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Rare-Earth-Metal Mixed Hydride/Aryloxide Complexes Bearing Mono(cyclopentadienyl) Ligands. Synthesis, CO_2 Fixation, and Catalysis on Copolymerization of CO_2 with Cyclohexene Oxide

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Hydrogenolysis of mono(cyclopentadienyl)-ligated rare-earth-metal bis(alkyl) complexes $Cp'Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**1a**), Dy (**1b**), Lu (**1c**); $Cp' = C_5Me_4SiMe_3$) with $PhSiH_3$ afforded the mixed hydride/alkyl complexes $[Cp'Ln(\mu\text{-}H)(CH_2SiMe_3)(THF)]_2$ (Ln = Y (**2a**), Dy (**2b**), Lu (**2c**)). The overall structure of complexes **2a**−**c** is a C_2-symmetric dimer containing a planar symmetric Ln_2H_2 core at the center of the molecule. Deprotonation of ArOH (Ar = $C_6H_2\text{-}{}^tBu_2\text{-}2,6\text{-}Me\text{-}4$) by the metal alkyl group of **2a**−**c** led to formation of the mixed hydride/aryloxide derivatives $[Cp'Ln(\mu\text{-}H)(OAr)]_2$ (Ln = Y (**3a**), Dy (**3b**), Lu (**3c**)), which adopt the dimeric structure through hydride bridges with *trans*-accommodated terminal aryloxide groups. Complexes **3a**−**c** swiftly reacted with CO_2 to generate the mixed formate/carbonate complexes $[Cp'Ln(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CH)(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2COAr)]_2$ (Ln = Y (**4a**), Dy (**4b**), Lu (**4c**)). The two Cp′Ln fragments in these complexes are bridged by the formate and carbonate species, respectively, to form two square-pyramidal geometries around the metal centers. Furthermore, complexes **3a**−**c** initiated the copolymerization of CO_2 and cyclohexene oxide (CHO) under mild conditions to afford polymers with modest molecular weights and high carbonate linkages (92−99%).

Introduction

Transition metal alkoxides have recently attracted great interest because of their ability to catalyze many reactions such as the enantioselective alkylation of aldehydes,[1a] asymmetric epoxidation of α,β-unsaturated ketones,[1b] decarboxylation of carboxylic acids,[1c] polymerization of lactones and lactides, and copolymerization of carbon dioxide with epoxides.[1d–g] Rare-earth-metal alkoxide complexes bearing two cyclopentadienyl ligands or non-cyclopentadienyl ligands have also been extensively studied.[2] In contrast, the mono(cyclopentadienyl)-ligated rare-earth-metal alkoxide complexes, which are expected to show unique reactivities, have been less explored, and well-defined examples have so far been limited almost to yttrium owing to difficulty in isolation and structural characterization,[3] although their transition metal counterparts are well known and can exhibit tremendous catalytic activity toward the polymerization of ethylene.[4] During our recent studies on preparation and reactivity of mono(cyclopentadinenyl)-ligated rare-earth-metal bis(alkyl)s and dihydrides,[5] we isolated the lutetium mixed hydride/alkyl complex $[Cp'Lu(\mu\text{-}H)(CH_2SiMe_3)(THF)]_2$,[5a] which represented a rare example of a mixed hydride/alkyl rare-earth-metal complex. We have now found that such mixed hydride/alkyl complexes can also be prepared for other rare-earth metals such as Y and Dy in a similar way. Moreover, these complexes, which are different from the rare-earth metallocene monohydride or monoalkyl complexes[6a,b] or the linked-cyclopentadienyl-amido rare-earth-metal monohydride or monoalkyl complexes,[6c–g] can serve as convenient precursors to the corresponding half-sandwich mixed hydride/aryloxide complexes via selective elimination of the alkyl group by the aromatic alcohol. This synthetic route is strikingly different from that reported by Schaverien,[3c] which allows us to isolate and characterize the

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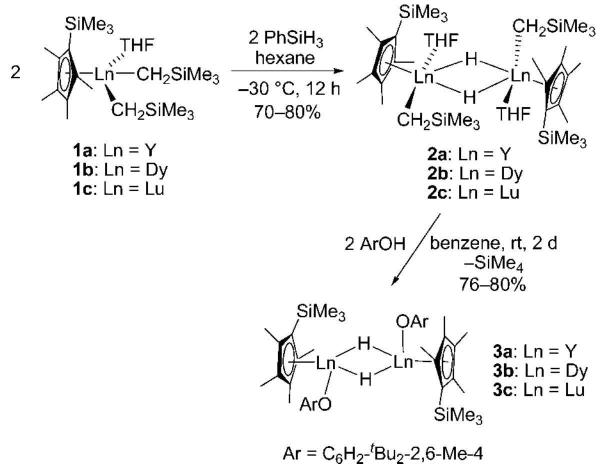
10.1021/om800170x CCC: $40.75

Scheme 1. Synthesis of Mono(cyclopentadienyl)-Ligated Rare-Earth-Metal Mixed Hydride/Alkyl and Mixed Hydride/Aryloxide Complexes



mixed hydride/aryloxide complexes of various rare-earth elements. In addition, these mixed hydride/aryloxide complexes exhibit high activity for CO_2 fixation and the copolymerization of CO_2 with cyclohexene oxide (CHO). The copolymerization of CO_2 with epoxides has received much current interest, 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. A variety of complexes based on transition metals such as zinc,[7] aluminum,[8] chromium,[9] cadmium and magnesium,[10] and cobalt[11] have been reported as efficient catalysts for the copolymerization of CO_2 with epoxides, whereas catalytic systems based on lanthanide elements, which usually need a cocatalyst, are few.[12] Herein we report the preparations and structures of half-sandwich rare-earth-metal mixed hydride/alkyl complexes, mixed hydride/aryloxide complexes, and their CO_2 fixation derivatives, as well as the preliminary results of the copolymerization of CO_2 with CHO.

