 h; (iv) O_2, 25 °C, 16 h, 85%.

Table 1. Electronic Spectroscopic Data for the Complexes

complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})[a]
1	489 (55), 1042 (13)
2	514 (129), 570 (131), 1017 (40)
3	627 (370), 1032 (6)

[a] Molar absorption coefficients calculated per dimer.

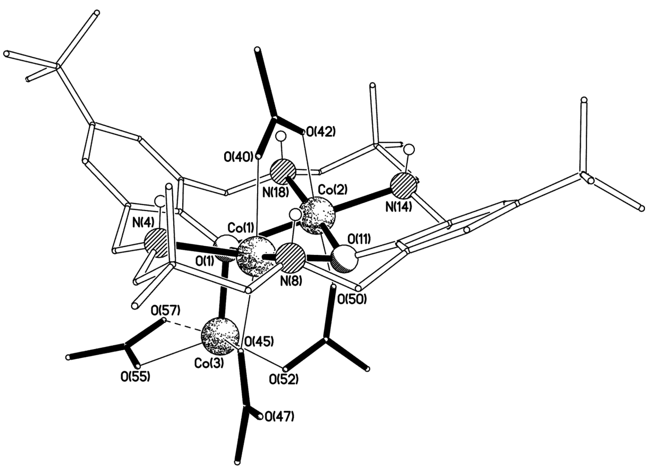


Figure 2. Molecular structure of **2**.

Table 2. Selected Bond Lengths (Å) for 2

Co(1)−O(1)	2.2273(17)	Co(1)−N(4)	2.133(2)
Co(1)−N(8)	2.112(2)	Co(1)−O(11)	2.0571(16)
Co(1)−O(40)	2.1055(15)	Co(1)−O(45)	2.1163(16)
Co(2)−O(1)	2.1897(16)	Co(2)−O(11)	2.0845(17)
Co(2)−N(14)	2.138(2)	Co(2)−N(18)	2.139(2)
Co(2)−O(42)	2.0739(16)	Co(2)−O(50)	2.0759(16)
Co(3)−O(1)	2.0075(15)	Co(3)−O(45)	2.0345(19)
Co(3)−O(52)	1.948(2)	Co(3)−O(55)	1.968(2)
C(1)−O(1)	1.370(3)	C(11)−O(11)	1.351(3)
Co(1)···Co(2)	3.0607(4)		

(1032 nm, 6 dm^3 mol^{-1} cm^{-1}) and a more intense transition at 627 nm (370 dm^3 mol^{-1} cm^{-1}) which corresponds to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of a cobalt(III) center in O_h geometry.[58] The significantly weaker $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition[a] of the cobalt(II) center is obscured by the tail of the cobalt(III) transition and by the slight red-shifting of an intense ligand-based absorption to 370 nm. The trimetallic complex **2** shows two different visible absorptions corresponding to d−d transitions in the separate cobalt environments. The $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ absorption from the two octahedral cobalt centers is slightly red-shifted to 514 nm (129 dm^3 mol^{-1} cm^{-1}) while a separate transition corresponding to the tetrahedral cobalt(II) center is observed at 573 nm (131 dm^3 mol^{-1} cm^{-1}). A broad transition at 1017 nm (40) is observed, too, from the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition on the octahedral cobalt centers, possibly with a contribution from the tetrahedral cobalt center, too. When the extinction coefficients of the two visible transitions are compared per metal center, the tetrahedral transition has double the intensity. As a result, while **1** is light pink, **2** has a very strong purple color.

The magnetic moment of **3** was measured using the Evans NMR method, giving an effective magnetic moment of 4.40 μ_B per dimer, which is consistent with one high-spin Co(II) center and a low-spin diamagnetic Co(III) center.[58,59]

X-ray Crystallography. Crystals of sufficient caliber for single-crystal X-ray diffraction analysis were grown of **2** and **3**, and the structures were analyzed. The crystal structure of **2** (Figure 1) is isomorphous with that of its zinc analogue;[60] the macrocyclic ligand has a dished conformation with all four N−H units on the same side of the ring. In general, the bonds to Co(1) and Co(2) are shorter than those in the zinc species, while the bonds to Co(3) are longer (Table S1). In particular, the Co(1)···Co(2) separation in **2** [3.0607(4) Å] is significantly shorter than the equivalent distance in the zinc analogue [3.1135(3) Å]. As was seen in a series of related zinc complexes (including the isomorphous species),[60] the Co(1)−O(1) and Co(2)−O(1) bonds are longer than their Co(1)−O(11) and Co(2)−O(11) counterparts, and related to this, the Ar−O(1) bond is longer than the Ar−O(11) bond. Both these observations can readily be explained by the presence of three cobalt centers bonded to O(1); cf. the two cobalt atoms bound to O(11).

