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Reactivity of Monocationic Bis(alkyl) and Dicationic Mono(alkyl) Yttrium Complexes toward Ketones and Carbon Dioxide

Yumiko Nakajima and Jun Okuda*

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany

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Cationic alkyl yttrium complexes $[Y(CH_2SiMe_3)_2(THF)_4][A]$ (**1a**, A = BPh_4; **1b**, A = $Al(CH_2SiMe_3)_4$) react with benzophenone and fluorenone at ambient temperature to produce bis(alkoxy) complexes *cis*-$[Y\{OC(CH_2SiMe_3)R'_2\}_2(THF)_4][BPh_4]$ (**3a**, R′ = Ph; **4a**, $R'_2 = C_{12}H_8$), while two isomers, *cis*- and *trans*-$[Y\{OC(CH_2SiMe_3)R'_2\}_2(THF)_4][Al(CH_2SiMe_3)_4]$ (**3b**, R′ = Ph; **4b**, $R' = C_{12}H_8$), were obtained from the reaction of the aluminate **1b** with benzophenone or fluorenone. The reaction of the crown ether-supported monocationic bis(alkyl) complex $[Y(CH_2SiMe_3)_2(12\text{-crown-}4)(THF)][A]$ (**1′a**, A = BPh_4; **1′b**, A = $Al(CH_2SiMe_3)_4$) with benzophenone or fluorenone results in the formation of *cis*-$[Y\{OC(CH_2SiMe_3)R'_2\}_2(12\text{-crown-}4)(THF)][A]$ (**3′a**, R′ = Ph, A = BPh_4; **4′a**, $R'_2 = C_{12}H_8$, A = BPh_4; **3′b**, R = Ph, A = $Al(CH_2SiMe_3)_4$). Complex **1a** reacts with carbon dioxide to produce a dinuclear carboxylato complex, $[Y(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CR)(\mu\text{-}\eta^1{:}\eta^2\text{-}O_2CR)(THF)_3]_2[BPh_4]_2$ (**6a**) (R = CH_2SiMe_3). The reaction of the crown ether complex $[Y(CH_2SiMe_3)_2(12\text{-crown-}4)(THF)][B(C_6H_4F\text{-}4)_4]$ (**1′c**) with carbon dioxide also produced a product of insertion, $[Y(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CR)_2(12\text{-crown-}4)]_2[B(C_6H_4F\text{-}4)_4]_2$ (**7′c**). The structures of **4a**, **6a**, and **7′c** were determined by single-crystal X-ray structural analysis. Reaction of the dicationic mono(alkyl) complex $[Y(CH_2SiMe_3)(THF)_5][BPh_4]_2$ (**2a**) with benzophenone, fluorenone, and carbon dioxide resulted in the formation of the corresponding dicationic alkoxy complex $[Y\{OC(CH_2SiMe_3)R'_2\}(THF)_5][BPh_4]_2$ (**8a**, R′ = Ph; **9a**, $R'_2 = C_{12}H_8$) and the carboxylato complex $[Y(O_2CR)(THF)_5][BPh_4]_2$ (**10a**).

Introduction

In the context of developing homogeneous ethylene,[1] α-olefin,[1e,f,2] and 1,3-diene[3] polymerization catalysts based on rare earth metals,[4] we and others have established that cationic alkyl complexes of the rare earth metals play a pivotal role as the active species.[1−3,5] Since the first isolation and structural characterization of a cationic alkyl lutetium complex in 2002,[6a] several complexes without any ancillary ligands $[YR_2(THF)_4][BPh_4]$ (R = CH_2SiMe_3, **1a**) and the dication $[YR(THF)_5][BPh_4]_2$ (**2a**) have been described.[5,6] These complexes contain labile THF ligands and a higher reactivity can be expected. In addition to the olefin insertion into the metal alkyl bond at a cationic metal center, initial studies have revealed a high reactivity of these complexes, including the C−H bond activation of pyridine.[6c,7] For further applications of these cationic rare earth metal alkyls, understanding their fundamental reactivity appears to be essential. Since a highly polarized rare earth metal−carbon bond is combined with a Lewis acidic cationic metal center, both nucleophilic and electrophilic properties can be anticipated for these complexes.[8] We have examined whether the trimethylsilylmethyl group of the cationic yttrium complexes still acts as a nucleophile.[9] Herein we report on the reactivity of the monocationic bis(alkyl) complex $[YR_2(THF)_4][A]$ (**1a**, A = BPh_4; **1b**, A = AlR_4) as well as the dicationic mono-

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* Corresponding author. Fax: +49 241 8092644. E-mail: jun.okuda@ac.rwth-aachen.de.

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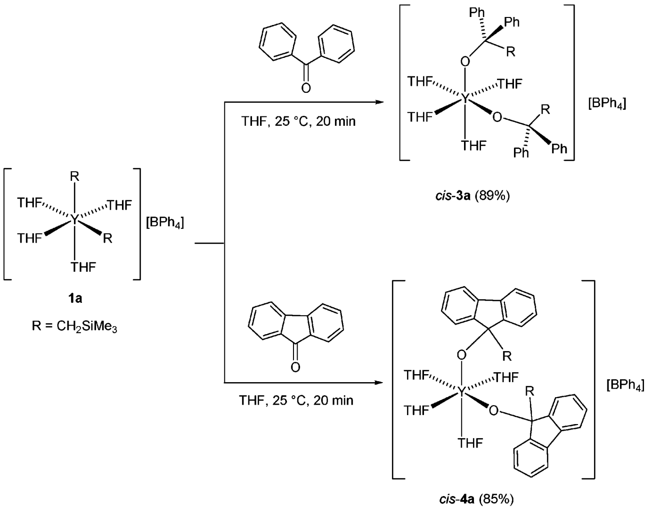
Scheme 1



(alkyl) complex [YR(THF)$_5$][BPh$_4$]$_2$ (**2a**) toward the C−O double bond of some ketones and carbon dioxide.

Results and Discussion

Reaction with Benzophenone and Fluorenone. The cationic bis(trimethylsilylmethyl) yttrium complex [YR$_2$(THF)$_4$][BPh$_4$] (**1a**) was found to be highly reactive toward aliphatic ketones (acetone, pentanone-3, acetophenone) in THF solution at ambient temperature, resulting in intractable mixtures of several compounds. Presumably both insertion of the C−O double bond into the Y−C bond and β-H deprotonation (enolization) occurred. When **1a** reacted with a 3-fold excess of benzophenone in THF at room temperature, the bis(alkoxy) complex, *cis*-[Y(OCRPh$_2$)$_2$(THF)$_4$][BPh$_4$] (**3a**), was formed as the only product and isolated in analytically pure form (Scheme 1). Likewise, the cationic complex **1a** reacted with excess fluorenone in THF at room temperature to give a similar complex, *cis*-[Y(OCRC$_{12}$H$_8$)$_2$(THF)$_4$][BPh$_4$] (**4a**), in high yield.

The bis(alkoxy) complexes *cis*-**3a** and *cis*-**4a** were identified by ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis. In the ^{1}H NMR spectrum of *cis*-**3a**, the two equivalent alkoxy groups give rise to one doublet and two triplets in the aromatic region, assigned to phenyl groups. The two equivalent trimethylsilylmethyl groups are observed as a singlet at δ 1.95 (CH$_2$Si) and δ −0.35 (SiMe$_3$). The ^{13}C NMR spectroscopic data of *cis*-**3a** are consistent with a structure containing two equivalent alkoxy ligands. The trimethylsilylmethyl groups exhibit only one set of methyl and methylene signals. The phenyl group gives rise to four signals in the aromatic region. Notably, the carbon atom attached to the alkoxy oxygen atom is recorded as a doublet at δ 83.5 with a coupling to yttrium ($^2J_{\mathrm{YC}} = 5.4$ Hz). This coupling to yttrium indicates a strong interaction of yttrium with the alkoxy ligand, as previously reported by Teuben et al. for the dinuclear benzamidinato yttrium complex [{PhC(NSiMe$_3$)$_2$}$_2$Y(μ-NHCMe=CHCN)]$_2$.[8c] In the ^{13}C NMR spectrum of this complex, the β-carbon atom bonded to the amido nitrogen was reported as a doublet with a coupling constant of $^2J_{\mathrm{YC}} = 5$ Hz. The NMR spectroscopic data of *cis*-**4a** are similar to those of *cis*-**3a**. Complex *cis*-**4a** exhibits one set of signals for the trimethylsilylmethyl group at δ 1.76 (CH$_2$Si) and δ −0.69 (SiMe$_3$) in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, a doublet was observed at δ 85.4 ($^2J_{\mathrm{YC}} = 3.7$ Hz) for the quaternary carbon of the alkoxy group.

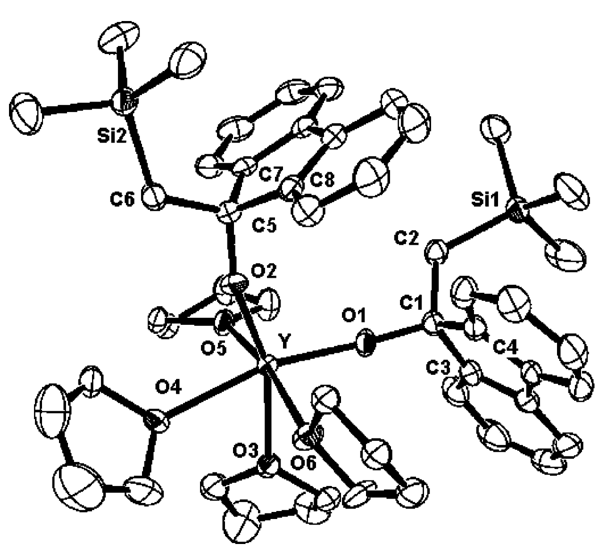


Figure 1. Molecular structure of *cis*-**4a** (ellipsoids drawn at the 50% probability level, tetraphenyl borate anion, disordered carbon atoms of a tetrahydrofuran, and hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Y−O1 2.0533(18), Y−O2 2.0680(18), C1−O1 1.402(3), C5−O2 1.406(3), Y−O1−C1 167.31(17), Y−O2−C5 156.01(17), C3−C1−O1 112.1(2), C4−C1−O1 111.3(2), C2−C1−O1 109.7(2), C7−C5−O2 109.1(2), C8−C5−O2 112.3(2), C6−C5−O2 110.1(2).