Results and Discussion

Syntheses and Structures of Mono(cyclopentadienyl) Rare-Earth-Metal Mixed Hydride/Alkyl Complexes. Following the literature procedure for the synthesis of $[Cp'Lu(\mu\text{-}H)(CH_2SiMe_3)(THF)]_2$ (**2c**),[5a] treatment of rare-earth-metal bis(alkyl) complexes bearing a mono(cyclopentadienyl) ligand, $Cp'Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**1a**), Dy (**1b**); Cp′ = $C_5Me_4SiMe_3$), with 1 equiv of $PhSiH_3$ was performed in hexane at −30 °C for 12 h to afford the corresponding mixed hydride/alkyl complexes $[Cp'Ln(\mu\text{-}H)(CH_2SiMe_3)(THF)]_2$ (Ln = Y (**2a**), Dy (**2b**)) through hydrogenolysis of one metal alkyl moiety (Scheme 1). Addition of an excess amount of $PhSiH_3$ would result in the replacement of another alkyl ligand to give dihydride complexes $[Cp'Ln(\mu\text{-}H)_2]_4(THF)$. Pure **2a** and **2b** were white powders, while **2c** was a yellow solid. They had good solubility in aromatic solvents but were almost insoluble in hexane. Complexes **2a**−**c** changed slowly to **1a**−**c** and other unknown hydride species in benzene or THF within several days at room temperature. X-ray analysis displayed that complexes **2a** and **2b** were dimers of C_2 symmetry, analogous to **2c** (Table 1). Each metal cordinates to a Cp′ unit, an alkyl ligand (CH_2SiMe_3), and a solvated THF molecule to form an Ln fragment (Figure 1 for **2a**). Two Ln fragments are connected by equivalent hydride bridges to form a rhombic Ln_2H_2 core with equal Ln−H bond lengths (Table 2). The ^1H NMR spectrum of complex **2a** showed a sharp triplet for the hydride ligands at δ 5.80 with a J_{Y-H} = 27.2 Hz in the temperature range −70 to 25 °C, reflecting that **2a** formed a stable dimeric structure in solution, consistent with its crystal structure in the solid state. Interestingly, the methylene protons of **2a** displayed variable resonances. At room temperature, only a broad resonance at δ −0.74 was observed, which, however, split into two doublets at δ −0.64 and −0.79, respectively, with a geminal proton coupling (J = 10.3 Hz) (Figure 2) when the temperature was lowered to −25 °C. This result suggests that the rotation of the methylene group around the Y−C(1) bond is restricted at low temperature.

Table 1. Summary of Crystallographic Data for Complexes 2a−c[a]

	2a	**2b**	**2c**
formula	$C_{40}H_{82}Y_2O_2Si_4$	$C_{40}H_{82}Dy_2O_2Si_4$	$C_{40}H_{82}Lu_2O_2Si_4$
fw	885.24	1032.42	1057.36
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.888(2)	9.9249(1)	9.867(1)
b, Å	11.153(3)	11.2281(1)	11.159(1)
c, Å	12.721(3)	12.7924(3)	12.709(1)
α, deg	73.878(3)	73.973(1)	73.567(1)
β, deg	85.735(3)	85.791(2)	85.782(1)
γ, deg	64.925(3)	64.861(1)	65.046(1)
V, Å^3	1219.2(5)	1238.8(1)	1215.2(2)
Z	1	1	1
D_c, g/cm^3	1.206	1.384	1.445
μ, cm^{-1}	24.95	31.17	41.65
no. of reflns collcd	6551	7304	9482
no. of reflns with $>I_o > 2\sigma(I_o)$	4435	5204	6442
no. of variables	231	231	231
R_{int}	0.0308	0.0184	0.0263
GOF	1.030	0.986	1.069
R	0.0394	0.0293	0.0315
R_w	0.0686	0.0748	0.0692
R (all data)	0.0619	0.0327	0.0369
R_w (all data)	0.0709	0.0760	0.0704

[a] Data for complex **2c** are cited from ref 5a.

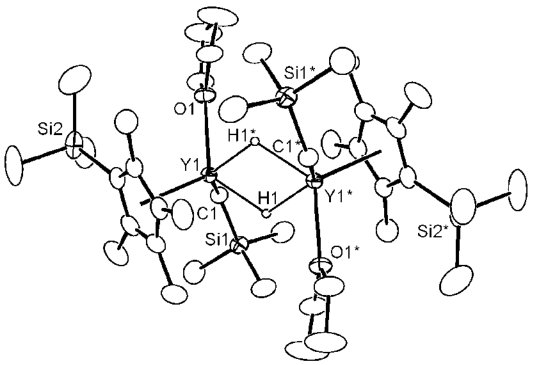


Figure 1. X-ray structure of **2a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2a−c[a]

	2a (Ln = Y)	**2b** (Ln = Dy)	**2c** (Ln = Lu)
Ln−C(Cp′)(av)	2.651 (3)	2.659 (4)	2.610 (4)
Ln(1)−O	2.396 (2)	2.426 (3)	2.360 (3)
Ln(1)−H(1)	2.21 (3)	2.09 (4)	2.12 (5)
Ln(1)−Ln(1)*	3.635 (1)	3.6457 (4)	3.5491 (4)
H(1)*−Ln(1)−H(1)	31.0 (7)	31.3 (11)	31.5 (12)

[a] Data for complex **2c** are cited from ref 5a.

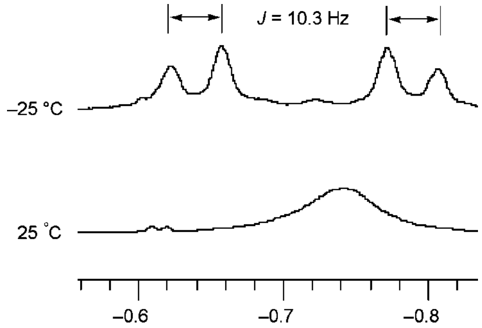


Figure 2. Methylene region in the ^{1}H NMR spectra of complex **2a**.