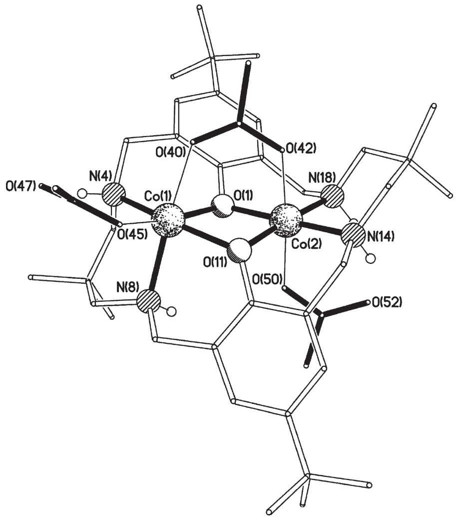


Figure 3. Molecular structure of **3**.

Table 3. Selected Bond Lengths (Å) for 3

Co(1)−O(1)	2.1530(17)	Co(1)−N(4)	2.128(2)
Co(1)−N(8)	2.158(2)	Co(1)−O(11)	2.0440(17)
Co(1)−O(40)	2.0993(19)	Co(1)−O(45)	2.0461(19)
Co(2)−O(1)	1.9307(18)	Co(2)−O(11)	1.9411(17)
Co(2)−N(14)	1.978(2)	Co(2)−N(18)	1.957(2)
Co(2)−O(42)	1.9060(18)	Co(2)−O(50)	1.9246(19)
C(1)−O(1)	1.353(3)	C(11)−O(11)	1.349(3)
O(40)−C(41)	1.236(3)	C(41)−O(42)	1.290(3)
Co(1)···Co(2)	3.0162(5)		

The solid-state structure determination of crystals of **3** (Figure 2) shows a very different conformation for the macrocyclic ligand compared to **2**. Instead of a dished conformation, here the macrocycle has a stepped conformation caused by the N(8) donor atom being cis to O(1) rather than trans as seen in the structure of **2**. This change places the O(45) acetate moiety in an equatorial position. This highlights the coordinative flexibility of L^1, an important consideration for the catalysis which requires a coordination vacancy for binding of the epoxide monomer. Complex **3** has already been shown by spectroscopic and magnetic measurements to be a mixed valence Co(III)/Co(II) complex. The solid state structure establishes the localization of these oxidations states. Inspection of the bond lengths around the two cobalt centers reveals a clear and consistent pattern with all of the bonds involving Co(2) being shorter than those involving Co(1), showing that the oxidation has localized on Co(2) (Table 2).[58] Furthermore, the bridging acetate C−O bond lengths C−O(42) and C−O(40) are of different lengths. The bond to O(40) is significantly shorter by 0.05 Å, suggesting it contains the most double-bond character, and hence O(42) is the anionic donor. Another interesting feature of the structure of **3** is that the Ar−O(1)/O(11) bond lengths are identical.

Copolymerization Results. The three complexes were tested for their catalytic activity for the copolymerization of CHO and CO_2 under 1 atm pressure. The bimetallic complexes were found to exhibit very high activities for this pressure, giving maximum TOFs ~20 times better than $[L^1Zn_2(OAc)_2]$ and comparable to the best systems reported.[41] As with the analogous zinc complexes, **2** shows significantly reduced activity compared to the bimetallic species, suggesting the externally coordinated metal center is less active than the macrocyclic sites, possibly hindering one face from attack by CHO and CO_2.