The structure of *cis*-**4a** was determined by a single-crystal X-ray diffraction study. Suitable single crystals were obtained from a CH$_2$Cl$_2$/Et$_2$O solution at −30 °C. The ORTEP diagram as well as selected bond distances and angles is depicted in Figure 1. The structure of *cis*-**4a** in the crystal is consistent with the above-mentioned spectroscopic data in solution. The coordination geometry around the yttrium center, coordinated by two *cis*-arranged alkoxy ligands and four THF molecules, is distorted octahedral. The structure of the starting complex **1b** with a tetrakis(trimethylsilylmethyl) aluminate counteranion also possesses two *cis*-arranged trimethylsilylmethyl ligands.[1g] The Y−O bond lengths of the alkoxy groups, Y−O1 = 2.0533(18) Å and Y−O2 = 2.0680(18) Å, are consistent with Y−O single bonds of terminal alkoxy groups coordinated to an yttrium center (1.99−2.12 Å).[10] The C−O bond lengths observed in both alkoxy groups are ca. 1.40 Å, corresponding to a normal C−O single bond. The bond angles of O1−C1−C2−4 and O2−C5−C6−8, 109−113°, indicate sp^3-character of the carbon atoms, and the angles at the alkoxy oxygen atoms, Y−O1−C1 167.31(17)° and Y−O2−C5 156.01(19)°, suggest pronounced π-donation. Preliminary experiments revealed that the monocationic bis(alkyl) complex of scandium, [ScR$_2$(THF)$_3$][BPh$_4$], also reacted with benzophenone to give the bis(alkoxy) complex [Sc(OCRPh$_2$)$_2$(THF)$_n$][BPh$_4$] (n = 3, 4).[11]

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(9) Not unexpectedly, the neutral yttrium tris(alkyl) complex [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] was found to react with 3 equiv of benzophenone to give a neutral tris(alkoxy) complex, [Y{OCPh$_2$(CH$_2$SiMe$_3$)}$_3$(THF)$_3$]. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ −0.05 (s, 27H, SiMe$_3$), 1.34 (m, β-THF), 1.92 (s, 6H, CH_2Si), 3.57 (m, α-THF), 7.09 (t, $^3J_{\mathrm{HH}} = 7.3$ Hz, 6H, *p*-Ph), 7.20 (t, $^3J_{\mathrm{HH}} = 7.8$ Hz, 12H, *m*-Ph), 7.59 (d, $^3J_{\mathrm{HH}} = 7.8$ Hz, 12H, *o*-Ph). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ −0.81 (SiMe$_3$), 25.6 (β-THF), 37.7 (CH$_2$Si), 68.5 (α-THF), 81.2 (d, $^2J_{\mathrm{YC}} = 5.2$ Hz, OC), 125.8 (*p*-Ph), 127.6 (*o*-Ph), 127.6 (*m*-Ph), 154.0 (*ipso*-Ph). Preliminary crystallography of [Y{OCPh$_2$(CH$_2$SiMe$_3$)}$_3$(THF)$_3$] showed a facial configuration.

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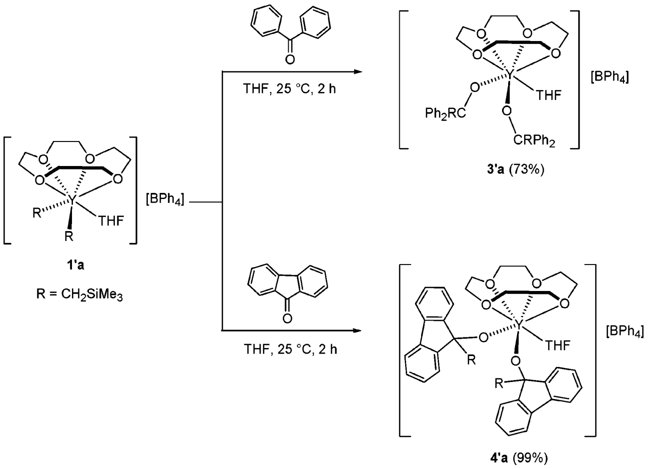
Scheme 2



The previously reported crown ether complex [YR$_2$(12-crown-4)(THF)][BPh$_4$] (**1′a**)[6c] also reacted with benzophenone and fluorenone in THF at room temperature to produce the corresponding bis(alkoxy) complexes **3′a** and **4′a** (Scheme 2). Complexes **3′a** and **4′a** exhibit two multiplets for the diastereotopic methylene protons of the coordinated crown ether. The trimethylsilylmethyl group of **3′a** is observed at δ 1.84 (CH$_2$-Si) and δ −0.36 (SiMe$_3$) in the ^{1}H NMR spectrum. Complex **4′a** exhibits one methylene signal and one methyl signal for the trimethylsilylmethyl group at δ 1.66 and δ −0.68. The quaternary carbon in **3′a** and **4′a** appears as a singlet at δ 83.2 and δ 84.5 in the ^{13}C NMR spectrum.

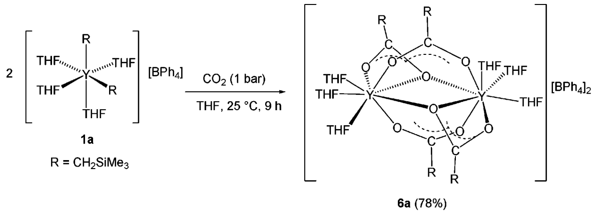
Changing the counteranion affected the reactivity of the cationic bis(alkyl) complex. The reaction of the tetrakis(trimethylsilylmethyl)aluminate complex, [YR$_2$(THF)$_4$][AlR$_4$] (**1b**), with benzophenone produced two isomeric bis(alkoxy) complexes, *cis*-**3b** and *trans*-**3b** in a 9:1 ratio (Scheme 3). Analogously, two isomers, *cis*-**4b** and *trans*-**4b**, were formed in the reaction of **1b** with fluorenone.

In the ^{1}H NMR spectrum of *cis*-**3b** and *trans*-**3b**, each complex shows one set of signals for alkyl groups, δ 1.97 (CH$_2$-Si) and δ −0.38 (SiMe$_3$) for *cis*-**3b** and δ 1.87 (CH$_2$Si) and δ −0.35 (SiMe$_3$) for *trans*-**3b**. In the ^{13}C NMR spectrum, *cis*-**3b** and *trans*-**3b** each exhibit one doublet at δ 83.6 ($^2J_{\mathrm{YC}} = 5.3$ Hz) and δ 82.2 ($^2J_{\mathrm{YC}} = 5.2$ Hz), which are assigned to the quaternary carbon atom, as a result of coupling to the yttrium center. Complexes *cis*-**4b** and *trans*-**4b** also exhibit doublets for the quaternary carbon atoms at δ 85.8 ($^2J_{\mathrm{YC}} = 6.1$ Hz) and δ 85.2 ($^2J_{\mathrm{YC}} = 5.0$ Hz), respectively. The spectra of *cis*-**3b** and *cis*-**4b** show almost identical signals to *cis*-**3a** and *cis*-**4a**. Only *cis*-**3b** was obtained when the reaction of **1b** with benzophenone was performed at −30 °C. Even after the solution of *cis*-**3b** was kept at room temperature overnight, formation of *trans*-**3b** was not observed. Furthermore, the high-temperature NMR spectra (+50 °C) of a mixture containing both *cis*-**3b** and *trans*-**3b** did not show any change in the molar ratio or in the chemical shifts, suggesting that the exchange between *cis*-**3b** and *trans*-**3b** does not occur at 50 °C.

Although the X-ray diffraction study using a single-crystal obtained from cold THF/pentane solution showed that complex **1b** has two alkyl groups *cis* to each other,[1g] *trans*-**1b** presumably exists in solution. The related monocationic dimethyl complex, [YMe$_2$(THF)$_5$][BPh$_4$], adopts a *trans* configuration.[3c] As shown previously, there is an equilibrium between the aluminate complex **1b** and the neutral tris(alkyl) complex [YR$_3$(THF)$_2$] (**5**) and [AlR$_3$(THF)] as a result of a transfer of an alkyl group between the aluminum center and the yttrium center depending on the solvent polarity.[12] On the basis of this observation, it is probable that an isomerization process occurs between *cis*-**1b** and *trans*-**1b** via the neutral tris(alkyl) complex **5** at room temperature (Scheme 4). Since the thermodynamically more stable *cis*-**1b** predominantly exists at low temperature, the *cis* complex **3b** was obtained as the sole product when the reaction was conducted at low temperature, whereas at higher temperatures both *cis* and *trans* isomers reacted with the ketone. On the other hand, no exchange reaction was observed on the NMR time scale between the bis(alkyl) cation **1a** with tetraphenylborate anion and tris(alkyl) **5**. This observation is consistent with the result that the reaction of **1a** with benzophenone or fluorenone produced only the *cis* isomer *cis*-**3a** or *cis*-**4a**.

In the case of the crown ether complex [YR$_2$(12-crown-4)(THF)][AlR$_4$] (**1′b**), the tetradentate crown ether ligand only allows complex **1′b** to adopt a *cis* configuration. Consequently, the reaction of **1′b** with benzophenone gave only one bis(alkoxy) complex, [Y(OCRPh$_2$)$_2$(12-crown-4)(THF)][AlR$_4$] (**3′b**) with *cis* alkoxy ligands.

Reaction with Carbon Dioxide. Carbon dioxide insertion into a lanthanide alkyl bond is a well-known reaction to give lanthanide carboxylato complexes, which serve as catalyst precursors for isoprene polymerization.[13] The bis(alkyl) monocation **1a** underwent insertion of carbon dioxide (1 bar) in THF at room temperature to produce the dinuclear cationic tetrakis(trimethylsilylacetato) complex [Y(μ-η^1:η^1-O$_2$CR)(μ-η^1:η^2-O$_2$CR)(THF)$_3$]$_2$[BPh$_4$]$_2$ (**6a**) in quantitative yield.