Syntheses and Structures of Mono(cyclopentadienyl) Rare-Earth-Metal Mixed Hydride/Aryloxide Complexes. Complex **2a** reacted with 2 equiv of ArOH (Ar = C_6H_2-$^{t}Bu_2$-2,6-Me-4) at room temperature for 2 days to give the corresponding mixed hydride/aryloxide yttrium complex **3a** ([Cp′Y(μ-H)(OAr)]$_2$) in a high yield via elimination of the metal alkyl moiety (Scheme 1). The hydride ligand remained untouched in the presence of excess ArOH, indicating the stable Ln−H fragment. A similar phenomenon had been observed in the reaction of lutetium dihydrides with excess butyrolactone.[5b] Monitoring the reaction by ^{1}H NMR spectroscopic technique showed that the upfield resonance at δ −0.74 for the methylene protons of the yttrium alkyl group in **2a** disappeared gradually; meanwhile new resonances at δ 1.62 and 2.30 arising from ^{t}Bu and CH_3 protons of the aryloxide unit in **3a** were observed. The triplet signals at δ 5.71 with a J_{Y-H} = 34.6 Hz could be assigned to the hydride ligands (μ-H) bridging to two yttrium atoms, indicating that **3a** adopted a dimeric structure in solution, in analogy to its precursor **2a** and other yttrium hydrides.[3c,13] Complexes **3b** and **3c** were synthesized according to a similar procedure described for **3a**. The overall solid-state structure of complexes **3a**−**c** characterized by X-ray diffraction analysis (Table 3) was a dimer, like that in solution state (Figure 3), containing C_2 symmetry in the center of the molecule. The hydride ligands bridge two metal atoms to form a symmetric Ln_2H_2 core. The structures of **3a**−**c** are strongly reminiscent of their congeners **2a**−**c** except for the absence of a THF molecule, which could be attributed to the coordination of the bulky aryloxide ligands. The Ln−H bond lengths in **3a**−**c** ranging from 2.09(3) to 2.15(2) Å (Table 4) are similar to those in **2a**−**c** (2.09(4)−2.21(3) Å) (Table 2) and also comparable to Lu−H found in [($C_5Me_4SiMe_2NCMe_3$)Lu(μ-H)(PMe_3)]$_2$ (1.93(6), 2.10(6) Å)[6e] and [$Et_2Si(C_5Me_4)(C_5H_5)$Lu(μ-H)]$_2$ (2.13(4), 2.16(4) Å)[14] and Y−H in [($C_5Me_4SiMe_2NCMe_3$)Y(μ-H)(THF)]$_2$ (1.98(6)−2.48(4) Å)[6g] and Yb−H in [$Me_2Si(C_5Me_4)(NCMe_2Et)$Yb($\mu$-H)(THF)]$_2$ (2.13(9)−2.57(5) Å).[6e] The average bond length of Ln−O$_{\text{terminal}}$ in **3a**−**c** (Y−O, 2.076(2) Å; Dy−O, 2.083(1) Å; Lu−O, 2.048(2) Å) is comparable to that of Y−O$_{\text{terminal}}$ (2.096(4), 2.059(3) Å) in [(C_5Me_5)Y($OC_6H_3Bu^{t}_2$)$_2$],[3a] but shorter than the bond distances between rare-earth metals and the oxygen of the neutral THF donor in **2a**−**c** (Y−O 2.396(2) Å, Dy−O 2.426(3) Å, Lu−O 2.360(3) Å). The Y···Y distance of 3.5721(7) Å in **3a** is comparable to 3.53 and 3.58 Å in methyl-bridged yttrium dimers [(C_5H_5)$_2$Y(μ-Me)]$_2$ and [(1,3-$Me_2C_5H_3$)$_2$Y(μ-Me)]$_2$, respectively.[15] The Ln−C(ring) bond distances varying from 2.575(3) to 2.626(3) Å fall in the normal range for the Ln−C(ring) bonds.[5]

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Table 3. Summary of Crystallographic Data for Complexes 3a−c and 4a−c

	3a	**3b**	**3c**	**4a**	**4b**	**4c**
fw	1005.26	1152.44	1177.38	1181.30	1328.48	1353.42
formula	$C_{54}H_{90}Y_2O_2Si_2$	$C_{54}H_{90}Dy_2O_2Si_2$	$C_{54}H_{90}Lu_2O_2Si_2$	$C_{58}H_{90}Y_2O_{10}Si_2$	$C_{58}H_{90}Dy_2O_{10}Si_2$	$C_{58}H_{90}Lu_2O_{10}Si_2$
fw	1005.26	1152.44	1177.38	1181.30	1328.48	1353.42
cryst syst	monoclinic	monoclinic	monoclini	monoclini	monoclini	monoclini
space group	*P*2 (1)/*n*	*P*2 (1)/*n*	*P*2 (1)/*n*	*P*2 (1)/*c*	*P*2 (1)/*c*	*P*2 (1)/*n*
a, Å	13.239 (1)	13.210 (1)	13.059 (1)	13.3954 (9)	13.403 (10)	12.239 (1)
b, Å	10.2802 (9)	10.234 (1)	10.168 (1)	13.4091 (9)	13.414 (10)	16.509 (1)
c, Å	20.597 (2)	20.566 (3)	20.550 (2)	17.599 (1)	17.451 (13)	15.141 (1)
α, deg	90	90	90	90	90	90
β, deg	91.044 (2)	91.110 (2)	91.842 (1)	106.135 (1)	105.954 (11)	91.539 (2)
γ, deg	90	90	90	90	90	90
V, $Å^3$	2802.7 (4)	2780.1 (6)	2727.1 (5)	3036.7 (3)	3017 (4)	3058.2 (5)
Z	2	2	2	2	2	2
D_c, g/cm^3	1.191	1.377	1.434	1.292	1.463	1.470
μ, cm^{-1}	21.38	27.45	36.79	19.94	25.50	33.01
no. of reflns collcd	9147	14 808	14 793	17 684	15 363	18 242
no. of reflns with $I_o > 2\sigma(I_o)$	4713	5422	5365	6625	5345	6945
no. of variables	289	289	289	339	339	343
R_{in}	0.0336	0.0207	0.0326	0.0279	0.0782	0.018
GOF	1.020	1.055	0.997	0.975	1.030	1.007
R	0.0405	0.0233	0.0234	0.0299	0.0290	0.0209
R_w	0.0845	0.0589	0.0422	0.0699	0.0954	0.0513
R (all data)	0.0681	0.0303	0.0348	0.0464	0.0352	0.0269
R_w (all data)	0.0900	0.0614	0.0434	0.0801	0.1050	0.0524