Polymerization Activities. At 80 °C and 1 atm CO_2 pressure, catalysts **1** (entry 1, see Table 4) and **3** (entry 2) show very similar activity, giving TOFs around 9 times higher than $[L^1Zn_2(OAc)_2]$ (entry 4) under the same conditions. This makes these complexes highly active for this copolymerization, under such a low pressure—indeed, they show a slight improvement in activity to the best reported system at similar temperatures.[44] In contrast, **2** (entry 3) shows poor activity, less even than its zinc analogue (entry 5). X-ray crystallography shows the bonds around the internally bound cobalt centers in **2** to be marginally shorter and therefore stronger than their zinc analogue, while those around the less active external center are slightly longer and weaker. This coupled with a probable increased sensitivity to trace impurities in the epoxide could account for the lower activity. Comparison of the TON and TOF per metal rather than per catalyst clearly shows a significant decrease in average activity per metal center for the trimetallic complexes, suggesting the externally coordinated metal is both significantly less active and a hindrance to copolymerization.

Selectivity. Direct comparison of **1** and $[L^1Zn_2(OAc)_2]$ shows that in this ligand system cobalt is considerably more active than zinc for this copolymerization, but also more selective for polymer formation, with little or no cyclic product observed by ^1H NMR. This is an improvement over the zinc catalysts which always produced around 3−4% cyclic carbonate as a byproduct. There is good literature precedent for the high selectivity of cobalt catalysts using both CHO and PO,[24,26,42,47,48,50,51] while many zinc catalysts produce a small of amount of cyclic carbonate.[11,19,30,31,41]

Table 4. Copolymerizations of CHO and CO_2 Catalyzed Using 1, 2, 3, and $[L^1Zn_x(OAc)_y]$ (Copolymerization Conditions: 80 °C, 1 atm CO_2)

catalyst	time (h)	TON[a]	TOF (h^{-1})[b]	TON per metal[c]	TOF per metal (h^{-1})[d]	% polymer[e]	M_n[f]	PDI[f]
1	2	340	172	170	86	> 99	5100	1.26
3	3	420	159	210	80	> 99	6300/2800	1.04/1.14
2	24	210	9	70	2.9	98	1100	1.22
$L^1Zn_2(OAc)_2$[41]	24	440	18	220	9.2	96	6200	1.19
$L^1Zn_3(OAc)_4$[60]	24	290	12	140	6	96	3400	1.21

[a] TON = number of moles of CHO consumed per mole of catalyst. [b] TOF = TON per hour. [c] Moles of epoxide consumed per mole of metal. [d] Moles of epoxide consider per mole of metal per hour. [e] Determined by comparison of the integrals of signals arizing from the methylene protons in the ^1H NMR spectra due to copolymer carbonate linkages (δ = 4.65 ppm), copolymer ether linkages (δ = 3.45 ppm), and the signals due to cyclic carbonate byproduct (δ = 4.0 ppm).[41] [f] Determined by SEC, in THF, using narrow polystyrene standards as calibrants. All the copolymers contained > 99% carbonate linkages, as observed by ^1H NMR.