(1)

Complex **6a** precipitated from THF solution and was identified on the basis of the ^{1}H and ^{13}C NMR spectra in pyridine-d_5 as well as by elemental analysis. In the ^{1}H NMR spectrum, signals for the trimethylsilylmethyl groups are observed at δ

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(11) The reaction of [Sc(CH$_2$SiMe$_3$)$_2$(THF)$_3$][BPh$_4$] with benzophenone produced the homologous scandium [Sc(OC(CH$_2$SiMe$_3$)Ph$_2$)$_2$(THF)$_4$][BPh$_4$] quantitatively. The resulting alkoxy complex was identified by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −0.22 (s, 18H, SiMe$_3$), 1.74 (m, β-THF), 1.79 (s, 4H, CH_2Si), 3.58 (m, α-THF), 6.69 (t, $^3J_{\mathrm{HH}} = 7.2$ Hz, 4H, 4-CH BPh$_4$), 6.83 (t, $^3J_{\mathrm{HH}} = 7.3$ Hz, 8H, 3-CH BPh$_4$), 7.06 (t, $^3J_{\mathrm{HH}} = 7.3$ Hz, 4H, *p*-Ph), 7.17 (t, $^3J_{\mathrm{HH}} = 7.7$ Hz, 8H, *m*-Ph), 7.24 (br, 8H, 2-CH BPh$_4$), 7.47 (d, $^3J_{\mathrm{HH}} = 7.1$ Hz, 8H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 0.35 (SiMe$_3$), 25.3 (β-THF), 33.1 (CH$_2$Si), 67.4 (α-THF) 86.1 (OC), 121.9 (4-CH BPh$_4$), 125.7 (3-CH BPh$_4$), 126.6 (*p*-Ph), 126.8 (*o*-Ph), 128.3 (*m*-Ph), 137.2 (2-CH BPh$_4$), 151.5 (*ipso*-Ph), 165.2 (q, $^1J_{\mathrm{BC}} = 49.5$ Hz, 1-CH BPh$_4$). HMQC (THF-d_8, 25 °C): −0.22−0.35, 1.79−33.1, 6.69−121.9, 6.83−125.7, 7.06−126.6, 7.17−128.3, 7.24−137.2, 7.47−126.8. Anal. Calcd for C$_{74}$H$_{94}$BO$_6$ScSi: Sc, 3.77. Found: Sc, 3.63.

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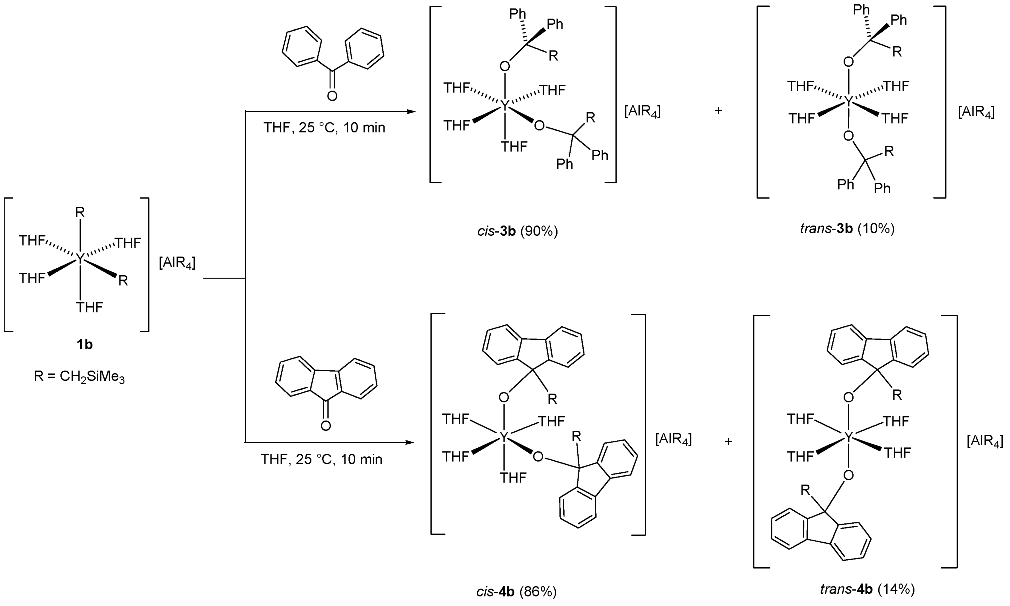
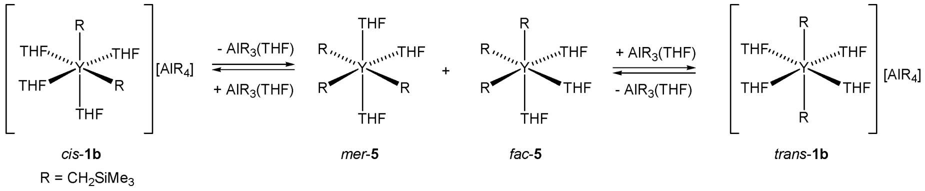
Scheme 3



Scheme 4



2.18 (CH_2Si) and δ 0.13 ($SiMe_3$) at room temperature. These resonances did not change their shape even at -50 °C, although **6a** has two sets of inequivalent carboxylato ligands according to its solid-state structure. The ^{13}C NMR spectrum is consistent with the ^1H NMR spectrum, and only one signal assigned to all four carboxylato carbon atoms was observed at δ 191.3. Ligand exchange between THF and pyridine-d_5 is fast when the cationic rare earth metal complex is dissolved in pyridine.[7]

The structure of **6a** in the solid state was determined by a single-crystal X-ray diffraction study. The ORTEP diagram together with selected bond lengths and angles is depicted in Figure 2. The crystal system is monoclinic, and the structure of **6a** possesses an inversion center on the center of the Y−Y′ axis. Complex **6a** contains two yttrium centers bridged by two symmetrical μ-η^1:η^1 and two unsymmetrical μ-η^1:η^2 carboxylato ligands. The Y···Y′ distance is 3.8632(6) Å. Each yttrium center is eight-coordinate and attached to two symmetrically bridging carboxylato oxygen atoms, one η^1 and two η^2 oxygen atoms of the unsymmetrically bridging μ-η^1:η^2 carboxylato, and three THF oxygen atoms. The coordination geometry can be described as triangular dodecahedron. Y−O (carboxylato) distances are in the range 2.2−2.6 Å, which are comparable with the Y−O single-bond distance of dimeric yttrium complexes bridged by a μ_2-oxo ligand.[10a,c] The Y−O2 bond length of the μ-η^1:η^2 carboxylato ligand of 2.3334(19) Å is slightly longer than the other Y′−O2 bond, 2.532(2) Å. This inequivalence in Y−O bond lengths of a bridging carboxylato ligand is observed in other structurally related dimeric yttrium carboxylato complexes.[14] Although several examples of structurally characterized cationic carboxylato rare earth metals or lanthanides are known,[15] complex **6a** is the first example of a cationic carboxylato rare earth metal complex that is prepared by insertion reaction of carbon dioxide.

In the course of the reaction, intermediates were detected by monitoring the reaction of **1a** with CO_2 by means of ^1H NMR spectroscopy. Immediately after CO_2 (ca. 10 equiv) was transferred into the NMR tube, all of the starting complex **1a** was consumed and the formation of three intermediates, **A**, **B**, and **C**, was observed. After 30 min, intermediate **A** disappeared and only **B** and **C** were detected in a ratio of 4:1. In the ^1H NMR spectrum, the intermediate **A** exhibits one set of resonances for the trimethylsilylmethyl bonded to yttrium, viz., one doublet at δ -0.93 (CH_2Si) and one singlet at δ -0.13 ($SiMe_3$). Intermediate **A** could not be fully characterized because of its short life time. The two other intermediates, **B** and **C**, exhibit one set of alkyl signals at δ 1.88 (CH_2Si) and 0.12 ($SiMe_3$) for **B** and δ 1.92 (CH_2Si) and 0.13 ($SiMe_3$) for **C**, respectively. The intermediates **B** and **C** also show a carboxylato carbon at δ 192.0 and 187.7 in the ^{13}C NMR spectrum. It was confirmed that both **B** and **C** are easily converted into the dimeric complex **6a** without any additional CO_2 molecule, as the mixture of **B** and **C** produced **6a** quantitatively in vacuum. These results indicate that **B** and **C** have already incorporated two CO_2 molecules on each yttrium center. On the basis of this observation, monomeric dicarboxylato complexes with *cis*/*trans* geometry are proposed for **B** and **C**.[13b]

The cationic crown ether-supported complex **1′** also reacted with carbon dioxide to produce a dinuclear yttrium tetracarboxylato complex. Although complex **1′a**, with a tetraphenylbo-

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[14] (a) Wang, X.; Guo, Y.; Wang, E.; Duan, L.; Xu, X.; Hu, C. *J. Mol. Struct.* **2004**, *691*, 171. (b) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711.

[15] (a) Sawase, H.; Koizumi, Y.; Suzuki, Y.; Shimoi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2730. (b) Schleid, T.; Meyer, G. Z. *Anorg. Allg. Chem.* **1990**, *583*, 46. (c) Ma, B.-Q.; Zhang, D.-S.; Gao, S.; Jin, T.-Z.; Yan, C.-H.; Xu, G.-X. *Angew. Chem., Int. Ed.* **2000**, *39*, 3644.

