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Alternating Copolymerization of Cyclohexene Oxide and Carbon Dioxide Catalyzed by Organo Rare Earth Metal Complexes

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ABSTRACT: The mono(cyclopentadienyl)-ligated rare earth metal bis(alkyl) complexes $(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**1a**), Dy (**1b**), Lu (**1c**), Sc (**1d**)) and polyhydride complexes $[(C_5Me_4SiMe_3)Ln(\mu\text{-}H)_2]_4(THF)_x$ (**2a**: Ln = Y, $x = 1$; **2b**: Ln = Dy, $x = 2$; **2c**: Ln = Lu, $x = 1$) are active as single-component catalysts, not only for the ring-opening homopolymerization of cyclohexene oxide (CHO), but also for the alternating copolymerization of CHO and CO_2. The homopolymerization of CHO in bulk took place much more rapidly than that in solution and afforded in high yields the corresponding polyether with $M_n = (50-80) \times 10^3$ and $M_w/M_n \cong 2$ in most cases. The copolymerization of CHO and CO_2 by **1a**−**c** and **2a**−**c** at 70−110 °C under 12 atm of CO_2 yielded the corresponding polycarbonate with $M_n = (14-40) \times 10^3$, $M_w/M_n = 4-6$, and carbonate linkages = 90−99% with TOF ranging from 1000 to 2000 g polymer/(mol-Ln h). In contrast, the Sc alkyl complex **1d** gave a polymer containing high ether linkages (carbonate linkages = 23%) under the similar conditions because of its higher activity for CHO homopolymerization. The stoichiometric reaction of the bis(alkyl) complexes **1a**, **c**, and **d** with CO_2 afforded quantitatively the corresponding bis(carboxylate) complexes $[(C_5Me_4SiMe_3)Ln(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CCH_2SiMe_3)_2]_2$ (Ln = Y (**3a**), Lu (**3b**), Sc (**3c**)), which adopt a dimeric structure through the carboxylate bridges. The isolated carboxylate complexes **3a**, **b** also showed moderate activity for the alternating copolymerization of CHO and CO_2, which thus constituted a rare example of a well-defined, catalytically active carboxylate intermediate that was isolated directly from the reaction of a true catalyst system.

Introduction

The copolymerization of CO_2 with epoxides has received much current interest[1] because it provides an environmentally friendly route to convert CO_2 into biodegradable polymers and a pathway to a value-added product incorporating the ubiquitous CO_2 molecule as a C1 feedstock. Since Inoue and co-workers first reported the copolymerization of CO_2 with propylene oxide by use of a mixture of $ZnEt_2$ and H_2O in 1969,[2a] extensive studies have been carried out in this area, and a variety of catalyst systems based on various metals such as zinc,[2] aluminum,[3] chromium,[4] cadmium,[5] and cobalt[6] have been reported. Despite these extensive researches and recent breakthroughs in this area, however, only Zn, Co, and Cr compounds were found to show significant activity for the copolymerization of CO_2 and epoxides.[1] Further exploration of new catalyst systems with these and other elements is therefore of obvious interest.

Rare earth metals have received much less attention in this area. Although a few rare-earth-containing multiple-component heterogeneous systems were reported for the copolymerization of CO_2 with propylene oxide[7] or cyclohexene oxide (CHO),[8] a well-defined homogeneous rare earth metal catalyst for the copolymerization of CO_2 and an epoxide has not been reported previously.[9] During our recent studies on mono(cyclopentadienyl)-supported rare earth metal bis(alkyl) and dihydride complexes,[10] we became interested in their reactivity toward CO_2 and epoxides. We report here that such half-sandwich rare earth metal complexes can act as excellent single-component catalysts for the copolymerization of CO_2 and cyclohexene oxide (CHO). The homopolymerization of CHO and isolation and reactivity of the CO_2-inserted carboxylate intermediates are also described.

Results and Discussion

Homopolymerization of Cyclohexene Oxide (CHO). The reactivity of the rare earth metal bis(alkyl) complexes $(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**1a**), Dy (**1b**), Lu (**1c**), Sc (**1d**)) and the polyhydride complexes $[(C_5Me_4SiMe_3)Ln(\mu\text{-}H)_2]_4(THF)_x$ (**2a**: Ln = Y, $x = 1$; **2b**: Ln = Dy, $x = 2$; **2c**: Ln = Lu, $x = 1$) (Chart 1) toward cyclohexene oxide (CHO) was first examined in toluene. All of these complexes showed an activity, albeit low, for the ring-opening polymerization of CHO in toluene (Table 1). In contrast, when the reaction was carried out in the absence of a solvent, the polymerization occurred much more rapidly and exothermally to yield the corresponding polyether with high molecular weight and moderate molecular weight distribution (Table 2 and Figure 1). Generally, the polymerization took place very fast at the early stage, leading to a conversion of higher than 50% within 30 min (Figure 1). At the later stage, the reaction became sluggish probably because of the difficulty of monomer diffusion. However, a conversion of as high as 70−85% could be achieved in 3 h in most cases.