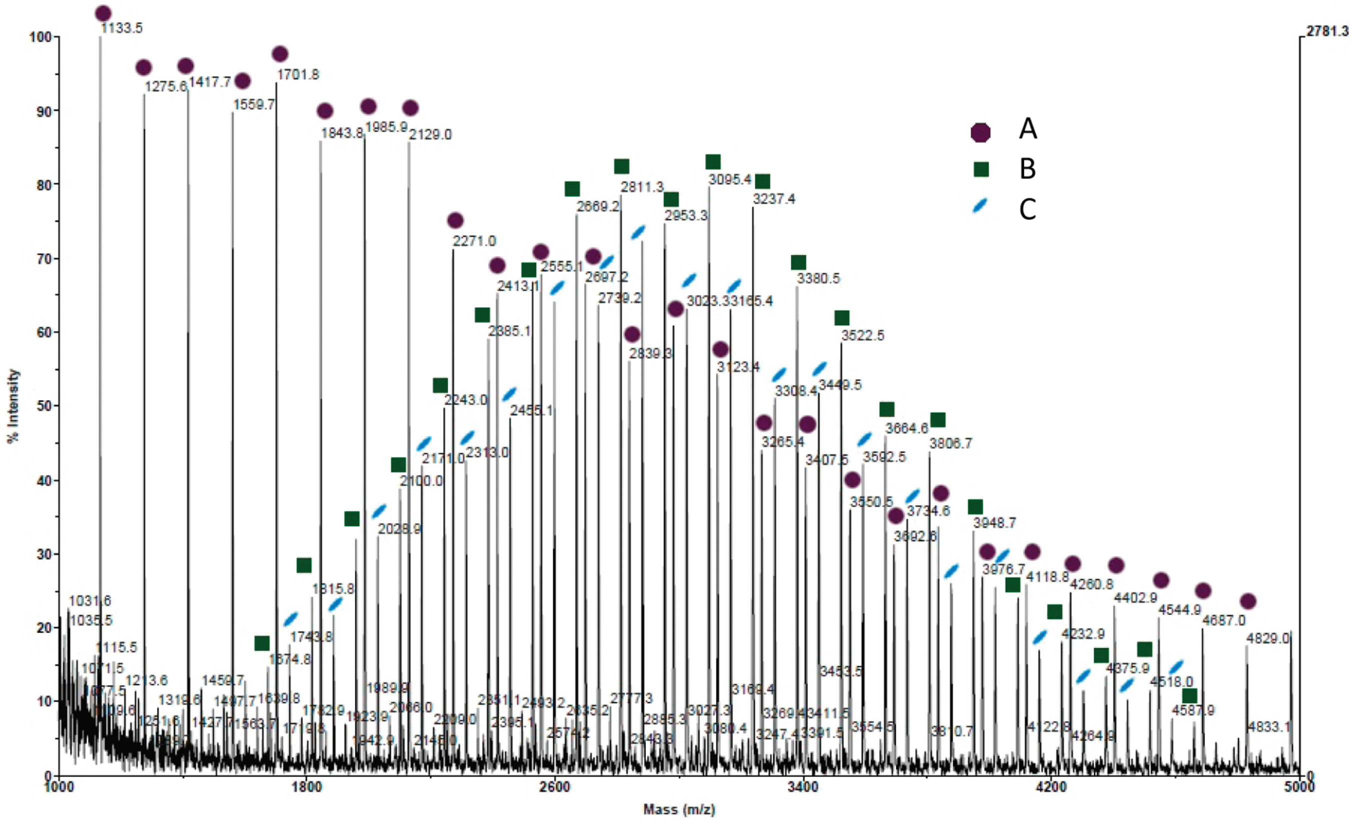


Figure 4. Accurate mass MALDI-TOF spectra for polymer produced by complex **3** (80 °C, 1 atm CO_2).