Carbon Dioxide Fixation of Mono(cyclopentadienyl) Rare-Earth-Metal Mixed Hydride/Aryloxide Complexes. When **3a** was exposed to a CO_2atmosphere (1 atm), the reaction took place rapidly even at 0 °C to generate a clean insertion product, $[Cp'Y(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CH)(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2COAr)]_2$ (**4a**), in a short period of time (5−30 min, 100% yield) (Scheme 2). Apparently, two carbon dioxide molecules inserted into Y−H bonds to form formate units, while another two carbon dioxide molecules inserted into Y−O bonds to generate carbonate species. The absorption at 1639 cm^{-1} in the IR spectrum of complex **4a** could be assigned to the C=O bond stretch of the formate groups, while the absorption at 1556 cm^{-1} was assigned to the carbonate functional group. This result was in agreement with the $^1H-^{13}C$ HMQC spectrum analysis. The resonances at δ 161.02 and 173.92 could be assigned to the carbonate carbon and the formate carbon, respectively. An X-ray diffraction study revealed that **4a** was a centrosymmetric dimer (Figure 4 and Table 3). The formate and carbonate species bridge two Cp′Y units to form two eight-membered rings perpendicular to each other at the core of the molecule. The oxygen atoms and the centroids of the Cp′ ligands generate pyramidal geometries around yttrium centers. The formate ligands coordinate to yttrium atoms asymmetrically, resulting in a large Y(1)−O(1)−C(1) bond angle of 175.4(1)° and a much smaller Y(1)*−O(2)−C(1) bond angle of 100.4(1)°. In contrast, the carbonate units bond to yttrium atoms symmetrically, leading to similar Y−O−C bond angles (Y(1)−O(3)−C(2), 134.5(1)° vs Y(1)*−O(4)−C(2), 136.5(1)°) (Table 5). The Y−O bond lengths ranging from 2.261(1) to 2.345(1) Å in **4a** are comparable to that in the complexes $\{(C_5Me_4)SiMe_2(CH_2\text{-}CH{=}CH_2)Y(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CCH_2SiMe_3)(\mu\text{-}\eta^1{:}\eta^2\text{-}$

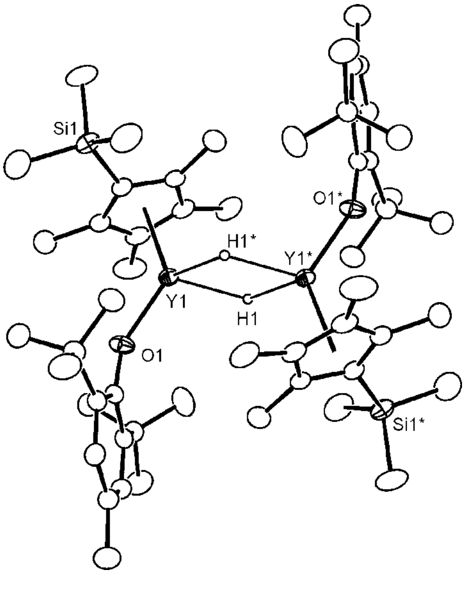
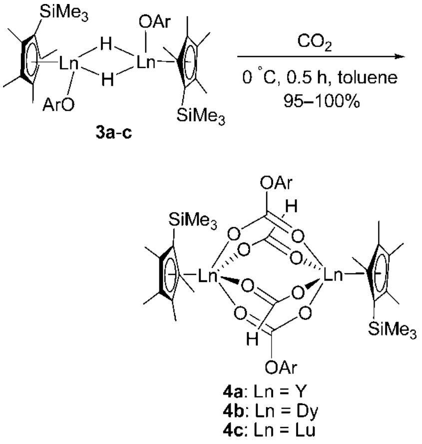


Figure 3. X-ray structure of **3a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3a−c

	3a (Ln = Y)	**3b** (Ln = Dy)	**3c** (Ln = Lu)
Ln−C(Cp′)(av)	2.618 (3)	2.626 (3)	2.575 (3)
Ln(1)−O(1)	2.076 (2)	2.083 (1)	2.048 (2)
Ln(1)−H(1)	2.15 (2)	2.14 (3)	2.09 (3)
Ln(1)⋯Ln(1)*	3.5721 (7)	3.5712 (4)	3.4516 (4)
Ln(1)*−Ln(1)−H(1)	33.8 (6)	32.2 (8)	33.0 (7)

Scheme 2. Reaction of Mono(cyclopentadienyl)-Ligated Rare-Earth-Metal Mixed Hydride/Aryloxido Complexes with CO_2



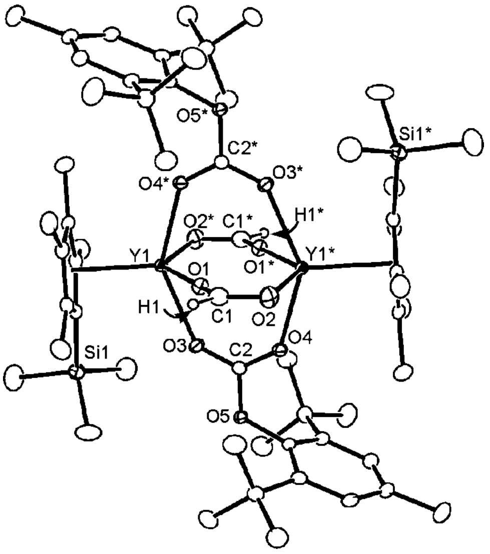


Figure 4. X-ray structure of **4a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4a−c

	4a (Ln = Y)	**4b** (Ln = Dy)	**4c** (Ln = Lu)
Ln−C(Cp′)(av)	2.623 (2)	2.627 (4)	2.579 (1)
Ln(1)−O(1)	2.276 (1)	2.296 (3)	2.229 (1)
Ln(1)−O(2)*	2.345 (1)	2.357 (3)	2.244 (1)
Ln(1)−O(3)	2.292 (1)	2.277 (3)	2.274 (1)
Ln(1)−O(4)*	2.261 (1)	2.310 (3)	2.221 (1)
Ln(1)···Ln(1)*	3.7505 (4)	3.759 (2)	3.6548 (3)
C(1)−O(1)	1.259 (3)	1.263 (5)	1.253 (3)
C(1)−O(2)	1.235 (3)	1.226 (5)	1.250 (3)
C(2)−O(3)	1.253 (2)	1.245 (4)	1.250 (3)
C(2)−O(4)	1.253 (2)	1.261 (4)	1.260 (3)
C(2)−O(5)	1.356 (2)	1.352 (4)	1.342 (3)
O(1)−Ln(1)−O(2)*	132.79 (6)	132.47 (9)	142.56 (6)
O(3)−Ln(1)−O(4)*	141.43 (1)	141.55 (9)	135.61 (6)
Ln(1)−O(1)−C(1)	175.4 (1)	174.1 (3)	134.2 (1)
Ln(1)*−O(2)−C(1)	100.4 (1)	99.3 (3)	134.5 (1)
Ln(1)−O(3)−C(2)	134.5 (1)	136.4 (2)	101.1 (1)
Ln(1)*−O(4)−C(2)	136.5 (1)	134.4 (2)	179.2 (1)
O(1)−C(1)−O(2)	122.9 (2)	123.2 (4)	127.4 (2)
O(3)−C(2)−O(4)	127.6 (1)	127.6 (3)	122.9 (2)