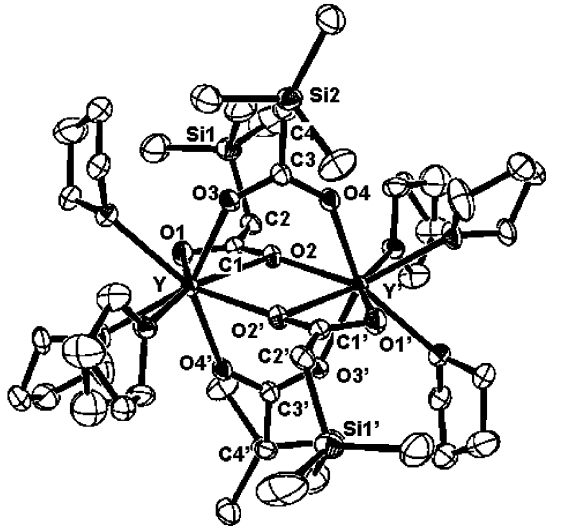


Figure 2. Molecular structure of **6a** (ellipsoids drawn at the 50% probability level, tetraphenylborate anion, tetrahydrofuran molecules in the lattice, and hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Y⋯Y′ 3.8632(6), O1−Y 2.333(2), O2−Y 2.3334(19), O2−Y′ 2.532(2), O3−Y 2.2693(19), O4−Y′ 2.2729(19), O1−C1−O2 118.9(3), O3−C3−O4 124.2(3), Si1−C2−C1 111.1(2), Si2−C4−C3 114.4(2).

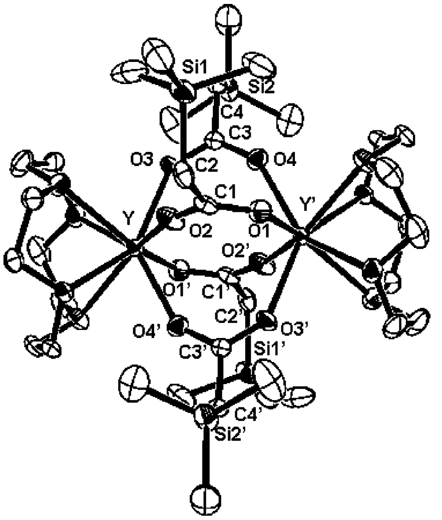
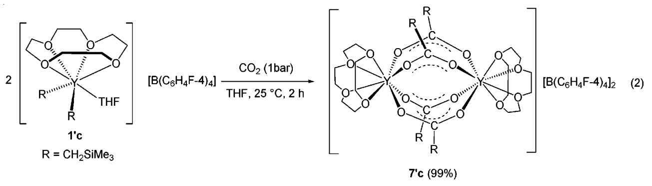


Figure 3. Molecular structure of **7′c** (ellipsoids drawn at the 50% probability level, tetra(*p*-fluorophenyl)borate, dichloromethane in the lattice, and hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Y⋯Y′ 4.0695(5), O2−Y 2.222(2), O3−Y 2.2534(19), O1−Y′ 2.2709(19), O4−Y′ 2.2392(19), O1−C1−O2 122.6(3), O3−C3−O4 123.5(3), Si1−C2−C1 112.4(2), Si2−C4−C3 113.5(2).

rate counteranion, reacted with carbon dioxide instantaneously, the resulting compound was found to be sparingly soluble in organic solvents and could not be identified. Therefore, the reaction of **1′** with carbon dioxide was performed using the more soluble derivative [YR$_2$(12-crown-4)(THF)][B(C$_6$H$_4$F-4)$_4$] (**1′c**), with a tetra(*p*-fluorophenyl)borate anion, to produce the di(yttrium) tetracarboxylato complex [Y(μ-η^1-η^1-O$_2$CR)$_2$(12-crown-4)]$_2$[B(C$_6$H$_4$F-4)$_4$]$_2$ (**7′c**) quantitatively. The reaction with carbon dioxide is faster than that of **1a**, and no intermediates were observed during the reaction, the final product **7′c** being obtained quantitatively after 2 h.



Complex **7′c** was identified by ^{1}H NMR, ^{13}C NMR, and IR spectra as well as by elemental analysis. Single crystals of **7′c** were obtained from cold CH$_2$Cl$_2$/Et$_2$O solution, and the structure of **7′c** was determined by X-ray structural analysis. The molecular structure is shown in Figure 3 together with selected bond lengths and bond angles. The crystal system is monoclinic, and a crystallographic inversion center relates both yttrium atoms. In **7′c**, the geometry around the yttrium center, surrounded by eight oxygen atoms, is square antiprismatic with the 12-crown-4 ether coordinating to the yttrium center via four oxygen atoms. In contrast to the structure of **6a**, all four carboxylato ligands bridge the two yttrium centers in a symmetrical μ-η^1-η^1 fashion and the Y−Y′ bond length (4.0695(5) Å) is slightly longer than that in **6a**. This can be accounted for by the increased valence electron number of the 11-electron fragment [Y(12-crown-4)] in **7′c** versus the 9-electron fragment [Y(THF)$_3$] in **6a**.

Reaction of the Dicationic Mono(alkyl) Complex. Due to the high ionic charge, the trimethylsilylmethyl group at the dicationic yttrium center in [YR(THF)$_5$][BPh$_4$]$_2$ (**2a**)[6c] was expected to be less nucleophilic than that in the monocationic complex **1**. However, the reaction of **2a** with benzophenone and fluorenone smoothly proceeded in THF to produce the corresponding alkoxy complexes [Y(OCRPh$_2$)(THF)$_5$][BPh$_4$]$_2$ (**8a**) and [Y(OCRC$_{12}$H$_8$)(THF)$_5$][BPh$_4$]$_2$ (**9a**), respectively (Scheme 5). Both complexes **8a** and **9a** exhibited one set of trimethylsilylmethyl and phenyl groups in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, one doublet assignable to the carbon atom attached to an oxygen atom appeared at δ 85.6 ($^2J_{\mathrm{YC}} = 5.2$ Hz) for **8a** and δ 88.1 ($^2J_{\mathrm{YC}} = 6.1$ Hz) for **9a** as a result of coupling to yttrium.

The dicationic complex **2a** also reacted with carbon dioxide (1 bar) in THF under insertion into the yttrium−carbon bond to produce the carboxylato complex [Y(O$_2$CR)(THF)$_5$][BPh$_4$]$_2$ (**10a**). In contrast to the reaction of the monocation **1a** with carbon dioxide, no intermediates were observed by ^{1}H NMR spectroscopic monitoring. The resulting complex **10a** was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy as well as elemental analysis. In the ^{1}H NMR spectrum, signals of the trimethylsilylmethyl group were observed at δ 2.19 (CH$_2$Si) and δ 0.13 (SiMe$_3$). In the ^{13}C NMR spectrum the carboxylato carbon signal appeared at δ 191.4. Since the spectra of **10a** were measured in pyridine-d_5, the coordination number of the solvent at the yttrium center is obscured. As a consequence of the double positive charge and by the number of THF molecules, we assume that this complex, [Y(O$_2$CCH$_2$SiMe$_3$)(THF)$_5$]$^{2+}$[BPh$_4$]$^-{}_2$, has a pentagonal bipyramidal configuration with a possibly chelating carboxylate ligand.[16] Carboxylato ligands at highly positively charged metal centers tend to be chelating, although the structure found in the dicationic tris(*tert*-butylsiloxy)silanolate yttrium complex [Y{OSi(O^{t}Bu)$_3$}(THF)$_6$]$^{2+}$[BPh$_4$]$^-{}_2$ with six THF ligands contains a nonchelating silanolate ligand.[5c]

Conclusion

Addition of metal alkyls such as Grignard or alkyl lithium reagents to carbonyl compounds is one of the most fundamental

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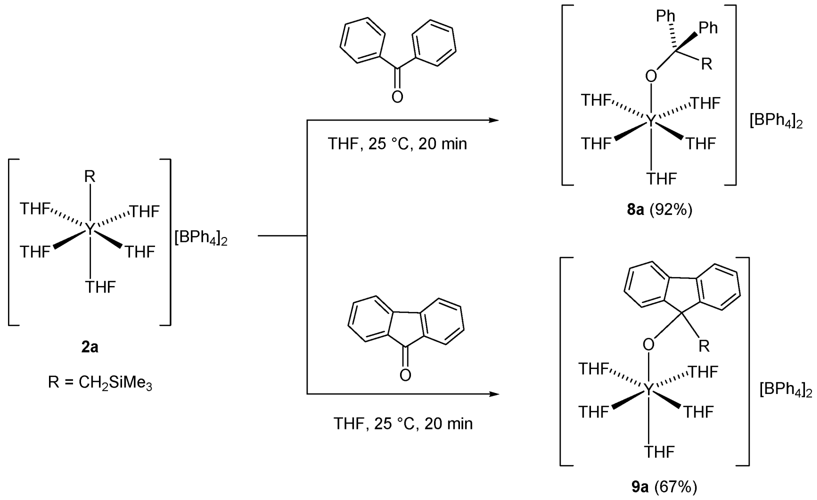
[16] Preliminary single-crystal X-ray analysis indicated that the solid-state structure of **10a** is mononuclear.

Scheme 5



reactions in organic synthesis.[17] In these reactions, competitive pathways such as enolization and reduction decrease the selectivity of the formation of the normally desired alcohol. It has recently been demonstrated that the addition of a lanthanide salt promotes the addition of organometallic reagents as a result of the Lewis acid-induced activation of the carbonyl group by the lanthanide salts.[18] Although $CeCl_3$ is the most commonly used reagent in these systems, any lanthanide or yttrium trichloride has been recognized to be applicable,[19] although there are not many examples for facile addition of well-defined alkyl lanthanide complexes to a carbonyl group.[8a,9] Despite the cationic charge,[20] the nucleophilicity of the trimethylsilylmethyl group in the cationic alkyl yttrium complexes **1** and **2** appears to be retained. Cationic alkoxy complexes were formed selectively as a result of insertion of the C−O double bond of a ketone into the yttrium−carbon bond. Notably, even the trimethylsilylmethyl group in dicationic **2** remains highly polarized and acts as a nucleophile. At the same time, the polarity of the trimethylsilymethyl group appears to be also pronounced, as facile C−H bond activation of pyridine by $[Y(CH_3)(THF)_6][BPh_4]_2$ has shown.[7] Application of cationic rare earth metal alkyl complexes for other C−C bond forming processes beyond olefin polymerization will depend on the ability to harness this strongly polarized bond.