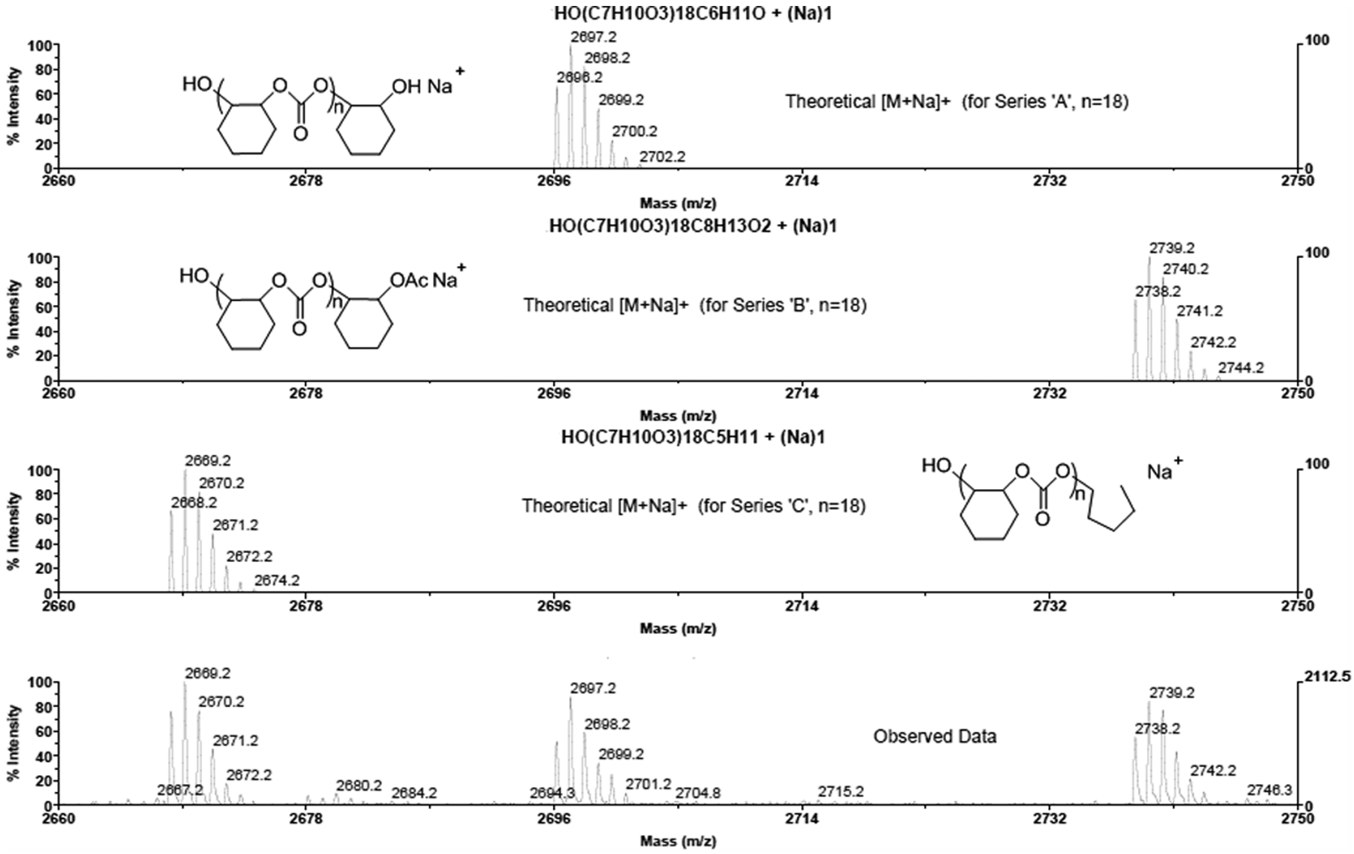


Figure 5. Comparison of theoretical and observed MALDI-TOF mass spectra for polymer series A, B, and C.

Table 5. Copolymerizations of CHO and CO_2 Catalyzed Using 1 and 3 with Variation of Pressure and Temperature

catalyst	T (°C)	time (h)	TON[a]	TOF (h^{-1})[b]	% carbonate[c]	% polymer[c]	M_n[d]	PDI[d]
1	100	1	410	410	> 99	> 99	4200	1.29
3	100	0.83	400	480	> 99	> 99	7300/3200	1.03/1.11
3	100	0.5	250	500	> 99	> 99	5000/2300	1.04/1.11
1	60	7	310	45	> 99	> 99	4900	1.04
3	60	7	110	15	93	95	750	1.28
3[e]	100	0.083	370	3700	> 99	> 99	8800/3900	1.04/1.09

[a] TON = number of moles of CHO consumed per mole of catalyst. [b] TOF = TON per hour. [c] Determined by comparison of the integrals of signals arizing from the methylene protons in the ^{1}H NMR spectra due to copolymer carbonate linkages (δ = 4.65 ppm), copolymer ether linkages (δ = 3.45 ppm), and the signals due to cyclic carbonate byproduct (δ = 4.0 ppm).[41] [d] Determined by SEC, in THF, using narrow polystyrene standards as calibrants. [e] Polymerization carried out at 10 atm CO_2 pressure.

The copolymers produced by both catalysts show bimodal molecular weight distributions in both the SEC analysis (Figure S3) and MALDI-ToF spectra (Figure S6). The mixed valence complex **3** produces a distinctly bimodal distribution of molecular numbers by SEC, the higher at 6300 and the lower 2800, both with very low polydispersity indices. The copolymer produced by **1** gives a much less pronounced bimodal distribution in the SEC analysis, with a lower molecular number (5100) and a slightly broader polydispersity of 1.26. The MALDI-TOF spectra show a similar pattern (Figure 4). The MALDI-ToF spectra for the analogous zinc catalyst shows several copolymer species with a variety of end groups, some of which are the result of Meerwein−Ponndorf−Verley−Oppenauer (MPVO) side reactions involving the catalyst and CHO, which produce alcohols that can act as chain transfer agents and lower the molecular weights.[41] The presence of such species is not observed using the cobalt catalysts, so we suggest the main cause of chain transfer with cobalt to be trace amounts of water.

