Cyclopentadienyl Yttrium Complexes Bearing a Fluorinated Aryloxide Functionality

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The ligand $C_5H_5(CH_2CAr^F{}_2OH)$ (**3**) (Ar^F = 3,5-$C_6H_3(CF_3)_2$) was prepared in moderate yield (65%) by ring opening of the epoxide $Ar^F{}_2C(O)CH_2$ (**2**) with NaCp. Epoxide **2** was accessible in two steps from commercially available precursors. Reaction of the dilithium salt of **3** with YCl_3 afforded the *ate* complex $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}_2Y^-Li^+\{THF\}_2$ (**4a**). Exposure of **4a** to vacuum resulted in partial desolvation to $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3\text{-}(CF_3)_2)_2]\}_2Y^-Li^+\{THF\}$ (**4b**). The chloride complex $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}$-$YCl\{THF\}_2$ (**5**) could only be prepared by protonolysis of $\{Y[N(SiMe_3)_2]_2(THF)_2(\mu\text{-}Cl)\}_2$ with 1 equiv of **3**. Metathesis reactions of **5** with 1 equiv of $NaN(SiMe_3)_2$, NaCp, and $LiCH(SiMe_3)_2$ afforded $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{N(SiMe_3)_2\}\{THF\}_n$ (**6a**, n = 2; **6b**, n = 1), $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{\eta^5\text{-}C_5H_5\}\{THF\}_n$ (**8a**, n = 2; **8b**, n = 1), and $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{CH(SiMe_3)_2\}\{THF\}_2$ (**9**), respectively. Metathesis of **5** with 2 equiv of $Na[N(SiMe_3)_2]$ or $LiCH(SiMe_3)_2$ afforded the anionic "*ate*" complexes $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}\{N(SiMe_3)_2\}_2Y^-Na^+\{THF\}_2$ (**7**) and $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C\text{-}(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}\{CH(SiMe_3)_2\}_2Y^-Li^+\{THF\}_2$ (**10**), respectively. The phenoxide $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3\}\{THF\}_2$ (**11**) could not be prepared by salt metathesis but was isolated by protonolysis of $Y[O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3][CH(SiMe_3)_2]_2[THF]_2$ with 1 equiv of **3**. The crystal structures of *ate* complex **4a** and phenoxide **11** were established by X-ray crystallography.

Introduction

During the past decade there has been tremendous development of alternative ligands to cyclopentadienyl for early transition metal and lanthanide chemistry.[1] Additionally many groups have been exploring the use of *hybrid* ligands that contain both Cp and a pendant anionic group.[1c,2,3] The preparation of Cp-alkoxide and Cp-amide mixed ligands has been particularly important because these ligands form metal complexes with coordination spheres that are more open than the corresponding bis(cyclopentadienyl) systems. Group 4 complexes containing these ligands have been extensively studied and have been widely applied to olefin polymerization chemistry.[3] In contrast, these ligands have not been very widely investigated in yttrium or lanthanide chemistry.[2c,4,5]

Many of the Cp-alkoxide ligands developed for use in group 4 chemistry are not well suited to group 3 and

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lanthanide chemistry because they possess insufficient steric bulk to satisfy the larger coordination sphere of these metals. In particular, many of the existing ligands bear no substituents on the alkoxide carbon. In other work, we have been exploring the use of perfluoroaryl-substituted amides with group 4 and lanthanide metals.[6] Fluorinated aryl groups are attractive substituents because they decrease the electron donor capacity of the heteroatom to which they are attached and they generally increase the solubility of the ligands and metal complexes that contain them relative to their nonfluorinated analogues. For these reasons, we have developed a Cp-alkoxide that possesses 3,5-bis(trifluoromethyl)phenyl groups on the alkoxide carbon.[7] An added benefit of this ligand design is that both the Cp and the alkoxide functions have low pK_a's, leading to improved stability in the presence of moderately acidic substrates (e.g., primary amines or phosphines, alkynes).[8]

In this contribution we report the synthesis of a new Cp-alkoxide ligand bearing fluorinated aryl substituents at the alkoxide carbon. The synthesis of several yttrium complexes of this ligand and the X-ray structure of two such complexes are described. Synthesis of the yttrium complexes did not always proceed simply, so the problems associated with ligand incorporation by salt metathesis and protonolysis are discussed in some detail.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques. Tetrahydrofuran (THF), hexane, and toluene were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. 3,5-Bis(trifluoromethyl)bromobenzene was purchased commercially (Aldrich) and used as received. Yttrium tris(2,6-di-*tert*-butylphenoxide),[9] $\{Y[N(SiMe_3)_2]_2(THF)_2(\mu\text{-}Cl)\}_2$,[10] and $Na^+\{CH_2S(O)Me_2\}^-$ [11] were prepared according to literature procedures.

^1H (360 MHz), ^{13}C (90.55 MHz), ^{19}F (338.86 MHz), and ^{29}Si (71.54 MHz) were recorded on a Bruker AMX-360 MHz spectrometer. All deuterated solvents were dried over activated 4 Å molecular sieves, and spectra were recorded using 5 mm tubes fitted with a Teflon valve (Brunfeldt) at room temperature unless otherwise specified. ^1H and ^{13}C NMR spectra were referenced to residual solvent resonances. ^{19}F NMR spectra were referenced to external CCl_3F, and ^{29}Si NMR spectra were referenced to external TMS. Melting points were recorded using a Büchi melting point apparatus and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, B.C. Despite the use of co-oxidants such as V_2O_5 and PbO_2, the analytical data for most complexes were consistently 2−4% low in carbon. This may be due to metal carbide formation. Mass spectra were recorded on a Kratos Concept H spectrometer using chemical ionization (methane) or electron impact (70 eV) methods.