Experimental Section

General Procedures. All operations were performed under an inert atmosphere of argon using Schlenk line and glovebox techniques. The starting materials, $[Y(CH_2SiMe_3)_2(THF)_4][BPh_4]$ (**1a**), $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)][BPh_4]$ (**1a′**), $[Y(CH_2SiMe_3)_2(THF)_4][AlR_4]$ (**1b**) ($R = CH_2SiMe_3$), $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)][AlR_4]$ (**1b′**), and $[Y(CH_2SiMe_3)(THF)_5][BPh_4]_2$ (**2a**), were prepared according to published procedures.[6c] $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)][B(C_6H_4F\text{-}4)_4]$ (**1′c**) was prepared from the reaction of $[YR_3(THF)_2]$ with $[PhNMe_2H][B(C_6H_4F\text{-}4)_4]$ and 12-crown-4 following the published procedures.[6c] All solvents were dried over sodium benzophenone ketyl and distilled. THF-d_8 was dried over sodium benzophenone ketyl, and CD_2Cl_2 and pyridine-d_5 were dried over calcium hydride. Benzophenone (Fluka) and fluorenone (Acros Organics) were purified by sublimation. CO_2 was obtained by Westfalen (DIN 32526-C1) and used without any purification. The ^1H and ^{13}C NMR were recorded on a Bruker DRX 400 spectrometer, Varian Unity 500 spectrometer, or Varian Unity 200 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to the residual solvent resonances. The ^{19}F NMR was recorded on a Bruker DRX 400 spectrometer, and the chemical shifts were referenced externally to CCl_3F. Elemental analyses were performed by the Microanalytical Laboratory of the department. The results occasionally show incorrect values for carbon content, despite acceptable hydrogen and yttrium measurements. We ascribe this difficulty to the sensitivity of the material and to the possibility of solvent loss during sample manipulation.[5c] Metal analyses were performed by complexometric titrations.[21]

Bis{1,1-diphenyl(2-trimethylsilyl)ethoxy}tetra(tetrahydrofuran)yttrium Tetraphenylborate (3a). To a solution containing **1a** (30 mg, 0.035 mmol) in THF (0.6 mL) was added solid benzophenone (20 mg, 0.11 mmol) at room temperature, and the reaction mixture was stirred for 20 min. After an excess amount of pentane was added, the reaction mixture was cooled to −30 °C to give pure **3a** as a white precipitate, which was washed with pentane (2 × 0.8 mL) and dried *in vacuo*; yield: 38 mg (0.031 mmol, 89%). ^1H NMR (400 MHz, THF-d_8, 25 °C): δ −0.35 (s, 18H, $SiMe_3$), 1.71 (br s, β-THF), 1.95 (s, 4H, CH_2Si), 3.56 (br s, α-THF), 6.70 (t, $^3J_{HH} = 7.2$ Hz, 4H, 4-C*H* BPh_4), 6.84 (t, $^3J_{HH} = 7.4$ Hz, 8H, 3-C*H* BPh_4), 7.18−7.30 (m, 20H, 2-C*H* BPh_4, *m*+*p*-Ph, 20H), 7.47 (d, $^3J_{HH} = 7.1$ Hz, 8H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 0.14 ($SiMe_3$), 26.3 (β-THF), 40.2 (CH_2Si), 68.2 (α-THF) 83.5 (d, $^2J_{YC} = 5.4$ Hz, O*C*), 121.8 (4-*C*H BPh_4), 125.7 (3-*C*H BPh_4), 127.1 (*p*-Ph), 128.2 (*o*-Ph), 128.8 (*m*-Ph), 137.1 (2-*C*H BPh_4), 151.7 (*ipso*-Ph), 165.1 (q, $^1J_{BC} = 49.4$ Hz, 1-*C*H BPh_4). Anal. Calcd for $C_{78}H_{102}BO_7Si_2Y$: C, 71.65; H, 7.86; Y, 6.80. Found: C, 71.59; H, 7.17; Y, 6.85.

Bis(trimethylsilylmethylfluorenoxy)tetra(tetrahydrofuran)yttrium tetraphenylborate (4a). Complex **1a** (30 mg, 0.035 mmol) was dissolved in THF (0.6 mL) and treated with solid fluorenone (20 mg, 0.11 mmol) at room temperature. After the reaction mixture

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[17] (a) Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980. (b) Davies, S. G. *Organo-Transition Metal Chemistry: Application to Organic Synthesis*; Pergamon: Oxford, 1982. (c) *Organometallics in Synthesis*, 2nd ed.; Schlosser, M., Ed.; Wiley: New York, 2002. (d) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994. (e) Tsuji, J. *Transition Metal Reagents and Catalysts*; Wiley: New York, 2001.

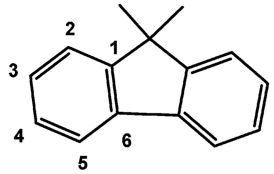
[18] (a) Imamoto, T. *Pure. Appl. Chem.* **1990**, *62*, 747. (b) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392. (c) Evans, W. J.; Feldman, J. D.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 4581.

[19] (a) Evans, W. J.; Ansari, M. A.; Feldman, J. D.; Doedens, R. J.; Ziller, J. W. *J. Organomet. Chem.* **1997**, *545-546*, 157. (b) Krasovskiy, A.; Kopp, F.; Knochel, P. *Angew. Chem., Int. Chem.* **2006**, *45*, 497.

[20] The disproportionation of a main group alkyl to give an ion pair has been studied in some detail: Fabicon, R. M.; Richey, H. G., Jr. *Organometallics* **2001**, *20*, 4018, and references therein.

[21] Arndt, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 775, and references therein.

was stirred for 20 min, excess pentane was added and the solution cooled to −30 °C, to afford a white precipitate. Washing the precipitate with excess pentane (× 2) and drying *in vacuo* afforded product **4a**; yield: 36 mg (0.029 mmol, 85%). Single crystals were obtained by cooling a solution of CH_2Cl_2/Et_2O (1:1 v/v) containing **4a**.



^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −0.69 (s, 18H, SiMe$_3$), 1.71 (br s, β-THF), 1.76* (C*H*$_2$Si), 3.57 (br s, α-THF), 6.76 (t, $^3J_{HH}$ = 7.2 Hz, 4H, 4-C*H* BPh$_4$), 6.83 (t, $^3J_{HH}$ = 7.3 Hz, 8H, 3-C*H* BPh$_4$), 7.19 (t, $^3J_{HH}$ = 7.3 Hz, 4H, C3-*H*), 7.24 (br, 8H, 2-C*H* BPh$_4$), 7.25* (C4-*H*), 7.34 (d, $^3J_{HH}$ = 7.3 Hz, 4H, C2-*H*), 7.64 (d, $^3J_{HH}$ = 7.6 Hz, 4H, C5-*H*). *The signals observed at δ 1.76 and 7.25 were assigned on the basis of an HSQC spectrum. ^{13}C NMR (100 MHz, 25 °C, THF-d_8): δ −1.07 (SiMe$_3$), 25.1 (β-THF), 34.6 (*C*H$_2$Si), 68.0 (α-THF), 85.4 (d, $^2J_{YC}$ = 3.7 Hz, O*C*), 120.3 (*C*5), 121.6 (4-*C*H BPh$_4$), 124.0 (*C*2), 125.4 (3-*C*H BPh$_4$), 128.0 (*C*3), 128.3 (*C*4), 136.8 (2-*C*H BPh$_4$), 139.4 (*C*1), 154.5 (*C*6), 164.9 (q, $^1J_{BC}$ = 39.4 Hz, 1-*C*H BPh$_4$). COSY (THF-d_8, 25 °C): 7.64−7.25, 7.34−7.19, 7.25−7.19, 6.83−6.76, 6.83−7.24. HSQC (THF-d_8, 25 °C): −0.69 to −1.07, 1.76−34.6, 6.76−121.6, 6.83−125.4, 7.19−128.0, 7.24−136.8, 7.25−128.3, 7.34−124.0, 7.64−120.3. Anal. Calcd for $C_{78}H_{98}BO_7Si_2Y$: C, 71.87; H, 7.58; Y, 6.82. Found: C, 70.15; H, 7.00; Y, 6.96. The elemental analysis indicated that five molecules of THF per yttrium are present, whereas the crystal structure determination by an X-ray diffraction study showed four THF molecules.

Bis{1,1-diphenyl(2-trimethylsilyl)ethoxy}(12-crown-4)(tetrahydrofuran)yttrium Tetraphenylborate (3a′). To a THF solution of **1′a** (50 mg, 0.048 mmol) was added solid benzophenone (40 mg, 0.22 mmol) at room temperature. After the reaction mixture was stirred for 2 h at room temperature, the solvent was removed *in vacuo*. The solid residue was washed with pentane (3 × 0.8 mL) and dried under reduced pressure to afford **3′a** as a white solid; yield: 41 mg (0.035 mmol, 73%). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −0.36 (s, 18H, SiMe$_3$), 1.70 (br s, β-THF) 1.84 (s, 4H, C*H*$_2$Si), 3.15 (m, 8H, 12-crown-4), 3.24 (m, 8H, 12-crown-4), 3.56 (br s, α-THF), 6.73 (t, $^3J_{HH}$ = 7.2 Hz, 4H, 4-CH BPh$_4$), 6.86 (t, $^3J_{HH}$ = 7.3 Hz, 8H, 3-CH BPh$_4$), 7.14 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 7.21 (t, $^3J_{HH}$ = 7.4 Hz, 8H, *m*-Ph), 7.25 (br, 8H, 2-CH BPh$_4$), 7.40 (d, $^3J_{HH}$ = 8.0 Hz, 8H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 0.37 (SiMe$_3$), 24.9 (β-THF), 39.2 (*C*H$_2$Si), 68.2 (12-crown-4), 68.3 (α-THF), 83.2 (d, $^2J_{YC}$ = 5.2 Hz, O*C*), 122.2 (4-*C*H BPh$_4$), 125.9 (3-*C*H BPh$_4$), 126.7 (*p*-Ph), 128.0 (*o*-Ph), 128.7 (*m*-Ph), 137.1 (2-*C*H BPh$_4$), 152.8 (*ipso*-Ph), 165.0 (q, $^1J_{BC}$ = 49.4 Hz, 1-*C*H BPh$_4$). HSQC (THF-d_8, 25 °C): −0.36−0.37, 1.70−24.9, 1.84−39.2, 3.15, 3.24−68.2, 3.56−68.3, 6.73−122.2, 6.86−125.9, 7.14−126.7, 7.21−128.7, 7.40−128.0, 7.25−137.1 Anal. Calcd for $C_{70}H_{86}BO_7SiY$: C, 70.34; H, 7.25; Y, 7.44. Found: C, 68.04; H, 7.60; Y, 7.17.