Copolymerization of Cyclohexene Oxide (CHO) and CO_2. The copolymerization of CHO and CO_2 was examined first by use of the bis(alkyl) complexes **1a**−**d** as catalysts under 12 atm CO_2 at 70 °C in toluene (Table 3). In the case of Y (**1a**), Dy (**1b**), and Lu (**1c**), the resulting copolymers all showed high carbonate linkages (>90%), high molecular weights, and moderate molec-

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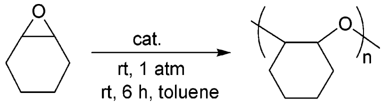
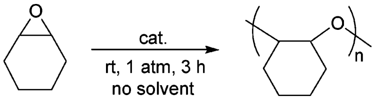
Table 1. Homopolymerization of Cyclohexene Oxide (CHO) in Toluene[a]



entry	cat	yield (%)	$M_n^b \times 10^{-3}$	M_w/M_n^b
1	$(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$ (**1a**)	15.0	38.0	2.01
2	$(C_5Me_4SiMe_3)Dy(CH_2SiMe_3)_2(THF)$ (**1b**)	12.5	21.7	1.79
3	$(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)$ (**1c**)	23.0	41.0	2.00
4	$(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1d**)	39.8	147.0	2.38
5	$[(C_5Me_4SiMe_3)Y(\mu\text{-}H)_2]_4(THF)$ (**2a**)	10.4	57.8	2.60
6	$[(C_5Me_4SiMe_3)Dy(\mu\text{-}H)_2]_4(THF)_2$ (**2b**)	8.1	52.6	1.88
7	$[(C_5Me_4SiMe_3)Lu(\mu\text{-}H)_2]_4(THF)$ (**2c**)	17.3	79.2	2.11

[a] Condition: [Ln] = 0.063 mmol; CHO: Ln = 400 (mol/mol); toluene: 2 mL. [b] Determined by GPC against polystyrene standard.

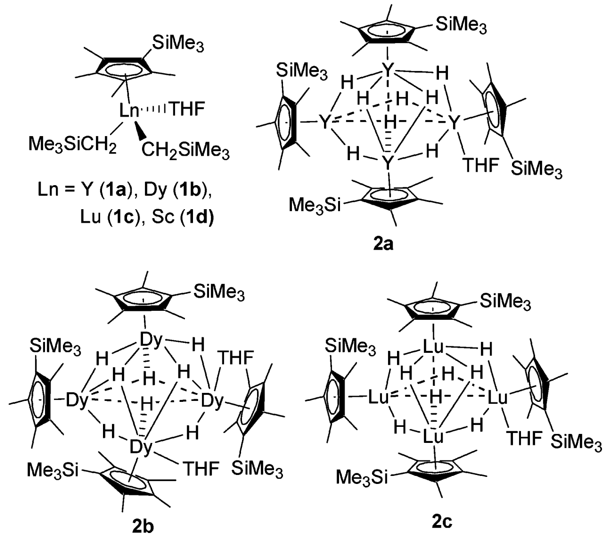
Table 2. Homopolymerization of Cyclohexene Oxide (CHO) in Bulk[a]



entry	cat	yield (%)	$M_n^b \times 10^{-3}$	M_w/M_n^b
1	$(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$ (**1a**)	82.7	45.0	2.06
2	$(C_5Me_4SiMe_3)Dy(CH_2SiMe_3)_2(THF)$ (**1b**)	71.7	30.6	2.27
3	$(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)$ (**1c**)	84.4	54.3	2.23
4	$(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1d**)	85.3	50.8	2.89
5	$[(C_5Me_4SiMe_3)Y(\mu\text{-}H)_2]_4(THF)$ (**2a**)	76.9	69.3	2.01
6	$[(C_5Me_4SiMe_3)Dy(\mu\text{-}H)_2]_4(THF)_2$ (**2b**)	60.0	65.5	2.22
7	$[(C_5Me_4SiMe_3)Lu(\mu\text{-}H)_2]_4(THF)$ (**2c**)	78.7	88.2	2.02

[a] Conditions: [Ln] = 0.063 mmol; CHO: Ln = 400 (mol/mol). [b] Determined by GPC against polystyrene standard.

Chart 1. Lanthanide Alkyl and Hydride Complexes Bearing Monocyclopentadienyl Ligand



ular weight distributions (Table 3, entries 1−3). The Lu complex **1c** showed the highest activity (1250 g polymer/(mol-Ln h)). In contrast, the Sc complex **1d** was much less efficient for the copolymerization, which yielded a copolymer containing high ether linkages (carbonate linkages = 23%, Table 3, entry 4), probably because of its higher activity for the homopolymerization of CHO in toluene as shown in Table 1.

Since the Lu complex **1c** showed the highest activity, it was then chosen as a catalyst for further investigation of the CHO/CO_2 copolymerization under various conditions. Table 4 summarizes the influence of the catalyst and CHO monomer concentrations. Under a constant CHO concentration (5.02 mol/L), increase of the catalyst concentration led to increase of the polymer yield to some extent (Table 4, entries 1−3, 5), but the highest TOF (turnover number frequency) was observed at [**1c**] = 12.3 mmol/L in the catalyst concentration range of 6.1−32.0 mmol/L. The molecular weight, molecular weight distribution, and carbonate linkage content of the resulting copolymers were not much influenced by the catalyst concentration. In contrast, when the CHO monomer concentration was raised under a constant catalyst concentration ([**1c**] = 12.3 mmol/L), the carbonate linkage content of the polymer products decreased significantly as a result of more CHO homocouplings (Table 4, entries 4−7).