$O_2CCH_2SiMe_3)\}_2$[16] (Y−O: 2.270(1) and 2.328(1) Å) and $[Cp'Y(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CCH_2SiMe_3)_2]_2$[12f] (Y−O: av 2.284(1) Å). These bond lengths are longer than $Y-O_{terminal}$ in **3a** (2.076(2) Å) and in $[(C_5Me_5)Y(OC_6H_3Bu^t{}_2)_2]$ (2.096(4) and 2.059(3) Å)[3a] but shorter than the bridging $Y-\eta^2$-O (2.40(2)−2.42(2) Å) in the yttrocene complex $(C_5H_5)_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$.[17] The Y···Y distance of 3.7505(4) Å is comparable to 3.7085(8) Å in $[Y(C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$,[6f] but much longer than that in its precursor **3a** due to the more specific crowding of the molecule. Product **4b** was prepared by reaction of CO_2 with **3b**, which is an analogue of **4a** (Table 3). The similar reaction between CO_2 and the lutetium **3c** afforded **4c** albeit with slightly different coordination geometry (Figure 5). The formate bridges coordinate to Lu metals symmetrically with similar Lu−O−C bond angles (Lu(1)−O(1)−C(1) = 134.2(1)°, Lu(1*)−O(2)−C(1) = 134.5(1)°), while the carbonate species connect to Lu metals asymmetrically with an almost linear angle Lu(1*)−O(4)−C(2) (179.2(1)°) and a much smaller Ln(1)−O(3)−C(2) angle (101.1(1)°) (Table 5). Nevertheless, in all complexes **4a−c**, the C−O bond lengths in both formate and carbonate moieties are similar, ranging from 1.226(3) to 1.261(3) Å, which are shorter than a C−O single bond, such as C(2)−O(5) (1.342(3)−1.356(2) Å) but longer than a C−O double bond, indicating that there are no localized C=O bonds. Interestingly, complexes **4a−c** retained their dimeric structures in THF solution, which was evident in the ^{1}H NMR spectrum of **4a** in THF-d_8 (Figure 6). The triplet resonance at δ 8.22 can be assigned to the methine proton of the formate species coupling with two yttrium atoms with a $^3J_{YOCH} = 2$ Hz, much smaller than 34.6 Hz of J_{YH}.[3,6] This is in contrast to the metallocene samarium allyl complex $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, which inserts CO_2 to form a bimetallic product existing in equilibrium with the THF-coordinated monomeric analogue.[16] The monomer−dimer equilibrium is also observable in β-diiminate zinc acetate and alkoxide systems depending on the concentration of the complex and temperature.[1g]

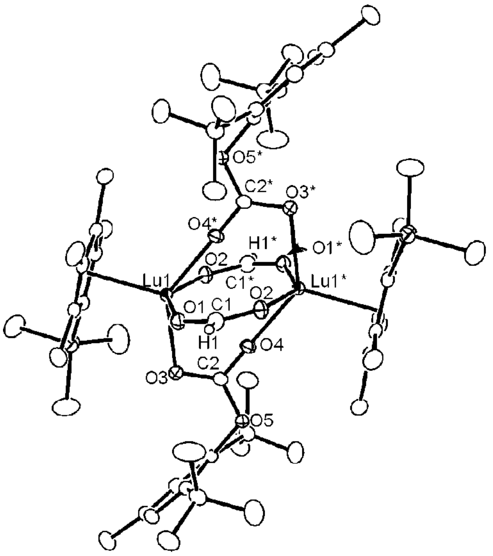


Figure 5. X-ray structure of **4c** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

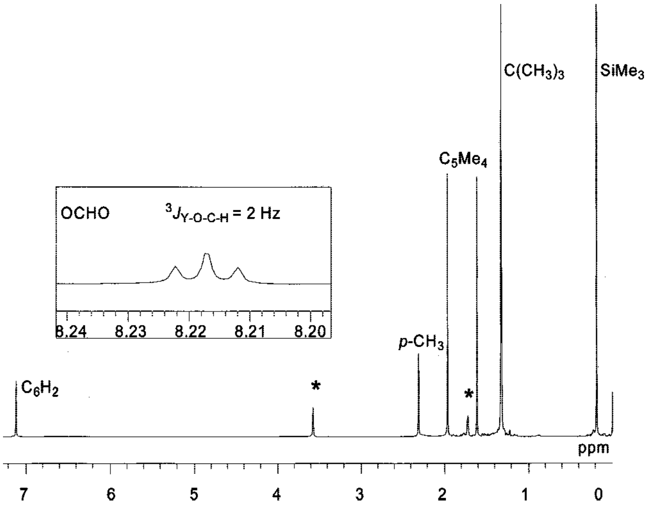


Figure 6. ^{1}H NMR spectrum of complex **4a** in THF-d_8.

CO_2 has been used successfully as an insertion substrate in transition metal chemistry. For example, CO_2 has been reported

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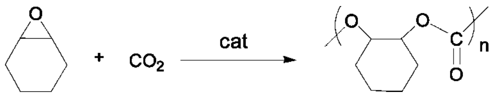
Table 6. Copolymerization of CO_2 with Cyclohexene Oxide (CHO) by Complexes 3a−c[a]



entry	cat	temp (°C)	time (h)	TON[b]	TOF[c](h^{-1})	M_n[d] × 10^{-3}	M_w/M_n[d]	carbonate linkages (%)[e]
1	**3a**	70	48	220	4.9	16.1	1.65	92
2	**3b**	70	48	176	3.7	13.7	3.30	92
3	**3c**	70	48	219	4.8	24.4	2.09	95
4	**3c**	50	24	trace	nd[f]	nd	nd	nd
5	**3c**	70	24	139	5.8	14.5	3.10	97
6	**3c**	90	24	187	7.8	25.6	5.69	98
7	**3c**	110	24	226	9.4	24.7	6.15	99

[a] Condition: 12 atm of CO_2, toluene: 2 mL, [Ln] = 16.3 mmol/L, [CHO] = 5.0 mol/L. [b] TON = mole cyclohexene oxide consumed by per mole catalyst (mol/mol·Ln). [c] TOF = mol/(mol·Ln h). [d] Determined by GPC against polystyrene standard. [e] Calculated by integration of methine resonances in ^1H NMR of copolymer ($CDCl_3$, 300 MHz). [f] nd: not determined.