Bis(trimethylsilylmethylfluorenoxy)(12-crown-4)(tetrahydrofuran)yttrium Tetraphenylborate (4a′). The reaction was performed in the same manner as the reaction of **1′a** with benzophenone. From the reaction of **1′a** (50 mg, 0.048 mmol) with fluorenone (40 mg, 0.22 mmol), complex **4′a** was obtained; yield: 56 mg (0.047 mmol, 99%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): δ −0.68 (s, 18H, SiMe$_3$), 1.66 (s, 4H, C*H*$_2$Si), 1.81 (m, β-THF), 2.99 (m, 8H, 12-crown-4), 3.16 (m, 8H, 12-crown-4), 3.75 (m, α-THF), 6.88 (t, $^3J_{HH}$ = 7.2 Hz, 4H, 4-C*H* BPh$_4$), 7.01 (t, $^3J_{HH}$ = 7.4 Hz, 8H, 3-C*H* BPh$_4$), 7.20 (t, $^3J_{HH}$ = 7.0 Hz, 4H, C3-*H*), 7.29 (m, 16H, 2-C*H* BPh$_4$ + C2,C4-*H*), 7.61 (d, $^3J_{HH}$ = 7.5 Hz, 4H, C5-*H*). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): δ −1.46 (SiMe$_3$), 25.5 (β-THF), 33.2 (*C*H$_2$Si), 67.2 (12-crown-4), 69.7 (α-THF), 84.5 (br s, O*C*), 119.7 (*C*5), 122.0 (4-*C*H BPh$_4$), 123.5 (*C*4), 125.8 (3-*C*H BPh$_4$), 127.5 (*C*3), 127.8 (*C*2), 136.0 (2-*C*H BPh$_4$), 138.8 (*C*1), 152.2 (*C*6), 164.0 (q, $^1J_{BC}$ = 49.4 Hz, 1-*C*H BPh$_4$). HSQC (CD$_2$Cl$_2$, 25 °C): 6.88−122.0, 7.01−125.8, 7.20−127.5, 7.29−123.5, 127.8, 136.0, 7.61−119.7. Anal. Calcd for $C_{70}H_{82}BO_7SiY$: C, 70.58; H, 6.94; Y, 7.46. Found: C, 69.31; H, 6.79; Y, 7.75.

***cis*/*trans*-Bis{1,1-diphenyl(2-trimethylsilyl)ethoxy}tetra(tetrahydrofuran)yttrium Tetrakis(trimethylsilyimethyl)aluminate (*cis/trans*-3b).** To the THF solution of **1b** (55 mg, 0.059 mmol) was added benzophenone (30 mg, 0.16 mmol) at room temperature. After the solution was stirred for 10 min at room temperature, excess pentane was added to the solution. The solution was cooled to −30 °C, and a colorless slurry was obtained. After removal of the supernatant and washing with excess pentane twice, a mixture of *cis*-**3b** (90%) and *trans*-**3b** (10%) was obtained as an oil. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −1.24 (br, 8H, AlC*H*$_2$), −0.38 (s, 18H, SiMe$_3$), −0.13 (s, 36H, AlCH$_2$Si*Me*$_3$), 1.70 (br s, β-THF), 1.97 (s, 4H, C*H*$_2$Si), 3.55 (br s, α-THF), 7.19 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 7.26 (t, $^3J_{HH}$ = 7.3 Hz, 8H, *m*-Ph), 7.48 (d, $^3J_{HH}$ = 7.0 Hz, 8H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 1.99 (sextet, $^3J_{HH}$ = 61.2 Hz, Al*C*H$_2$), 0.15 (SiMe$_3$), 4.22 (AlCH$_2$Si*Me*$_3$), 26.3 (β-THF), 40.2 (*C*H$_2$Si), 68.2 (α-THF), 83.6 (d, $^2J_{YC}$ = 5.3 Hz, O*C*), 127.1 (*p*-Ph), 128.2 (*o*-Ph), 128.7 (*m*-Ph), 151.6 (*ipso*-Ph). *trans*-**3b**: ^{1}H NMR (400 MHz, THF-d_8, 25 °C) δ −1.24 (s, 8H, AlC*H*$_2$), −0.35 (s, 18H, SiMe$_3$), −0.13 (s, 36H, AlCH$_2$Si*Me*$_3$), 1.70 (br s, β-THF), 1.87 (s, 4H, C*H*$_2$Si), 3.55 (br s, α-THF), 7.02 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 7.09 (t, $^3J_{HH}$ = 7.3 Hz, 8H, *m*-Ph), 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 8H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 1.99 (sextet, $^3J_{HH}$ = 61.9 Hz, Al*C*H$_2$), 0.05 (SiMe$_3$), 4.22 (AlCH$_2$Si*Me*$_3$), 26.3 (β-THF), 38.9 (*C*H$_2$Si), 68.2 (α-THF), 82.2 (d, $^2J_{YC}$ = 5.2 Hz, O*C*), 125.8 (*p*-Ph), 127.7 (*o*-Ph), 128.5 (*m*-Ph), 154.3 (*ipso*-Ph). Since **3b** was obtained as an oil, elemental analysis was not performed.

Reaction of 1b with Benzophenone at −30 °C. A THF solution containing **1b** (30 mg, 0.032 mmol) and a THF solution containing benzophenone (15 mg, 0.082 mmol) were mixed together at −30 °C. The reaction mixture was gradually warmed to room temperature and stirred for 30 min. The reaction mixture was again cooled at −30 °C after excess pentane was added, and a colorless slurry was obtained at the bottom of the reaction vessel. After removal of the supernatant, washing with excess pentane (×2), and drying *in vacuo*, complex *cis*-**3b** was obtained as the sole product.

Bis(trimethylsilylmethylfluorenoxy)tetra(tetrahydrofuran)yttrium Tetrakis(trimethylsilylmethyl)aluminate (4b). The reaction of **1b** (35 mg, 0.038 mmol) with fluorenone (20 mg, 0.11 mmol) was carried out at room temperature in the same manner as the reaction of **1b** with benzophenone. A mixture of *cis*-**4b** (86%) and *trans*-**4b** (14%) was obtained as an oily slurry. *cis*-**4b**: ^{1}H NMR (400 MHz, THF-d_8, 25 °C) δ −1.24 (br, 8H, AlC*H*$_2$), −0.70 (s, 18H, SiMe$_3$), −0.12 (s, 36 H, AlCH$_2$Si*Me*$_3$), 1.70 (br s, β-THF), 1.79 (s, 4H, C*H*$_2$Si), 3.56 (br s, α-THF), 7.19 (t, $^3J_{HH}$ = 7.34 Hz, 4H, C3-*H*), 7.26 (t, $^3J_{HH}$ = 7.54 Hz, 4H, C4-*H*), 7.34 (d, $^3J_{HH}$ = 7.53 Hz, 4H, C2-*H*), 7.63 (d, $^3J_{HH}$ = 7.28 Hz, 4H, C5-*H*). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ −0.85 (SiMe$_3$), 1.99 (sextet, $^1J_{AlC}$ = 60.6 Hz, Al*C*H$_2$SiMe$_3$), 4.2 (AlCH$_2$Si*Me*$_3$), 26.4 (β-THF), 34.8 (*C*H$_2$Si), 67.4 (α-THF), 85.8 (d, $^2J_{YC}$ = 6.1 Hz, O*C*), 120.6 (*C*5), 124.3 (*C*2), 128.3 (*C*3), 128.6 (*C*4), 139.7 (*C*1), 154.7 (*C*6). COSY (THF-d_8, 25 °C): 7.19−7.34, 7.26, 7.26−7.63. HSQC (THF-d_8, 25 °C): 7.19−128.3, 7.26−128.6, 7.34−124.3, 7.63−120.6. *trans*-**4b**: ^{1}H NMR (400 MHz, THF-d_8, 25 °C) δ −1.24 (br, 8H, AlC*H*$_2$), −0.69 (s, 18H, Si*Me*$_3$), −0.12 (s, 36 H, AlCH$_2$Si*Me*$_3$), 1.70 (br s, β-THF), 1.78 (s, 4H, C*H*$_2$Si), 3.56 (br s, α-THF), 7.07 (t, $^3J_{HH}$ = 7.28 Hz, 4H, C3-*H*), 7.12 (t, $^3J_{HH}$ = 7.0 Hz, 4H, C4-*H*), 7.51 (d, $^3J_{HH}$ = 7.3 Hz, 4H, C2-*H*), 7.53 (d, $^3J_{HH}$ = 7.3 Hz, 4H, C5-*H*). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ −0.81 (SiMe$_3$), 1.99 (sextet,

$^1J_{\mathrm{AlC}}$ = 60.6 Hz, Al*C*H$_2$SiMe$_3$), 4.22 (AlCH$_2$Si*Me*$_3$), 26.4 (β-THF), 36.8 (*C*H$_2$Si), 68.2 (α-THF), 85.2 (d, $^2J_{\mathrm{YC}}$ = 5.0 Hz, O*C*), 119.7 (*C*5), 125.2 (*C*2), 127.2 (*C*3), 127.6 (*C*4), 139.6 (*C*1), 157.1 (*C*6). COSY (THF-d_8, 25 °C): 7.07−7.51, 7.12−7.53. HSQC (THF-d_8, 25 °C): 7.07−127.2, 7.12−127.6, 7.51−125.2, 7.53−119.7.