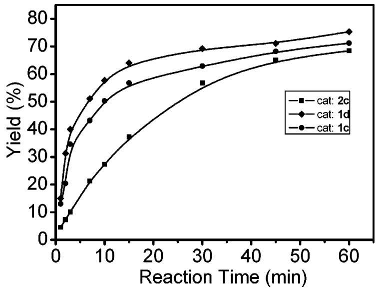
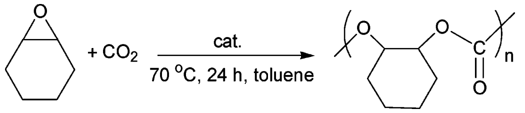


Figure 1. Bulk polymerization of CHO by **1c**, **1d**, and **2c**: Plots of conversion versus reaction time. Condition: Ln = 0.063 mmol; CHO: Ln = 400 (mol/mol), room temperature, 1 atm.

The reaction temperature also showed significant influence on the copolymerization (Table 5). The polymer yield increased gradually when the temperature was raised in the range of 50−110 °C. At 110 °C, the turnover frequency (TOF) increased to 2000 g polymer/(mol-Lu h), and the carbonate linkages of the resulting copolymer reached 97% (Table 5, entry 4). When the temperature was raised to 130 °C or higher, a decrease in polymer yield and molecular weight was observed (Table 5, entry 5). The similar temperature influence was also observed previously in other catalyst systems.[1b,2e,2q,4b,c]

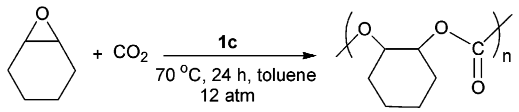
Table 3. Copolymerization of Cyclohexene Oxide (CHO) with CO_2 by Organolanthanide Bisalkyl Complexes[a]



entry	cat	TON[b]	TOF[c]	M_n[d] × 10^{-3}	M_w/M_n[d]	carbonate linkages (%)[e]
1	$(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$ (**1a**)	24.0	1000	19.1	4.30	94
2	$(C_5Me_4SiMe_3)Dy(CH_2SiMe_3)_2(THF)$ (**1b**)	17.2	716	14.5	3.99	93
3	$(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)$ (**1c**)	30.0	1250	23.0	4.03	92
4	$(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1d**)	13.6	567	8.4	3.68	23

[a] Conditions: 12 atm of CO_2, [Ln] = 16.3 mmol/L, [CHO] = 6.5 mol/L. [b] TON = kg/mol-Ln. [c] TOF = g/(mol-Ln h). [d] Determined by GPC against polystyrene standard. [e] Calculated by the integration of the methine resonances in the ^1H NMR of the copolymer ($CDCl_3$, 300 MHz).

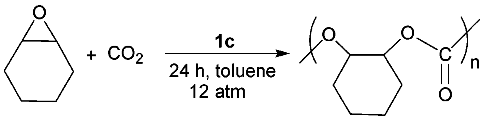
Table 4. Concentration Influence on Copolymerization of Cyclohexene Oxide (CHO) with CO_2 by 1c



entry	[**1c**] (mmol/L)	[CHO] (mol/L)	TON[a]	TOF[b]	M_n[c] × 10^{-3}	M_w/M_n[c]	carbonate linkages (%)[d]
1	6.1	5.02	6.7	278	nd	nd	90
2	19.7	5.02	27.5	1146	22.1	4.50	92
3	32.0	5.02	20.5	854	18.1	4.11	90
4[e]	12.3	3.78	18.9	395	16.8	2.45	97
5	12.3	5.02	31.0	1292	21.1	5.62	94
6	12.3	6.50	31.2	1300	18.1	5.21	91
7	12.3	8.00	32.4	1350	16.9	4.52	72

[a] TON = kg/mol-Ln. [b] TOF = g/(mol-Ln h). [c] Determined by GPC against polystyrene standard. [d] Calculated by the integration of the methine resonances in the ^1H NMR of the copolymer ($CDCl_3$, 300 MHz). [e] 48 h.

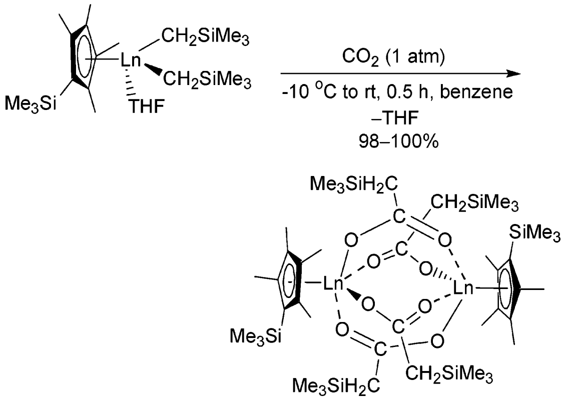
Table 5. Temperature Influence on Copolymerization of Cyclohexene Oxide (CHO) with CO_2[a]



entry	temp (°C)	TON[b]	TOF[c]	M_n[d] × 10^{-3}	M_w/M_n[d]	carbonate linkages (%)[e]
1	50	15.0	625	12.6	2.46	92
2	70	31.0	1292	21.1	5.62	94
3	90	44.0	1833	25.9	4.96	95
4	110	48.0	2000	23.7	6.03	97
5	130	46.0	1917	20.1	6.81	95

[a] Condition: [**1c**] = 12.3 mmol/L, [CHO] = 5.02 mol/L. [b] TON = kg/mol-Ln. [c] TOF = g/(mol-Ln h). [d] Determined by GPC against polystyrene standard. [e] Calculated by the integration of the methine resonances in the ^1H NMR of the copolymer ($CDCl_3$, 300 MHz).