Both the copolymers show a higher molecular number series of peaks (~5400), assigned to chains end-capped with hydroxyl groups (series A, Figures 4 and 5, $[HO(C_7H_{10}O_3)_n$-$C_6H_{11}ONa]^+$, 23 + 142.1n + 116.1), and a lower molecular number series (~3200), assigned to two series of peaks: one end-capped with the expected acetate group (series C, Figures 4 and 5, $[HO(C_7H_{10}O_3)_nC_8H_{13}O_2Na]^+$, 23 + 142.1$n$ + 158.2) and the other end-capped with an alcohol (pentanol) group (series B, Figures 4 and 5 $[HO(C_7H_{10}O_3)_n$-$C_5H_9Na]^+$, 23 + 142.1n + 88.2).[61] The most significant difference between the copolymers is that those produced from **3** show a much greater proportion of the higher molecular weight series (end-capped with hydroxyl groups) than those produced from **1** (see Figure S6). The hydroxyl end-groups are proposed to arise via a series of chain transfer reactions initiated by trace amounts of water. These chain transfer reactions must be occurring more rapidly than the propagation reactions as the polydispersity indices of all the copolymers are narrow (< 1.20). These end-groups are commonly observed for this polymerization;[44] however, we have not yet ascertained the reason for their increased presence in the polymers produced by **3**.

Copolymerization Conditions. If the polymerization temperature is increased to 100 °C, a significant increase in activity is observed for both **1** and **3**. However, **3** is more active at higher temperatures, with a maximum TOF of 500 h^{-1} (entry 3, Table 5), ~5 times the best reported catalyst at this pressure, albeit at higher temperature.[44] If the polymerization is run for 50 min, until stirring becomes difficult due to the increased viscosity, a higher conversion affords a higher molecular weight copolymer with a small reduction in activity due to the decreased stirring (entry 2). In contrast, at 60 °C, **1** is significantly more active than **3**. Indeed, **1** shows activity at 60 °C that is more than double that of $[L^1Zn_2(OAc)_2]$ at 100 °C.[41] Detailed and ongoing kinetic investigations are likely to shed further light on the contrasting behavior of catalysts **1** and **3** with temperature.

When the CO_2 pressure was increased to 10 atm, the activities of both catalysts increased markedly. It is particularly noteworthy that, under such conditions, **3** shows a TOF of 3700 h^{-1}, achieving greater than 30% conversion in just 5 min. This activity is among the highest reported for this copolymerization.[18,29] The excellent carbonate and polymer selectivity is retained, while the molecular weight is increased slightly (~9000), a little over half that expected if all three acetate groups initiate. As van Meerendonk et al. have reported,[62] the molecular weights for this polymerization are generally lower than those expected.

Discussion. Catalysts **1**−**3** are particularly significant for three reasons: (1) the high activities observed at low carbon dioxide pressure, (2) the introduction of the macrocyclic ligand system, and (3) the improved activity on substituting Zn(II) for Co(II)/Co(III).

The high TON and TOF observed at atmospheric pressure of CO_2 is very unusual—so far only a handful of catalysts are active under such conditions; ours is competitive/slightly more active than the best reported systems.[19,32,33,41−43,60,63]

However, of greater significance is that the current catalysts use a novel ligand system: the reduced Robson macrocycle. So far, the most active catalysts have been restricted to salen (or derivatives thereof) or β-diiminate ligands. The introduction of the reduced Robson ligand enables further insights into catalyst structure−activity relationships. The macrocyclic coordination environment is key to activity: neither phenoxydiamine zinc complexes nor bimetallic phenoxytetraamine dizinc complexes ("open" bimetallic analogues of the macrocyclic system) show any activity for CO_2−CHO copolymerizations.[41] The donor groups are also very important—we have found, and it has been reported, that related complexes using the Robson ligand (i.e., with imine vs amine donors) are all inactive.[64] It is proposed that weaker amine donors, in combination with the increased flexibility of the reduced system, facilitate the coordination/decoordination reactions: enabling both epoxide binding, bidentate carbonate coordination (vide infra), and possibly facilitating CO_2 insertion. Nakano et al. and Luinstra et al. have both observed that a bidentate coordination mode of the carbonate growing polymer chain is particularly favorable for assisting CO_2 insertion reactions and preventing decarboxylation.[44,65] Complexes **1** and **3** show bidentate coordinaton of acetate groups, both in the solid state and in solution. This bidentate coordination is facilitated by the flexibility of the ligand coordination geometry, where either an all-cis or a cis, cis, cis, trans geometry is feasible for the amine donors, and by the presence of two close metal centers over which the carboxylate can bind in a bridging fashion.