Bis{1,1-diphenyl(2-trimethylsilyl)ethoxy}(12-crown-4)(tetrahydrofuran)yttrium Tetrakis(trimethylsilylmethyl)aluminate (3b′). Complex **1′b** (30 mg, 0.034 mmol) was dissolved in THF, and benzophenone (20 mg, 0.11 mmol) was added at room temperature. The reaction mixture was stirred for 2 h at room temperature. To the reaction mixture was added excess pentane to terminate the reaction. After cooling the reaction mixture at −30 °C, a colorless slurry was obtained. The resulting slurry was washed with pentane twice and dried *in vacuo*. Complex **3′b** was obtained as an oily compound. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −1.24 (br, 8H, AlC*H*$_2$), −0.35 (s, 18H, SiMe$_3$), −0.11 (s, 36H, AlCH$_2$Si*Me*$_3$), 1.70 (br s, β-THF), 1.91 (s, 4H, C*H*$_2$Si), 3.56 (br s, α-THF), 3.66 (m, 16H, 12-crown-4), 7.16 (t, $^3J_{\mathrm{HH}}$ = 7.28 Hz, 4H, *p*-Ph), 7.23 (t, $^3J_{\mathrm{HH}}$ = 7.41 Hz, 8H, *m*-Ph), 7.46 (d, $^3J_{\mathrm{HH}}$ = 7.78 Hz, 8H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 0.37 (SiMe$_3$), 2.1 (sextet, $^1J_{\mathrm{AlC}}$ = 60.3 Hz, Al*C*H$_2$), 4.3 (AlCH$_2$Si*Me*$_3$), 26.4 (β-THF), 39.3 (*C*H$_2$Si), 68.2 (α-THF), 68.5 (12-crown-4), 83.3 (d, $^2J_{\mathrm{YC}}$ = 5.2 Hz, O*C*), 126.8 (*p*-Ph), 128.0 (*m*-Ph), 128.7 (*o*-Ph), 152.7 (*ipso*-Ph).

Tetrakis{(trimethylsilylacetato}hexa(tetrahydrofuran)yttrium Tetraphenylborate (6a). A glass ampule equipped with a Teflon valve was charged with **1a** (30 mg, 0.035 mmol) and THF (1 mL). After degassing of the ampule at −195 °C, carbon dioxide (1 bar) was transferred at room temperature. The reaction mixture was stirred at room temperature, and a white solid of complex **6a** was gradually formed over hours. After 9 h, volatiles were removed *in vacuo* and complex **6a** was obtained in good yield: 24 mg (0.014 mmol, 78%). ^{1}H NMR (400 MHz, pyridine-d_5, 25 °C): δ 0.13 (s, 36H, SiMe$_3$), 2.18 (s, 8H, C*H*$_2$Si), 1.60 (m, β-THF), 3.63 (m, α-THF), 7.13 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 8H, 4-C*H* BPh$_4$), 7.31 (t, 16H, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 3-C*H* BPh$_4$), 8.10 (br s, 16H, 2-C*H* BPh$_4$). ^{13}C NMR (100 MHz, pyridine-d_5, 25 °C): δ −0.95 (SiMe$_3$), 30.3 (*C*H$_2$Si), 25.8 (β-THF), 67.8 (α-THF), 122.3 (4-*C*H BPh$_4$), 126.2 (3-*C*H BPh$_4$), 137.2 (2-*C*H BPh$_4$), 165.1 (q, $^1J_{\mathrm{BC}}$ = 49.0 Hz, 1-*C*H BPh$_4$), 191.3 (s, *C*O). IR (KBr): ν = 3055, 3036, 2982, 2897, 1591, 1579, 1553 (ν_{sym} CO, RCO$_2$), 1480, 1431 (ν_{asym} CO, RCO$_2$), 1375, 1240, 1114, 1032, 1015, 855, 734, 705, 680, 638, 612 cm^{-1}. Anal. Calcd for $C_{92}H_{132}B_2O_{14}Si_4Y_2$: C, 62.29; H, 7.50; Y, 10.02. Found: C, 62.95; H, 7.75; Y, 10.09.

Monitoring the Reaction of 1a with Carbon Dioxide. The NMR sample tube was charged with **1a** (10 mg, 0.012 mmol) and THF-d_8. After the solution was evacuated at −195 °C, carbon dioxide (1 bar, 0.09 mmol) was transferred into the sample tube using a balloon. The sample tube was kept at room temperature and the reaction was followed by taking a ^{1}H NMR spectrum. The molar ratio of complexes was calculated on the relative integral intensity to TMS. After 10 min, complex **1a** was completely consumed and intermediates **A**, **B**, and **C** were observed. The relative integral intensities of methyl signals are 5%, 76%, and 19%, respectively. After 30 min, only **B** and **C** were observed with yields of 80% and 20%. At the end of the reaction, single crystals of **6a**, which were suitable for X-ray diffraction study, were obtained in the NMR sample tube. **A**: ^{1}H NMR (200 MHz, THF-d_8, 25 °C) δ −0.93 (d, $^2J_{\mathrm{YH}}$ = 3.2 Hz, C*H*$_2$Si), −0.13 (s, SiMe$_3$). **B**: ^{1}H NMR (400 MHz, THF-d_8, 25 °C) δ 0.12 (s, SiMe$_3$), 1.72 (br s, β-THF), 1.88 (s, C*H*$_2$Si), 3.56 (br s, α-THF), 6.69 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 4-C*H* BPh$_4$), 6.83 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 3-C*H* BPh$_4$), 7.25 (br, 2-C*H* BPh$_4$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ −1.01 (SiMe$_3$), 26.4 (β-THF), 30.2 (d, $^3J_{\mathrm{YC}}$ = 2.6 Hz, *C*H$_2$Si), 68.2 (α-THF), 121.8 (4-*C*H BPh$_4$), 125.7 (3-*C*H BPh$_4$), 137.2 (2-*C*H BPh$_4$), 165.2 (q, $^1J_{\mathrm{BC}}$ = 49.4 Hz, BPh$_4$), 192.0 (*C*O). **C**: ^{1}H NMR (400 MHz, THF-d_8, 25 °C) δ 0.13 (s, SiMe$_3$), 1.72 (br s, β-THF), 1.92 (s, C*H*$_2$Si), 3.56 (br s, α-THF), 6.69 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 4H, 4-C*H* BPh$_4$), 6.83 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 8H, 3-C*H* BPh$_4$), 7.25 (br, 8H, 2-C*H* BPh$_4$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ −0.72 (SiMe$_3$), 26.4 (β-THF), 30.5 (*C*H$_2$Si), 68.2 (α-THF), 121.8 (4-*C*H BPh$_4$), 125.7 (3-*C*H BPh$_4$), 137.2 (2-*C*H BPh$_4$), 165.2 (q, $^1J_{\mathrm{BC}}$ = 49.4 Hz, 1-*C*H BPh$_4$), 187.7 (*C*O).

Reaction of 1a with Carbon Dioxide under Reduced Pressure. A THF solution containing compound **1a** (60 mg, 0.069 mmol) was charged into the reaction vessel equipped with a Teflon valve. After the evacuation of the reaction mixture at −195 °C, carbon dioxide (1 bar) was transferred into the reaction vessel at room temperature. After the reaction mixture was stirred for 10 min at room temperature, the solvent was removed under reduced pressure. On starting the evacuation, a large amount of white crystalline **6a** formed at the bottom of the vessel. Complete removal of the solvent and washing the resulting crystals with THF (×2) afforded clean **6a**; yield: 43 mg (0.024 mmol, 70%).

(12-Crown-4)tetrakis{(trimethylsilylacetato}yttrium Tetra(*p*-fluorophenyl)borate (7′c). A THF solution (1 mL) of [Y(CH$_2$SiMe$_3$)$_2$(12-crown-4)(THF)][B(C$_6$H$_4$F-4)$_4$] (**1′c**) (80 mg, 0.089 mmol) was charged in an ampule. After the solution was degassed at −195 °C, carbon dioxide (1 bar) was transferred into the reaction vessel at room temperature. The reaction mixture was stirred at room temperature for 2 h. Removal of the solvent *in vacuo* afforded a slurry. Washing the residue with pentane (0.8 mL × 1) gave **7′c** as a white solid: yield 81 mg (0.044 mmol, 99%). From a CH$_2$Cl$_2$/Et$_2$O solution at −30 °C, a single crystal of **7′c** was obtained. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −0.09 (s, 36H, SiMe$_3$), obscured in residual THF (C*H*$_2$Si), 3.81 (br, 16H, 12-crown-4), 4.13 (br, 16H, 12-crown-4), 6.61 (t, $^3J_{\mathrm{HH}}$ = $^3J_{\mathrm{HF}}$ = 8.2 Hz, 16H, 3-C*H* B(C$_6$*H*$_4$F-4)$_4$), 7.14 (br m, 16H, 2-C*H* B(C$_6$*H*$_4$F-4)$_4$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ −1.48 (SiMe$_3$), 30.9 (*C*H$_2$Si), 71.5 (12-crown-4), 112.3 (dq, $^2J_{\mathrm{CF}}$ = 18.2 Hz, $^3J_{\mathrm{BC}}$ = 3.1 Hz, 3-CH B(*C*$_6$H$_4$F-4)$_4$), 137.6 (2-CH B(*C*$_6$H$_4$F-4)$_4$), 159.4 (q, $^1J_{\mathrm{BC}}$ = 49.7 Hz 1-CH B(*C*$_6$H$_4$F-4)$_4$,), 160.9 (d, $^1J_{\mathrm{CF}}$ = 237.6 Hz, B(*C*$_6$H$_4$F-4)$_4$), 180.9 (*C*O). ^{19}F NMR (376.4 MHz, THF-d_8, 25 °C): δ −125.01 (B(C$_6$H$_4$*F*-4)$_4$). THF coordinated at yttrium was obscured by THF-d_8 signals in the ^{13}C NMR spectrum. IR (KBr): ν = 3081,3017, 2957, 2888, 1615, 1581 (ν_{sym} CO, RCO$_2$), 1489, 1443 (ν_{asym} CO, RCO$_2$), 1381, 1298, 1285, 1251, 1211, 1157, 1131, 1114, 1072, 1018, 934, 867, 853, 814, 780, 707, 633, 552. cm^{-1}. Anal. Calcd for $C_{84}H_{108}B_2F_8O_{10}Si_4Y_2$: C, 54.91; H, 5.92; Y, 9.68. Found: C, 54.45; H, 5.66; Y, 8.82.