Scheme 1. Stoichiometric Reaction of CO_2 with Rare Earth Metal Alkyl Complexes



Ln = Y (**3a**), Lu (**3b**), Sc (**3c**)

Table 6 summarizes some representative results of the CHO/CO_2 copolymerization catalyzed by the rare earth metal polyhydride complexes $[(C_5Me_4SiMe_3)Ln(\mu\text{-}H)_2]_4(THF)_x$ (**2a**: Ln = Y, x = 1, **2b**: Ln = Dy, x = 2; **2c**: Ln = Lu, x = 1). The general polymerization behaviors observed for the hydrides **2a**–**c** were basically similar to those for the alkyl complexes **1a**–**c** and need not be further discussed.

Isolation and Reactivity of the CO_2-Insertion Intermediates. To gain more information on the mechanistic aspects of the copolymerization reactions, isolation and structural characterization of some reaction intermediates were attempted. Since all of our complexes were active for the homopolymerization of CHO, it was difficult to isolate a structurally characterizable intermediate in the reaction with CHO. However, the corresponding CO_2-insertion intermediates were successfully isolated and structurally characterized in the reactions of the alkyl complexes **1a**, **c**, and **d** with CO_2. The CO_2 insertion reaction took place very rapidly at both of the two alkyl groups, which finished within a few minutes even at low temperature under 1 atm of CO_2 (Scheme 1). Each alkyl group reacted with one molecule of CO_2 to yield the corresponding carboxylate complexes $[(C_5Me_4SiMe_3)Ln(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CCH_2SiMe_3)_2]_2$ (Ln = Y (**3a**), Lu (**3b**), Sc (**3c**)) in almost quantitative yields.

Complexes **3a**–**c** are isostructural and isomorphous. The X-ray structure of the Y complex **3a** is shown in Figure 2. Some selected bond distances for **3a**–**c** are summarized in Table 7. Complexes **3a**–**c** all adopt a dimeric structure through the carboxylate bridges. There is a crystallographic inversion center at the center of the molecule. The C–O bond lengths in **3a**–**c** are

Table 6. Copolymerization of Cyclohexene Oxide (CHO) with CO_2 by Organolanthanide Polyhydride Complexes[a]

entry	cat	temp (°C)	time (h)	TON[b]	TOF[c]	M_n[d] × 10^{-3}	M_w/M_n[d]	carbonate linkages (%)[e]
1	2a	70	48	21.0	437	34.5	4.39	97
2	2b	70	48	17.7	368	29.6	7.48	99
3	2c	70	48	25.8	538	39.7	4.67	96
4	2c	50	48	13.0	270	21.0	4.76	93
5	2c	90	48	30.1	631	30.0	4.49	96
6	2c	110	24	31.4	1310	21.5	9.83	98
7	2c	130	7.5	27.7	3693	12.6	10.68	95
8	2c	90	24	26.9	1121	39.8	4.49	99
9	2c[f]	90	24	17.6	732	27.8	4.95	98
10	2c[g]	90	24	24.2	1007	2.53	7.40	87

[a] Condition: 12 atm CO_2, [Ln] = 16.3 mmol/L, [CHO] = 3.8 mol/L, in toluene, unless otherwise noted. [b] TON = kg/mol-Ln. [c] TOF = g/(mol-Ln h). [d] Determined by GPC against polystyrene standard. [e] Calculated by the integration of the methine resonances in the ^1H NMR of the copolymer ($CDCl_3$, 300 MHz). [f] In THF. [g] In chlorobenzene.

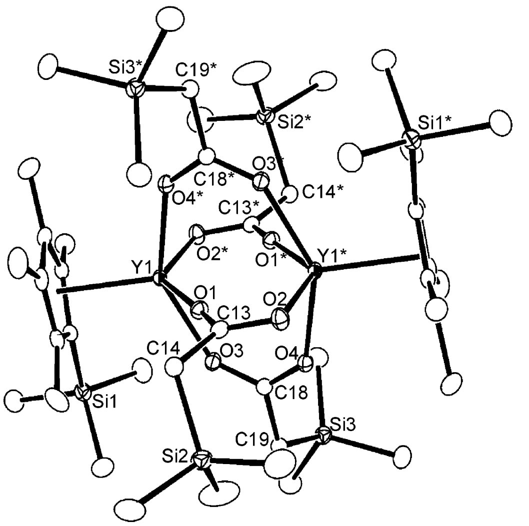


Figure 2. X-ray structure of 3a with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 7. Selected Bond Distances (Å) for 3a−c

	3a (Ln = Y)	**3b** (Ln = Lu)	**3c** (Ln = Sc)
Ln−C(Cp′) (av)	2.646(3)	2.599(3)	2.496(1)
Ln−O (av)	2.284(1)	2.236(1)	2.128(1)
Ln···Ln*	3.6457(6)	3.6034(3)	3.5696(6)
C(13)−O(1)	1.280(3)	1.283(3)	1.272(2)
C(13)−O(2)	1.262(3)	1.260(3)	1.258(2)
C(18)−O(3)	1.275(3)	1.271(3)	1.270(2)
C(18)−O(4)	1.263(3)	1.264(3)	1.261(2)

within the range of 1.258(2)−1.283(3) Å and are typical for delocalized carboxylate species. Other bond distances and angles in **3a**−**c** are also normal and need not be further discussed.