Finally, the significant improvement in activity on substitution of Zn(II) centers with Co(II) centers provides an interesting analogy with zinc-dependent metalloenzymes, in particular phosphatases, amidases, and proteases, which show dramatic improvements in rate for the same substitution.[66−69] This so-called enzymatic "hyperactivity" (i.e., on substitution of Zn(II) with Co(II)) has also been observed in well-defined, biomimetic complexes, some of which are reactivity models for the enzymes.[68] In the current catalysis, the increase in activity on substituting Zn(II) for Co(II) might, at first sight, appear difficult to rationalize. After all, Zn(II) and Co(II) have similar Lewis acidities and as such should have similar affinities for epoxide binding.[70] However, various experimental and theoretical studies, albeit using different ancillary ligands, propose that the rate-determining step is ring-opening by the nucleophilic metal carbonate growing polymer chain.[19,71] Therefore, by analogy to these other systems, we expect our complexes to show rate-determining step(s) dependent on epoxide ring-opening. This is supported by the fact that complexes **1** and **3** show essentially the same TON and TOF; in contrast, if the rate were to depend significantly on epoxide *binding*, then it would be expected that complex **3**, which has a much more Lewis acidic Co(III) center, would show a higher TOF than catalyst **1**. It is worth noting that this similarity in reactivity is not caused by the in situ oxidation of complex **1**, as the reaction mixture retains the pink color of the Co(II/II) complex throughout the experiment. We consider it likely that the rate enhancement on substituting Co(II) for Zn(II) is due to the increased nucleophilicity of the cobalt carbonate propagating species compared to its Zn analogue. In fact, exactly such hypotheses have been advanced to rationalize the hyperactivity of the cobalt metalloenzymes and biomimetic complexes.[66−69]

Conclusions

In conclusion, we have synthesized three new cobalt complexes from the same macrocyclic ligand: a dicobalt(II) complex, a mixed valence Co(II)/Co(III) complex, and a tricobalt complex analogous to our previously reported trizinc complex. While the tricobalt complex **2** showed a reduced activity compared to zinc, probably due to its stability, the bimetallic complexes **1** and **3** show unprecedented activity for the copolymerization of CHO and CO_2 under atmospheric pressure, giving a maximum TOF of 500 h^{-1}, over 20 times higher than the analogous zinc complex. In this ligand system, cobalt is a more active and more selective metal. The copolymers produced are of low molecular weight due to chain transfer reactions, most probably involving water. High pressure/temperature copolymerizations using catalyst **3** show that it is highly active and thermally robust, giving one of the highest TOFs yet reported for this copolymerization.

Experimental Section

Materials and Methods. The synthesis of H_2L^1 was carried out in air and has been previously reported.[41] The synthesis of the metal complexes **1**, **2**, and **3** were conducted under a nitrogen atmosphere, using either standard anaerobic techniques or in a nitrogen-filled glovebox. All solvents and reagents were obtained from commercial sources (Aldrich and Merck). Toluene was distilled from sodium and stored under nitrogen. Cyclohexene oxide (CHO) was distilled from CaH_2 and stored under nitrogen. All solvents were thoroughly degassed before use. Research grade carbon dioxide was used for copolymerization studies.

^1H and $^{13}C\{^1H\}$ NMR spectra were performed on a Bruker AV-400 instrument, unless otherwise stated. All mass spectrometry measurements were performed using a Fisons Analytical (VG) Autospec spectrometer. All IR spectra were performed neat on a Perkin-Elmer Spectrum 100 ATR-IR instrument.

Elemental analyses were determined by M_r Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7. SEC data were collected using a Polymer laboratories PL GPC-50 instrument with THF as the eluent, at a flow rate of 1 mL min^{-1}. Two Polymer laboratories Mixed D columns were used in series. Narrow M_w polystyrene standards were used to calibrate the instrument.

Synthesis of 1. H_2L^1 (0.4 g, 0.72 mmol) and $Co(OAc)_2$ (0.26 g, 1.44 mmol) were dissolved in dry toluene (10 mL) in a Schlenk tube and left to stir overnight, producing a pinky-red solution. The solvent was removed in vacuo, and the pink powder was dried under vacuum overnight. This proved sufficient to remove both toluene and acetic acid from the product, and no further purification was necessary (0.44 g, 0.56 mmol, 79% unoptimized). IR ($\nu_{C=O}$, cm^{-1}, neat): 1575 and 1419. *m*/*z* (FAB): 727 ($[M - OAc]^+$, 100%). Anal. Calcd for $C_{38}H_{60}Co_2N_4O_6$: C, 58.01; H, 7.69; N, 7.12. Found: C, 57.93; H, 7.69; N, 7.05.