to insert into M−C bonds of $(C_5H_5)_2Ti\text{-}(CH_3)_2$[18] and M−H bonds of $[(C_5H_5)Ti(\mu\text{-}H)]_2(C_{10}H_8)$,[19] $Ru(dmpe)_2H_2$,[20] and $(C_5H_5)_2Zr(H)(\mu\text{-}H)(\mu\text{-}N^tBu)Ir(C_5Me_5)$,[21] generating carboxylate or mixed hydride/terminal formate derivatives, respectively, although in some cases, decaboxylation or CO_2 extrusion might occur.[22] In contrast, only a few examples of CO_2 reaction with rare-earth-metal complexes have been reported,[5c,12f,16,17,23] and CO_2 insertion into M−H and M−O bonds simultaneously in one molecule like **3a−c** is really rare.[5c]

Mono(cyclopentadienyl) Rare-Earth-Metal Mixed Hydride/Aryloxide Complexes Catalyze the Copolymerization of CO_2 with Cyclohexene Oxide. The copolymerization of CO_2 and CHO was successfully performed with complexes **3a−c** in the absence of a cocatalyst under 12 atm of CO_2 at 70 °C for 48 h in toluene (TON: 139−220 mol/(mol·Ln)) (Table 6). The resulting copolymers showed high contents of carbonate linkages (>92%) and moderate molecular weights and molecular weight distributions. The Lu and Y complexes showed similar activities, which were higher than that of the Dy counterpart (Table 6, entries 1−3). The copolymerization also showed a strong temperature dependence. When the reaction was performed at 50 °C, only a trace amount of product could be isolated. At 70 °C, a TON of 139 mol/mol·Ln was obtained, which reached 226 mol/(mol·Ln) when the temperature was increased to 110 °C. Meanwhile the content of carbonate linkages of the resulting copolymer increased gradually to 99% at 110 °C, indicating that the CO_2 insertion reaction was favored at elevated temperature. The molecular weight of the product increased when the temperature was raised to some extent, but dropped slightly when the temperature was over 90 °C, which was accompanied by the broadened molecular weight distribution (Table 6, entries 4−7). This could be imputed to the effect of the ceiling temperature where the depolymerization and decomposition reactions became obvious, in agreement with previous reports.[7e,9b,12f,24]

Conclusion

We have demonstrated that mono(cyclopentadienyl)-ligated mixed hydride/aryloxide complexes of varying lanthanide elements can be synthesized easily by the acid−base reaction between the mixed hydride/alkyl complexes and an aryl alcohol. These complexes can swiftly fix CO_2 molecule to generate mixed formate/carboxylate derivatives of novel structures. Moreover, they can also act as moderately active initiators for the copolymerization of CO_2 and cyclohexene oxide under mild conditions to produce alternating copolymers without requirement of a cocatalyst.

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. 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 JNM-EX 300 (FT, 300 MHz for ^1H; 75 MHz for ^{13}C) and JNM-EX 400 spectrometers. The NMR assignments were confirmed by the $^1H-^{13}C$ HMQC and $^1H-^{13}C$ HMBC experiments. Elemental analyses were performed by Chemical Analysis Team, Advanced Development and Supporting Center, RIKEN. IR spectra were recorded on a Shimadzu FTIR-8100 M spectrometer using Nujol mulls between KBr disks. The molecular weight and molecular weight distribution of the polymers were measured 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. Cyclohexene oxide was dried over molecular sieves (4 Å) for 2 days and distilled from CaH_2 under reduced pressure. CO_2 (Purity grade, 99.995%), $PhSiH_3$, and 2,6-di-*tert*-butyl-4-methylphenol were used as purchased. Complexes **1a−c** and **2c** were prepared according to the literature procedure.[5a,12f]

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

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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 the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydride atoms in complexes **2a**,**b** and **3a**−**c** and the methine protons of formate units in **4a**−**c** were located by difference Fourier synthesis, and their coordinates and isotropic parameters were refined. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

[Cp′Y(*μ*-H)(CH_2SiMe_3)(THF)]$_2$ (2a). Under −30 °C, to a hexane solution (10 mL) of Cp′Y(CH_2SiMe_3)$_2$(THF) (**1a**) (4.366 g, 8.256 mmol) was added dropwise 1 equiv of cold $PhSiH_3$ (0.892 g, 8.256 mmol) under stirring. The reaction mixture was kept at this temperature overnight to afford white crystalline **2a** deposited on the bottom of the flask. After decantation of the upper clear solution, the solid was washed with hexane (3 × 2 mL) and dried in vacuo to afford a white powder of **2a** in 74% yield (2.704 g, 3.055 mmol). Colorless blocks for X-ray analysis were isolated from the hexane/toluene (2:1 (v/v)) solution at −30 °C in 3−4 days. ^{1}H NMR (300 MHz, C_6D_6, 22 °C): −0.74 (s, 4H, $C\mathit{H}_2SiMe_3$), 0.38 (s, 18H, $CH_2Si\mathit{Me}_3$), 0.46 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.36 (s, 8H, THF), 2.15 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.37 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 3.85 (s, 8H, THF), 5.80 (t, J_{Y-H} = 27.2 Hz, 2H, *μ*-H). ^{13}C NMR (75 MHz, C_6D_6, 22 °C): 3.08 ($C_5Me_4Si\mathit{Me}_3$), 5.24 ($CH_2Si\mathit{Me}_3$), 12.37 ($C_5\mathit{Me}_4SiMe_3$), 15.30 ($C_5\mathit{Me}_4SiMe_3$), 25.24 (THF), 39.31 ($\mathit{C}H_2SiMe_3$), 71.77 (THF), 113.40 (*ipso*-$C_5Me_4SiMe_3$), 123.22 ($\mathit{C}_5Me_4SiMe_3$), 126.40 ($\mathit{C}_5Me_4SiMe_3$). IR (Nujol): ν 1323, 1242, 1171, 1130, 1018, 849, 754, 721 cm^{-1}. Anal. Calcd for $C_{40}H_{82}O_2Si_4Y_2$: C, 54.27; H, 9.34. Found: C, 53.81; H, 9.26.