Complexes **3a**−**c** all showed one set of well-resolved ^1H and ^{13}C NMR resonances in THF-d_8. Their NMR spectra remained almost unchanged at the temperature range from −70 to 70 °C, which is in contrast with what was observed previously for the samarocene carboxylate complex $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CH_2)]$. In the latter case, two sets of ^1H NMR resonances were observed in THF-d_8 because of the existence of an equilibrium between monomeric and dimeric forms.[9a] These results might suggest that the dimeric structure of **3a**−**c** could remain intact in solution.

It is also noteworthy that the isolated carboxylate complexes **3a**, **b** could also catalyze the CHO/CO_2 copolymerization (Table 8), although the activity was lower than those of their alkyl precursors under the same conditions. Therefore, complexes **3a**, **b** represent a rare example of well-defined active carboxylate intermediates that were isolated directly from a true catalyst reaction system. Since the reaction of the alkyl complexes **1a**−**c** with CO_2 was much faster than that with CHO in toluene, the CHO/CO_2 copolymerization in the present systems must be initiated by insertion of CO_2 into a Ln−CH_2SiMe_3 bond, followed by nucleophilic attack of the resulting carboxylate species to CHO. To form an alternating copolymer, the insertion of CO_2 into the Ln−O(CHO) bond should be faster than that of CHO.

Table 8. Copolymerization of Cyclohexene Oxide (CHO) with CO_2 by Carboxylate complexes 3a,b[a]

cat	TON[b]	TOF[c]	M_n[d] × 10^{-3}	M_w/M_n[d]	carbonate linkages (%)[e]
3a	25.1	523	12.7	2.73	92
3b	34.0	708	17.4	2.66	94

[a] Condition: [Ln] = 12.3 mmol/L, [CHO] = 5.02 mol/L, 12 atm CO_2, 90 °C, 48 h, in toluene. [b] TON = kg/mol-Ln. [c] TOF = g/(mol-Ln h). [d] Determined by GPC against polystyrene standard. [e] Calculated by the integration of the methine resonances in the ^1H NMR of the copolymer ($CDCl_3$, 300 MHz).

In the reactions of the polyhydride complexes **2a**−**c** with CO_2, a structurally characterizable species was not isolated. However, a methylene diolate species $[CH_2O_2]^{2-}$ rather than a formate $[CHO_2]^-$ might be formed as shown by appearance of new signals at δ 4.6−4.8 in the ^1H NMR spectrum. The formation of such a methylene diolate species (e.g., $[(C_5Me_4SiMe_3)Y]_4(O_2CH_2)_2(Me_3SiCC(H)C(H)CSiMe_3)$) has been recently confirmed in the reaction of the yttrium tetrahydride complex $[(C_5Me_4SiMe_3)Y(\mu\text{-}H)]_4(Me_3SiCC(H)C(H)CSiMe_3)$ with CO_2.[10e] We found that this isolated methylene diolate complex $[(C_5Me_4SiMe_3)Y]_4(O_2CH_2)_2(Me_3SiCC(H)C(H)CSiMe_3)$ was also active for the copolymerization of CO_2 and CHO at 70 °C and 12 atm of CO_2 (TOF = 554 g polymer/(mol-Ln h), $M_n = 14.2 \times 10^3$, $M_w/M_n = 2.15$, carbonate linkage = 93%).

Conclusion

We have demonstrated that rare earth metal half-sandwich bis(alkyl) complexes such as **1a**−**c** and hydride complexes such as **2a**−**c** can act as excellent single-component catalysts for the alternating copolymerization of CO_2 and cyclohexene oxide (CHO) to give the corresponding poly(carbonate) with high molecular weight and moderate molecular distribution. The homopolymerization of CHO can also be achieved by use of these complexes. The isolation of the CO_2-insertion intermediates **3a**, **b** and their catalytic behavior in the copolymerization of CHO and CO_2 suggest that the present CHO/CO_2 copolymerization is initiated by insertion of CO_2 into a metal−alkyl bond, followed by nucleophilic attack of the resulting carboxylate species to CHO. In the copolymerization catalyzed by the polyhydride complexes **2a**−**c**, however, the first step might be formation of a methylene diolate species through insertion of one molecule of CO_2 into two Ln−H bonds.

Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. ^1H and ^{13}C NMR spectra were recorded on a JNM-EX 300 (FT, 300 MHz for ^1H; 75 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by the $^1H-^{13}C$ HMQC experiments when necessary. Elemental analyses were performed by the Chemical Analysis Team, Advanced Development and Supporting Center, RIKEN. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer using Nujol mulls between KBr disks. The molecular weight and molecular weight distribution of the polymers were measure by GPC (TOSOH HLC-8220 GPC; column, Super HZM-H ×3; temperature, 40 °C; eluent, THF; polystyrene standard). Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze−pump−thaw method (three times), and dried over fresh Na chips in the glovebox. Cyclohexane oxide was dried over molecular sieves (4A) for 2 days and distilled from CaH_2 under reduced pressure. CO_2 (purity grade, 99.995%) was used as received. Complexes **1a**, **1c**, **1d**, **2a**, and **2c** were prepared according to literature.[10c−f]

$(C_5Me_4SiMe_3)Dy(CH_2SiMe_3)_2(THF)$ (1b). To a hexane solution (15 mL) of $Dy(CH_2SiMe_3)_3(THF)_2$ (2.168 g, 3.811 mmol), which was prepared from the reaction of $DyCl_3$ and $LiCH_2SiMe_3$, was added 1 equiv of $C_5Me_4H(SiMe_3)$ (0.741 g, 3.811 mmol). The reaction mixture was stirred at room temperature for 1.5 h. The concentrated solution was cooled at −30 °C overnight to give colorless crystals of **1b** (2.066 g, 3.430 mmol, 90%). The ^1H NMR spectrum of **1b** was not informative because of the influence of the paramagnetic Dy(III) ion. IR (Nujol): 1377, 1349, 1323, 1250, 1238, 1130, 1038, 1016, 854, 818, 750, 721, 671, 630 cm^{-1}. Anal. Calcd for $C_{24}H_{51}OSi_3Dy$: C, 47.85; H, 8.53. Found: C, 47.13; H, 8.34.