Synthesis of 2. H_2L^1 (0.3 g, 0.54 mmol) and $Co(OAc)_2$ (0.29 mg, 1.62 mmol) were dissolved in dry toluene (10 mL), in a Schlenk tube, and left to stir overnight, producing a deep purple solution. The solvent was removed in vacuo, and the purple powder was dried under vacuum overnight. This proved sufficient to remove both toluene and acetic acid from the product, and no further purification was necessary (0.42 g, 0.44 mmol, 83%). IR ($\nu_{C=O}$, cm^{-1}, neat): 1581 and 1425. *m*/*z* (FAB): 727 ($[M - Co(OAc)_2]^+$, 100%). Anal. Calcd for $C_{42}H_{66}Co_3N_4O_{10}$: C, 52.34; H, 6.90; N, 5.81. Found: C, 52.24; H, 6.85; N, 5.79.

Synthesis of 3. H_2L^1 (0.3 g, 0.54 mmol) and $Co(OAc)_2$ (0.19 g, 1.08 mmol) were dissolved in dry toluene (10 mL), in a Schlenk tube, and left to stir overnight, producing a pinky-red solution. The solution was then opened to air and left stirring overnight, during which time the solution turned olive green. The solvent was removed in vacuo, and the product was dried under vacuum overnight. This proved sufficient to remove both toluene and acetic acid from the product, and no further purification was necessary (0.39 g, 0.46 mmol, 85%). IR ($\nu_{C=O}$, cm^{-1}, neat): 1572 and 1386. *m*/*z* (FAB): 727 ($[M - 2OAc]^+$, 100%). Anal. Calcd for $C_{40}H_{63}Co_2N_4O_8$: C, 56.80; H, 7.51; N, 6.62. Found: C, 56.75; H, 7.60; N, 6.58.

Copolymerization Conditions. *Low-Pressure Polymerization.* Cyclohexene oxide (2.5 mL, 25 mmol) and complex (0.025 mmol) were added to a Schlenk tube. The cyclohexene oxide was degassed, before being left stirring under 1 atm CO_2, at 80 °C, for *x* hours. The crude reaction mixture was then taken up in CH_2Cl_2, and a 0.2 mL of a 5% solution of HCl/MeOH was added. The solution was evaporated in air, after which the product was dried in vacuo overnight. No further purification of the polymer was undertaken as the vacuum was sufficient to remove unreacted cyclohexene oxide.

High-Pressure Polymerization. A Parr reaction vessel was placed in an oven at 140 °C overnight, after which it was removed and placed under vacuum for 3 h. Separately, **3** (0.166 g, 0.198 mmol) was added to a Schlenk and placed under vacuum for 3 h. The reaction vessel was then charged with nitrogen, and cyclohexene oxide (10 mL, 99 mmol) was transferred into it. The vessel was evacuated, placed under 1 atm CO_2, and heated to temperature. The Schlenk containing **3** was charged with nitrogen and cyclohexene oxide (10 mL, 99 mmol) was added. Once all **3** was dissolved, the Schlenk was degassed before being charged with CO_2. The solution was transferred into the reaction vessel, which was immediately pressurized to 10 atm CO_2 and allowed to stir at pressure and temperature for 5 min. The vessel was then placed into an ice bath to cool before being vented in a fume hood. The crude reaction mixture was taken up in CH_2Cl_2, and a 0.5 mL of a 5% solution of HCl/MeOH was added. The solution was evaporated in air, after which the product was dried in vacuo overnight.

The turnover number was calculated as [(isolated yield − weight catalyst)/142.1]/moles catalyst.

The copolymers were analyzed by ^1H NMR spectroscopy, where the protons adjacent to the carbonate linkage resonated at 4.6 ppm, while the absence of a peak at 3.45 ppm showed there were no polyether linkages. The copolymer tacticity was determined by $^{13}C\{^1H\}$ NMR spectroscopy and analyzed as described by Nozaki et al.[72] The copolymers were all atactic.

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Supporting Information Available: X-ray crystallographic data in CIF format for the crystal structures of **2** and **3**; ^1H and $^{13}C\{^1H\}$ NMR spectra of the polymer; nominal MALDI-TOF mass spectra of the polymers produced by **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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