[Cp′Dy(*μ*-H)(CH_2SiMe_3)(THF)]$_2$ (2b). Following the same procedure described for the preparation of **2a**, the reaction of Cp′Dy(CH_2SiMe_3)$_2$(THF) (**1b**) (2.112 g, 3.506 mmol in 8 mL of cold hexane) with $PhSiH_3$ (0.379, 3.506 mmol) afforded **2b** in 70% yield (1.266 g, 1.227 mmol). Single crystals suitable for X-ray analysis were isolated as colorless blocks from the hexane/toluene (2:1 (v/v)) solution at −30 °C in 3−4 days. The ^{1}H NMR spectrum of **2b** was not informative because of the influence of the paramagnetic Dy(III) ion. IR (Nujol): ν 1325, 1246, 1180, 1130, 1039, 846, 754, 721 cm^{-1}. Anal. Calcd for $C_{40}H_{82}O_2Si_4Dy_2$: C, 46.53; H, 8.01. Found: C, 46.01; H, 7.44.

[Cp′Y(*μ*-H)(OC_6H_2-^{t}Bu$_2$-2,6-Me-4)]$_2$ (3a). To a benzene (10 mL) solution of **2a** (1.130 g, 1.277 mmol) was added 2 equiv of 2,6-di-*tert*-butyl-4-methylphenol (0.563 g, 2.553 mmol in 5 mL benzene) at room temperature, and the reaction mixture was stirred for 2 days. Removal of solvent in vacuo was followed by washing the residue with hexane (2 × 2 mL) to give a white solid of **3a** in 76% yield (0.976 g, 0.971 mmol). Recrystallization from benzene solution at room temperature afforded good colorless crystals for X-ray analysis in 4−5 days. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): 0.36 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.62 (s, 36H, C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 2.02 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.24 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.30 (s, 6H, C_6H_2-^{t}Bu$_2$-2,6-*Me*-4), 5.71 (t, J_{Y-H} = 34.6 Hz, 2H, *μ*-H), 7.13 (s, 4H, $C_6\mathit{H}_2$-^{t}Bu$_2$-2,6-Me-4). ^{13}C NMR (75 MHz, C_6D_6, 22 °C): 2.62 ($C_5Me_4Si\mathit{Me}_3$), 12.13 ($C_5\mathit{Me}_4SiMe_3$), 14.93 ($C_5\mathit{Me}_4SiMe_3$), 21.48 (C_6H_2-^{t}Bu$_2$-2,6-*Me*-4), 33.04 (C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 35.34 (C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 118.12 (*ipso*-$C_5Me_4SiMe_3$), 125.66 ($\mathit{C}_5Me_4SiMe_3$), 126.48, ($\mathit{C}_5Me_4SiMe_3$), 126.51 (*m*-C_6H_2), 129.82 (*p*-C_6H_2), 136.18 (*o*-C_6H_2), 157.78 (*ipso*-C_6H_2). IR (Nujol): ν 3049, 2852, 1462, 1453, 1421, 1377, 1311, 1263, 1187, 1018, 867, 831 cm^{-1}. Anal. Calcd for $C_{54}H_{90}O_2Si_2Y_2$: C, 64.51; H, 9.02. Found: C, 63.97; H, 8.79.

[Cp′Dy(*μ*-H)(OC_6H_2-^{t}Bu$_2$-2,6-Me-4)]$_2$ (3b). Following a similar procedure to that described for the preparation of **3a**, treatment of **2b** (0.730 g, 0.707 mmol) with 2,6-di-*tert*-butyl-4-methylphenol (0.312 g, 1.414 mmol) generated a crystalline light yellow solid of complex **3b** (0.578 g, 0.502 mmol, 71%). Recrystallization from benzene solution at room temperature afforded good colorless crystals for X-ray analysis in 4−5 days. The ^{1}H NMR spectrum of **3b** was not informative because of the influence of the paramagnetic Dy(III) ion. IR (Nujol): ν 3088, 2850, 1462, 1454, 1421, 1377, 1315, 1261, 1193, 1016, 883, 831 cm^{-1}. Anal. Calcd for $C_{54}H_{90}O_2Si_2Dy_2$: C, 56.28; H, 7.87. Found: C, 55.42; H, 7.62.

[Cp′Lu(*μ*-H)(OC_6H_2-^{t}Bu$_2$-2,6-Me-4)]$_2$ (3c). In the same manner, complex **3c** was isolated by reaction of **2c** (0.137 g, 0.130 mmol) with 2 equiv of 2,6-di-*tert*-butyl-4-methylphenol (0.057 g, 0.260 mmol) as a colorless solid in 80% yield (0.122 g, 0.104 mmol). Colorless single crystals for X-ray analysis were isolated by evaporating slowly the saturated benzene solution in a glovebox at room temperature. ^{1}H NMR (270 MHz, C_6D_6, 22 °C): 0.35 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.62 (s, 36H, C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 2.03 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.28 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.30 (s, 6H, C_6H_2-^{t}Bu$_2$-2,6-*Me*-4), 7.14 (s, 2H, C_6H_2), 9.64 (s, 2H, *μ*-H). ^{13}C NMR (75 MHz, C_6D_6, 22 °C): 2.93 ($C_5Me_4Si\mathit{Me}_3$), 12.44 ($C_5\mathit{Me}_4SiMe_3$), 15.32 ($C_5\mathit{Me}_4SiMe_3$), 21.66 (C_6H_2-^{t}Bu$_2$-2,6-*Me*-4), 33.37 (C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 35.71 (C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 117.51 (*ipso*-$\mathit{C}_5Me_4SiMe_3$), 125.80 ($\mathit{C}_5Me_4SiMe_3$), 125.84 ($\mathit{C}_5Me_4SiMe_3$), 126.70 (*m*-C_6H_2), 129.41 (*p*-C_6H_2), 136.18 (*o*-C_6H_2), 158.29 (*ipso*-C_6H_2). IR (nujol): ν 3075, 2852, 1460, 1455, 1421, 1377, 1311, 1273, 1200, 1018, 908, 833 cm^{-1}. Anal. Calcd for $C_{54}H_{90}O_2Si_2Lu_2$: C, 55.08; H, 7.70. Found: C, 54.50; H, 7.58.