$[(C_5Me_4SiMe_3)Dy(\mu\text{-}H)_2]_4(THF)_2$ (2b). A toluene solution (15 mL) of **1b** (1.050 g, 1.743 mmol) in a 100-mL Schlenk flask equipped with a J. Young valve was frozen in liquid nitrogen, pumped, and refilled with H_2. The mixture was allowed to warm to room temperature and stirred for 2 h. For complete conversion, a second charge of H_2 was carried out in an identical way, and the mixture was further stirred for 2 h. Evaporation of the solvent under reduced pressure afforded a light-yellow powder, which after recrystallization from THF/hexane at −30 °C yielded crystals of **2b** (0.596 g, 0.378 mmol, 88%). The ^1H NMR spectrum of **2b** was not informative because of the influence of the paramagnetic Dy(III) ion. IR (Nujol): 1460, 1377, 1325, 1244, 1198, 1132, 1018, 978, 846, 835, 684 cm^{-1}. Anal. Calcd for $C_{56}H_{108}O_2Si_4Dy_4$: C, 42.68; H, 6.91. Found: C, 41.96; H, 6.77.

$[(C_5Me_4SiMe_3)Y(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CCH_2SiMe_3)_2]_2$ (3a). A benzene solution (10 mL) of $(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$ (**1a**) (0.20 g, 0.38 mmol) in a Schlenk tube was frozen in a cold bath (−10 °C), evacuated under vacuum, and then backfilled with carbon dioxide (1 atm). The cold bath was removed, and the mixture was stirred at ambient temperature for 10 min. The volatiles were removed under reduced pressure to afford white powder of complex **3a** (0.20 g, 0.185 mmol, 98%). Recrystallization from THF/benzene at room temperature gave single crystals suitable for X-ray analysis. ^1H NMR (300 MHz, THF-d_8, 22 °C): 0.16 (s, 36H, $O_2CCH_2Si\mathit{Me}_3$), 0.27 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.88 (s, 8H, $O_2C\mathit{CH}_2SiMe_3$), 1.97 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.15 (s, 12H, $C_5\mathit{Me}_4SiMe_3$). ^{13}C NMR (100 MHz, THF-d_8, 22 °C): −0.40 (12C, $O_2CCH_2Si\mathit{Me}_3$), 2.82 (6C, $C_5Me_4Si\mathit{Me}_3$), 12.03 (4C, $C_5\mathit{Me}_4SiMe_3$), 13.54 (4C, $C_5\mathit{Me}_4SiMe_3$), 30.94 (4C, $O_2C\mathit{C}H_2SiMe_3$), 114.86 (d, J_{C-Y} = 2.5 Hz, 2C, *ipso*-$\mathit{C}_5Me_4SiMe_3$), 123.27 (4C, $\mathit{C}_5Me_4SiMe_3$), 126.81 (4C, $\mathit{C}_5Me_4SiMe_3$), 185.04 (4C, $O_2\mathit{C}CH_2SiMe_3$). IR (Nujol): ν = 1566, 1458, 1440, 1373, 1331, 1248, 1134, 1107, 849, 752, 721 cm^{-1}. Anal. Calcd for $C_{44}H_{86}O_8Si_6Y_2$: C, 48.50; H, 7.68. Found: C, 47.91; H, 7.28.

$[(C_5Me_4SiMe_3)Lu(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CCH_2SiMe_3)_2]_2$ (3b). Following the procedure described for the preparation of **3a**, the reaction of $(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)$ (**1c**) (0.200 g, 0.325 mmol in 10 mL of benzene) with carbon dioxide afforded **3b** (0.202 g, 0.161 mmol, 99%). ^1H NMR (300 MHz, THF-d_8, 22 °C): 0.18 (s, 36H, $O_2CCH_2Si\mathit{Me}_3$), 0.27 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.90 (s, 8H, $O_2C\mathit{CH}_2SiMe_3$), 1.97 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.16 (s, 12H, $C_5\mathit{Me}_4SiMe_3$). ^{13}C NMR (75 MHz, THF-d_8, 22 °C): −0.28 (12C, $O_2CCH_2Si\mathit{Me}_3$), 2.89 (6C, $C_5Me_4Si\mathit{Me}_3$), 12.17 (4C, $C_5\mathit{Me}_4SiMe_3$), 14.48 (4C, $C_5\mathit{Me}_4SiMe_3$), 31.07 (4C, $O_2C\mathit{C}H_2SiMe_3$), 113.88 (2C, *ipso*-$\mathit{C}_5Me_4SiMe_3$), 122.38 (4C, $\mathit{C}_5Me_4SiMe_3$), 125.89 (4C, $\mathit{C}_5Me_4SiMe_3$), 185.22 (4C, $O_2\mathit{C}CH_2SiMe_3$). IR (Nujol): ν = 1572, 1454, 1377, 1331, 1246, 1136, 1107, 849, 829, 750, 721 cm^{-1}. Anal. Calcd for $C_{44}H_{86}O_8Si_6Lu_2$: C, 41.89; H, 6.87. Found: C, 40.97; H, 6.67.