{1,1-Diphenyl(2-trimethylsilyl)ethoxy}penta(tetrahydrofuran)yttrium Bis(tetraphenylborate) (8a). Complex **2a** (70 mg, 0.060 mmol) was reacted with benzophenone (30 mg, 0.16 mmol) in THF (0.7 mL) at room temperature for 20 min. All volatiles were removed under reduced pressure, and the resulting solid was washed with pentane (2 × 0.8 mL) and dried *in vacuo* to afford **8a** as a yellow powder; yield: 75 mg (0.056 mmol, 92%). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ −0.38 (s, 9H, SiMe$_3$), obscured in residual THF (C*H*$_2$Si), 1.70 (br s, β-THF), 3.55 (br s, α-THF), 6.72 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 16H, 4-C*H* BPh$_4$), 6.86 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 16H, 3-C*H* BPh$_4$), 7.26 (br, 16H, 2-C*H* BPh$_4$), 7.45 (br, 4H, *p*-Ph), 7.55 (br, 2H, *m*-Ph), 7.74 (br, 4H, *o*-Ph). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ −0.07 (SiMe$_3$), 26.4 (β-THF), 40.0 (*C*H$_2$Si), 68.2 (α-THF), 85.6 (d, $^2J_{\mathrm{YC}}$ = 5.2 Hz, O*C*), 122.0 (4-*C*H BPh$_4$), 125.8 (3-*C*H BPh$_4$), 128.2 (*p*-Ph), 129.0 (*o*-Ph), 129.5 (*m*-Ph) 137.1 (2-*C*H BPh$_4$), 149.1 (*ipso*-Ph), 165.1 (q, $^1J_{\mathrm{BC}}$ = 54.8 Hz, 1-*C*H BPh$_4$). Anal. Calcd for $C_{85}H_{101}B_2O_6SiY$: C, 72.21; H, 7.50; Y, 6.55. Found: C, 74.28; H, 7.17; Y, 6.63.

{(Trimethylsilylmethyl)fluorenoxy}penta(tetrahydrofuran)yttrium Bis(tetraphenylborate) (9a). Complex **2a** (25 mg, 0.021 mmol) was dissolved in THF (0.6 mL) and treated with fluorenone (20 mg, 0.11 mmol) at room temperature. After the solution was stirred for 20 min, all volatiles were removed *in vacuo*. The residue was washed with pentane (2 × 0.8 mL) and dried *in vacuo* to give

Table 1. Experimental Data for Crystal Structure Determinations of Complexes 4a, 6a, and 7′c

	4a	**6a**	**7'c**
empirical formula	$C_{74}H_{90}BO_6Si_2Y$	$C_{92}H_{132}B_2O_{14}Si_4Y_2 \cdot 2(C_4H_8O)$	$C_{84}H_{108}B_2F_8O_{16}Si_4Y_2 \cdot CH_2Cl_2$
M_r	1231.36	1917.98	1922.43
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$	$C2/c$
a (Å)	21.6997(11)	12.4231(10)	29.708(2)
b (Å)	12.2426(6)	13.6526(11)	13.3582(11)
c (Å)	24.9387(13)	29.791(2)	23.4492(19)
α (deg)			
β (deg)	94.546(2)	93.001(2)	92.171(2)
γ (deg)			
V (Å^3)	6604.4(6)	5045.9(7)	9299.0(12)
Z	4	2	4
D_{calc} (g·cm^{-3})	1.238	1.262	1.373
T (K)	130	130	130
μ(Mo Kα) (mm^{-1})	0.971	1.253	1.428
F(000)	2616	2040	3992
cryst size	0.19 × 0.20 × 0.46	0.23 × 0.26 × 0.44	0.16 × 0.28 × 0.47
θ range (deg)	2.33−26.58	2.22−28.57	2.17−29.58
no. of reflns collected	79 201	33 647	66 746
no. of reflns obsd [$I > 2\sigma(I)$]	9484	7947	8431
no. of indep reflns (R_{int})	13 772 (0.1020)	12 334 (0.0605)	12 971(0.0819)
no. of data/restraints/params	13 772/0/753	12 334/0/554	12 971/0/529
absorp corr	empirical	empirical	empirical
goodness-of-fit on F^2	1.021	1.005	1.014
R_1, wR_2 [$I > 2\sigma(I)$]	0.0504, 0.1040	0.0548, 0.1242	0.0506, 0.1151
R_1, wR_2 (all data)	0.0891, 0.1179	0.1008, 0.1416	0.0973, 0.1341
largest diff peak and hole (e Å^{-3})	0.545 and −0.352	0.604 and −0.404	1.432 and −1.363

9a as a yellow powder; yield: 19 mg (0.014 mmol, 67%). ^{1}H NMR (400 MHz, pyridine-d_5, 25 °C): δ −0.50 (s, 9H, SiMe$_3$), 1.60 (m, β-THF), 2.40 (s, 2H, CH_2Si), 3.64 (m, α-THF), 7.09 (t, $^3J_{HH}$ = 7.2 Hz, 8H, 4-CH BPh$_4$), 7.26 (t, $^3J_{HH}$ = 7.4 Hz, 16H, 3-CH BPh$_4$), 7.30 (t, $^3J_{HH}$ = 7.5 Hz, 2H, C$_{12}H_8$), 7.47 (t, $^3J_{HH}$ = 7.5 Hz, 2H, C$_{12}H_8$), 7.69 (d, $^3J_{HH}$ = 7.5 Hz, 2H, C$_{12}H_8$), 7.88 (d, $^3J_{HH}$ = 7.5 Hz, 2H, C$_{12}H_8$), 8.05 (br, 16H, 2-C$_H$ BPh$_4$). ^{13}C NMR (100 MHz, pyridine-d_5, 25 °C): −0.71 (SiMe$_3$), 25.8 (β-THF), 31.2 (CH$_2$Si), 67.9 (α-THF), 88.1 (d, $^2J_{YC}$ = 6.1 Hz, OC), 121.1 (C_{12}H$_8$), 122.4 (4-CH BPh$_4$), 124.5 (C_{12}H$_8$), 126.2 (3-CH BPh$_4$), 128.4 (C_{12}H$_8$), 129.6 (C_{12}H$_8$), 137.2 (2-CH BPh$_4$), 139.6 (C_{12}H$_8$), 151.2 (C_{12}H$_8$), 165.1 (q, $^1J_{BC}$ = 49.4 Hz, 1-CH BPh$_4$). Anal. Calcd for $C_{85}H_{99}B_2O_6SiY$: C, 75.33; H, 7.36; Y, 6.56. Found: C, 75.49; H, 7.43; Y, 6.30.

(Trimethylsilylacetato)penta(tetrahydrofuran)yttrium Bis(tetraphenylborate) (10a). In an ampule, complex **2a** (75 mg, 0.064 mmol) was dissolved in THF (1.2 mL) and exposed to 1 bar of CO$_2$ for 22 h at room temperature. After all volatiles were removed under reduced pressure, the resulting solid was washed with pentane (2 × 0.8 mL). After drying *in vacuo*, the carboxylato complex was obtained as a white solid; yield: 60 mg (0.049 mmol, 77%). ^{1}H NMR (400 MHz, pyridine-d_5, 25 °C): δ 0.13 (s, 9H, SiMe$_3$), 2.19 (s, 2H, CH_2Si), 1.60 (m, 20H, β-THF), 3.64 (m, 20H, α-THF), 7.10 (t, $^3J_{HH}$ = 7.2 Hz, 8H, 4-CH BPh$_4$), 7.27 (t, $^3J_{HH}$ = 7.5 Hz, 16H, 3-CH BPh$_4$), 8.06 (br, 16H, 2-CH BPh$_4$). ^{13}C NMR (100 MHz, pyridine-d_5, 25 °C): δ −0.91 (SiMe$_3$), 25.8 (β-THF), 30.4 (CH$_2$Si), 67.9 (α-THF), 122.4 (4-CH BPh$_4$), 126.3 (3-CH BPh$_4$), 137.2 (2-CH BPh$_4$), 165.8 (q, $^1J_{BC}$ = 49.4 Hz, 1-CH BPh$_4$), 191.4 (CO). IR (KBr): ν = 3055, 3036, 2983, 2898, 1612, 1557 (ν_{asym} CO, RCO$_2$), 1480, 1441 (ν_{asym} CO, RCO$_2$), 1375, 1251, 1112, 1032, 1014, 856, 733, 704, 634, 612 cm^{-1}. Anal. Calcd for $C_{73}H_{91}B_2O_7SiY$: C, 71.92; H, 7.52; Y, 7.29. Found: C, 71.50; H, 7.40; Y, 7.35.

Crystal Structure Analysis of 4a, 6a, and 7′c. The diffraction data of **4a**, **6a**, and **7′c** were collected on a Bruker SMART Apex CCD area detector diffractometer.[22] The SADABS program was used for absorption correction.[22] The structure of **4a** was solved using the Patterson method, and the structures of **6a** and **7′c** were solved by direct methods using the SHELXS-97 program,[23] followed by successive cycles of full-matrix least-squares refinement on F^2. In the structure of **4a**, two carbons of a yttrium-coordinated tetrahydrofuran are disordered with 61.0% and 38.1% occupancy for each site. In the lattice of **6a**, two disordered tetrahydrofuran molecules are included with 56.4% and 43.6% occupancy, respectively. In the lattice of **7′c**, one disordered methylene chloride molecules was included with occupancy of 50:50. All non-hydrogen atoms except the disordered carbon and chloride atoms were refined anisotropically. Hydrogen atoms of methylene, methyl, and phenyl groups were included in the structure factor calculations in idealized positions. Least-squares refinement was carried out using SHELXL-97.[24] Relevant crystallographic data for **4a**, **6a**, and **7′c** are summarized in Table 1.

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Supporting Information Available: CIF files of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, and bond lengths and angles for **4a**, **6a**, and **7′c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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