{Cp′Y(*μ*-η^1:η^1-O_2CH)(*μ*-η^1:η^1-$O_2COC_6H_2$-^{t}Bu$_2$-2,6-Me-4)}$_2$ (4a). A 50 mL Schlenk tube containing a benzene (10 mL) solution of **3a** (0.200 g, 0.199 mmol) was cooled to −10 °C. Removal of N_2 and solvent under reduced pressure was followed by backfilling with carbon dioxide (1 atm). The reaction mixture was stirred for 0.5 h at 0 °C. The volatile was removed off under reduced pressure to give a white powder of complex **4a** (0.235 g, 0.199 mmol, 100%). Recrystallization from a mixture of hexane/THF (1:1 v/v) yielded good colorless cubic crystals for X-ray analysis. ^{1}H NMR (400 MHz, THF-*d*$_8$, 22 °C): 0.20 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.33 (s, 36H, C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 1.62 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 1.97 (s, 12H, $C_5\mathit{Me}_4SiMe_3$), 2.32 (s, 6H, C_6H_2-^{t}Bu$_2$-2,6-*Me*-4), 7.12 (s, 4H, $C_6\mathit{H}_2$-^{t}Bu$_2$-2,6-Me-4), 8.22 (t, J_{Y-H} = 2 Hz, 2H, OC(H)O). ^{13}C NMR (75 MHz, THF-*d*$_8$, 22 °C): 2.44 ($C_5Me_4Si\mathit{Me}_3$), 10.91 ($C_5\mathit{Me}_4SiMe_3$), 13.74 ($C_5\mathit{Me}_4SiMe_3$), 21.55 (C_6H_2-^{t}Bu$_2$-2,6-*Me*-4), 31.72 (C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 36.13 (C_6H_2-$^t\mathit{Bu}_2$-2,6-Me-4), 116.95 (*ipso*-$C_5Me_4SiMe_3$), 125.26 ($\mathit{C}_5Me_4SiMe_3$), 127.26 (*m*-C_6H_2), 128.39 ($\mathit{C}_5Me_4SiMe_3$), 135.03 (*p*-C_6H_2), 142.53 (*o*-C_6H_2), 148.12 (*ipso*-C_6H_2), 161.02 (O_2CO) 173.92 (OC(H)O). IR (Nujol): ν 3072, 2852, 1639, 1554, 1462, 1377, 1338, 1244, 1203, 1113, 1028, 837 cm^{-1}. Anal. Calcd for $C_{58}H_{90}O_{10}Si_2Y_2$: C, 58.97; H, 7.68. Found: C, 58.79; H, 7.58.

{Cp′Dy(*μ*-η^1:η^1-O_2CH)(*μ*-η^1:η^1-$O_2COC_6H_2$-^{t}Bu$_2$-2,6-Me-4)}$_2$ (4b). Following the same procedure described for the formation of **4a**, reaction of **3b** (0.150 g, 0.130 mmol in 15 mL of benzene) with CO_2 at 0 °C in a period of 0.5 h afforded **4b** as a light yellow powder (0.165 g, 0.124 mmol, 95%). Recrystallization from a mixture of hexane/THF (1:1 v/v) yielded good colorless cubic crystals for X-ray analysis. The ^{1}H NMR spectrum of **4b** was not informative because of the influence of the paramagnetic Dy(III) ion. IR (Nujol): ν 3074, 2855, 1647, 1557, 1460, 1375, 1334, 1244, 1203, 1112, 1028, 837 cm^{-1}. Anal. Calcd for $C_{58}H_{90}O_{10}Si_2Dy_2$: C, 52.83; H, 6.83. Found: C, 52.63; H, 6.62.

{Cp′Lu(*μ*-η^1:η^1-O_2CH)(*μ*-η^1:η^1-$O_2COC_6H_2$-^{t}Bu$_2$-2,6-Me-4)}$_2$ (4c). The reaction of **3c** (0.130 g, 0.110 mmol in 8 mL of benzene) with CO_2 by the same manner described above yielded complex **4c**, selectively (0.149 g, 0.110 mmol, 100%). Recrystallization from a mixture of hexane/THF (1:1 v/v) yielded good colorless cubic crystals for X-ray analysis. ^{1}H NMR (300 MHz, THF-*d*$_8$, 22 °C): 0.20 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.33 (s, 36H, C_6H_2-

^{t}*Bu*$_2$-2,6-Me-4), 1.61 (s, 12H, C$_5$*Me*$_4$SiMe$_3$), 1.98 (s, 12H, C$_5$*Me*$_4$SiMe$_3$), 2.32 (s, 6H, C$_6$H$_2$-^{t}Bu$_2$-2,6-*Me*-4), 7.12 (s, 4H, C$_6$*H*$_2$-^{t}Bu$_2$-2,6-Me-4), 8.34 (s, 2H, OC(H)O). ^{13}C NMR (75 MHz, THF-*d*$_8$, 22 °C): 2.33 (C$_5$Me$_4$Si*Me*$_3$), 10.84 (C$_5$*Me*$_4$SiMe$_3$), 13.69 (C$_5$*Me*$_4$SiMe$_3$), 21.45 (C$_6$H$_2$-^{t}Bu$_2$-2,6-*Me*-4), 31.64 (C$_6$H$_2$-^{t}*Bu*$_2$-2,6-Me-4), 36.06 (C$_6$H$_2$-^{t}*Bu*$_2$-2,6-Me-4), 115.84 (*ipso*-*C*$_5$Me$_4$SiMe$_3$), 124.13 (*C*$_5$Me$_4$SiMe$_3$), 127.42 (*m*-C$_6$H$_2$), 129.03 (*C*$_5$Me$_4$SiMe$_3$), 135.25 (*p*-C$_6$H$_2$), 142.70 (*o*-C$_6$H$_2$), 148.17 (*ipso*-*C*$_6$H$_2$), 162.03 (O$_2$CO), 174.07 (OC(H)O). IR (Nujol): ν 3074, 2865, 1659, 1556, 1454, 1377, 1344, 1242, 1192, 1111, 1031, 837 cm^{-1}. Anal. Calcd for $C_{58}H_{90}O_{10}Si_2Lu_2$: C, 51.47; H, 6.70. Found: C, 51.33; H, 6.54.

Copolymerization of CO$_2$ and CHO. A typical procedure for the copolymerization of CHO and CO$_2$ (Table 6, 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 backfilled with N$_2$. A toluene solution (2.0 mL) of **3a** (0.0251 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 mmol/L, [CHO] = 5.0 mol/L). The autoclave was pressurized to 11 atm with CO$_2$ and then heated to 70 °C, and the pressure rose to about 12 atm. The mixture was stirred at 70 °C for 48 h and then cooled to room temperature. The viscous reaction mixture was dissolved with chloroform and poured into methanol, filtered, washed with methanol, and then dried at 60 °C for 24 h under vacuum to give a white powder of polycarbonate (1.56 g). The percentage of the carbonate linkages was calculated from the relative intensities of the ^{1}H 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: Experimental details, ORTEP drawings, and tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for **2a**,**b**, **3a**−**c**, and **4a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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