$[(C_5Me_4SiMe_3)Sc(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CCH_2SiMe_3)_2]_2$ (3c). Following the procedure described for the preparation of **3a**, the reaction of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1d**) (0.100 g, 0.206 mmol) with carbon dioxide gave **3c** (0.103 g, 0.103 mmol, 100%). ^1H NMR (300 MHz, THF-d_8, 22 °C): 0.19 (s, 36H, $O_2CCH_2Si\mathit{Me}_3$), 0.27 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.87 (s, 8H, $OCO\mathit{CH}_2SiMe_3$), 1.94 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.12 (s, 12H, $C_5\mathit{Me}_4SiMe_3$). ^{13}C NMR (75 MHz, THF-d_8, 22 °C): −0.01 (12C, $O_2CCH_2Si\mathit{Me}_3$), 2.70 (6C, $C_5Me_4Si\mathit{Me}_3$), 12.42 (4C, $C_5\mathit{Me}_4SiMe_3$), 15.01 (4C, $C_5\mathit{Me}_4SiMe_3$), 30.51 (4C, $O_2C\mathit{C}H_2SiMe_3$), 117.36 (2C, *ipso*-$\mathit{C}_5Me_4SiMe_3$), 125.83 (4C, $\mathit{C}_5Me_4SiMe_3$), 128.70 (4C, $\mathit{C}_5Me_4SiMe_3$), 181.67 (4C, $O_2\mathit{C}CH_2SiMe_3$). IR (Nujol): ν = 1586, 1454, 1375, 1337, 1246, 1115, 849, 714, 633 cm^{-1}. Anal. Calcd for $C_{44}H_{86}O_8Si_6Sc_2$: C, 52.76; H, 8.66. Found: C, 52.47; H, 8.43.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox under a microscope and were sealed in thin-walled glass capillaries. Data collections were performed at −80 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinement was performed on F^2 anisotropi-

Table 9. Summary of Crystallographic Data for 1b, 2b, and 3a−c

	1b	**2b**	**3a**	**3b**	**3c**
formula	$C_{24}H_{51}DyOSi_3$	$C_{56}H_{108}Dy_4O_2Si_4$	$C_{44}H_{86}Y_2O_8Si_6$	$C_{44}H_{86}Lu_2O_8Si_6$	$C_{44}H_{86}Sc_2O_8Si_6$
fw	602.42	1575.78	1089.49	1261.61	1001.59
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*Pbcn*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a, Å	10.481(1)	18.289(1)	24.544(3)	24.314(1)	24.084(1)
b, Å	15.919(3)	20.571(1)	11.863(1)	11.7846(8)	11.750(7)
c, Å	18.973(3)	17.594(1)	22.834(2)	22.748(1)	22.837(1)
α, deg	90	90	90	90	90
β, deg	100.303(2)	90	120.886(2)	120.985(1)	121.604(1)
γ, deg	90	90	90	90	90
V, $Å^3$	3114.4(9)	6619.2(9)	5705.6(10)	5587.8(6)	5503.9(6)
Z	4	4	4	4	4
*D*c, g/cm^3	1.285	1.581	1.268	1.500	1.209
μ, cm^{-1}	25.26	45.70	21.93	36.85	4.21
reflns collcd	18456	37549	16697	16642	16302
reflns with $I_o > 2\sigma(I_o)$	7125	7553	6159	6216	6031
no. variables	275	328	284	284	284
R_{int}	0.0319	0.0552	0.0532	0.0224	0.0372
GOF	1.044	1.076	0.973	0.986	0.999
R	0.0335	0.0285	0.0375	0.0205	0.0373
R_w	0.0848	0.0569	0.0559	0.0509	0.0971
R (all data)	0.0532	0.0759	0.0794	0.0276	0.0491
R_w (all data)	0.0912	0.0806	0.0586	0.0517	0.0998

cally for all the non-hydrogen atoms by the full-matrix least-squares method. The hydride ligands were found by difference Fourier synthesis and were refined isotropically. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. The crystallographic data and processing parameters for **1b**, **2b**, and **3a−c** are summarized in Table 9.

Homopolymerization of Cyclohexene Oxide (CHO). A typical procedure for bulk CHO polymerization (Table 2, entry 1): to neat CHO (2.473 g, 25.2 mmol) in a 50-mL flask was added **1a** (0.033 g, 0.063 mmol; CHO/**1a** (mol/mol) = 400) under magnetic stirring at room temperature in the glovebox. Polymerization took place immediately with an exotherm. After 3 h, the reaction was terminated by addition of a large amount of methanol. The polymer product was collected by filtration, washed with methanol, and then dried at 60 °C for 24 h in a vacuum to give a white powder (2.045 g, 82.7%).

Copolymerization of Cyclohexene Oxide and CO_2. A typical procedure for the copolymerization of CHO and CO_2 (Table 3, entry 1): a 100-mL stainless steel autoclave with a stir bar inside was put into a 70 °C oil bath, dried under vacuum for 1 h, cooled to room temperature, and then backfilled with N_2. A toluene solution (1.0 mL) of **1a** (0.026 g, 0.05 mmol) was injected into the autoclave with a syringe under N_2. CHO (1.963 g, 20.0 mmol) was then loaded ([Y] = 16.3 mM, [CHO] = 6.5 M). The autoclave was pressured to 11 atm with CO_2 and then heated to 70 °C, at which the pressure rose to about 12 atm. The mixture was stirred at 70 °C for 24 h and then cooled to room temperature. The viscous reaction mixture was dissolved with chloroform and poured into methanol to precipitate a white solid polymer product. The polymer product was collected by filtration, washed with methanol, and then dried at 60 °C for 24 h in a vacuum to give a white powder (1.20 g). The percentage of the carbonate linkages was calculated from the relative intensities of the ^1H NMR signals of the methine protons adjacent to the carbonate linkages (δ 4.62) and ether linkages (δ 3.42).

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Supporting Information Available: ORTEP drawings and tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for **1b**, **2b**, **3a**, **3b**, and **3c** and ^1H NMR charts for poly(cyclohexene oxide) and a typical CO_2/CHO copolymer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For reviews on the copolymerization of epoxides and CO_2, see: (a) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174. (b) Super, M.; Beckman, E. J. *Macromol. Symp*. **1998**, *127*, 89−108. (c) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. *Acc. Chem. Res*. **2004**, *37*, 836−844. (d) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed*. **2004**, *43*, 6618−6639.

(2) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym Phys.* **1969**, *7*, 287−292. (b) Kuran, W.; Listoś, T. *Macromol. Chem. Phys*. **1994**, *195*, 977−984. (c) Kuran, W.; Listoś, T. *Macromol. Chem. Phys.* **1994**, *195*, 1011−1015. (d) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577−7579. (e) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107−116. (f) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487−12496. (g) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc*. **2003**, *125*, 11911−11924. (h) Cheng. M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc*. **2001**, *123*, 8738−8749. (i) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284−14285. (j) Cheng, Ming; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun*. **2000**, 2007−2008. (k) Cheng, Ming; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed*. **2002**, *41*, 2599−2602. (l) Dinger, M. B.; Scott, M. J. *Inorg. Chem*. **2001**, *40*, 1029−1036. (m) Cheng, Ming; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019. (n) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008−11009. (o) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501−5510. (p) Nakano, K.; Nozaki, K.; Hiyama, T. *Macromolecules* **2001**, *34*, 6325−6332. (q)

Zhang, M.; Chen, L.; Qin, G.; Liu, B.; Yan, Z.; Li, Z. *J. Appl. Polym. Sci.* **2003**, *87*, 1123−1128. (r) Super, M.; Berluche, E.; Costello, C.; Bechman, E. *Macromolecules* **1997**, *30*, 368−372.

(3) Jung, J. H.; Ree, M.; Chang, T. *J. Polym. Sci: Part A: Polym. Chem*. **1999**, *37*, 3329−3336.

(4) (a) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335−6342. (b) Stamp, L. M.; Mang, S. A.; Holmes, A. B.; Knight, K. A.; Miguel, Y. R.; McConvey, I. F. *Chem. Commun.*, **2001**, 2502−2503. (c) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules*, **2000**, *33*, 303−308. (d) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586−7591.

(5) Darensbourg, D. J.; Niezgoda, S. A.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 4690−4698.

(6) (a) Lu, X.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574−3577. (b) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484−5487. (c) Lu, X.; Liang, B.; Zhang, Y.; Tian. Y.; Wang, Y.; Bai, C.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732−3733.

(7) (a) Chen, X.; Shen, Z.; Zhang, Y. *Macromolecules* **1991**, *24*, 5305−5308. (b) Liu, B.; Zhao, X.; Wang, X.; Wang, F. *J. Polym. Sci: Part A: Polym. Chem.* **2001**, *39*, 2751−2754. (c) Quan, Z.; Min, J.; Zhou, Q.; Xie, D.; Liu, J.; Wang, X.; Zhao, X.; Wang, F. *Macromol. Symp*. **2003**, *195*, 281−286. (d) Liu, B.; Zhao, X.; Wang, X.; Wang, F. *Polymer* **2003**, *44*, 1803−1808. (e) Tan, C.-S.; Hsu, T.-J. *Macromolecules* **1997**, *30*, 3147−3150.

(8) Hsu, T.-J. Tan, C.-S. *Polymer* **2001**, *42*, 5143−5150.

(9) For examples of stoichiometric reactions of CO_2 with organolanthanide complexes, see: (a) Evans, W. J.; Seibel, C. A.; Ziller, J. W.; Doedens, R. *Organometallics* **1998**, *17*, 2103−2112. (b) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711−7712. (c) Schumann, H.; Meese-Marktscheffel, J. A.; Dietrich, A.; Görlitz, F. *J. Organomet. Chem.* **1992**, *430*, 299−315. See also ref 10e.

(10) (a) Hou, Z. *Bull. Chem. Soc. Jpn*. **2003**, *76*, 2253−2266. (b) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1−22. (c) Tardif, O.; Nishiura, M.; Hou, Z. *Organometallics* **2003**, *22*, 1171−1173. (d) Cui, D.; Tardif, O.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 1312−1313. (e) Tardif, O.; Hashizume, D.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 8080−8081. (f) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910−13911. (g) Cui, D.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 959−962. (h) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962−965.

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