3,3′,5,5′-Tetrakis(trifluoromethyl)benzophenone (1). A solution of 3,5-bis(trifluoromethyl)bromobenzene (15.6 g, 53.2 mmol) in 150 mL of diethyl ether was prepared under argon in a 500 mL Schlenk flask and cooled to −78 °C. A 2.2 M solution of *n*-BuLi in hexanes (24.2 mL, 53.2 mmol) was added via syringe over 5 min with rapid stirring. Stirring was continued for 30 min before the cold solution was added via cannula to a 1 L flask containing a solution of diethyl carbonate (3.17 g, 26.6 mmol) in 100 mL of diethyl ether. After addition was complete, the reaction mixture was allowed to warm to 0 °C and was quenched with 200 mL of distilled water. The mixture was extracted with 3 × 200 mL of diethyl ether, and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and removal of the solvent from the filtrate yielded ketone **1** as a yellow solid. Recystallization from a mixture of toluene and hexane afforded pure **1** as colorless crystals. Yield: 9.08 g (75%). Mp: 136−137 °C. NMR ($CDCl_3$): ^1H δ 8.23 (s, 4H, *o*-aryl*H*), 8.19 (s, 2H, *p*-aryl*H*); $^{13}C\{^1H\}$ δ 205 (*C*O), 146.37 (*ipso*-aryl*C*), 132.53 (q, *m*-aryl*C*, $^2J_{CF} = 34$ Hz), 127.47 (*o*-aryl*C*), 122.90 (*p*-aryl*C*), 122.77 (q, *C*F_3, $^1J_{CF} = 272$ Hz); $^{19}F\{^1H\}$ δ −63.30 (CF_3).

1,1-Di(3,5-bis(trifluoromethyl)phenyl)ethylene Oxide (2). A solution of **1** (2.00 g, 4.41 mmol) in 50 mL of THF was placed in a 250 mL Schlenk flask and cooled to −10 °C under an argon atmosphere. A 0.6 M DMSO solution of $Na^+[CH_2SO(CH_3)_2]^-$ (7.5 mL, 4.5 mmol) was added to the flask rapidly by syringe. The reaction mixture was quenched with ice water 10 min after the addition. The resulting mixture was extracted with diethyl ether (3 × 100 mL), and the combined extracts were dried over anhydrous $MgSO_4$, filtered, and taken to dryness. The resulting white solid was redissolved in a minimum of ether and further dried over activated 4 Å molecular sieves. After removal of solvent, the solid was recrystallized from a hexane−toluene mixture to afford pure epoxide **2** as colorless crystals. Yield: 1.61 g (78%). Mp: 79−80 °C. NMR ($CDCl_3$): ^1H δ 7.90 (s, 2H, *p*-aryl*H*), 7.79 (s, 4H, *o*-aryl*H*), 3.36 (s, 2H, CH_2); $^{13}C\{^1H\}$ 140.4 (*ipso*-aryl*C*), 132.4 (q, *C*CF_3, $^2J_{CF} = 34$ Hz), 127.5 (*o*-aryl*C*), 122.9 (*p*-aryl*C*), 122.85 (q, *C*F_3, $^1J_{CF} = 273$ Hz), 77.2 (*C*O), 56.9 (*C*H_2O); $^{19}F\{^1H\}$ δ −63.21 (CF_3).

2-Cyclopentadienyl-1,1-di(3,5-bis(trifluoromethyl)phenyl)ethanol (3). A solution of epoxide **2** (2.90 g, 6.2 mmol) in THF (50 mL) was placed in a 500 mL Schlenk flask and cooled to −78 °C. To this stirred solution was added a solution of NaCp (0.81 g, 9.2 mmol) in THF (50 mL) by cannula. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 3 h. The reaction mixture was quenched with distilled water (200 mL), and the organic products were extracted with diethyl ether (3 × 200 mL). The combined ether extracts were dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to yield a dark red oil, which solidified on standing. The crude material was recrystallized from hexane−toluene to yield white crystalline **3** as a mixture of two diene isomers in approximately 2:1 ratio. The major isomer was identified as the 1-alkyl-substituted diene, while the minor isomer was the 2-alkyl-substituted compound; the 5-alkyl (substituted at the sp^3 carbon) isomer was not observed. Yield (based on epoxide): 2.15 g (65%). Mp: 104−105 °C. Major isomer **3a** (1-alkylCp): NMR (benzene-d_6) ^1H δ 7.82 (m, 4H, *o*-aryl*H*), 7.60 (m, 2H, *p*-aryl*H*), 6.00 (m, 1H, Cp-*H3*), 5.67 (dq, 1H, Cp-*H4*, $J = 5.3$, 1.5 Hz), 5.57 (m, 1H, Cp-*H2*), 2.58 (br s, 2H, CH_2CO), 2.44 (q, 2H, Cp-*H5*), 2.16 (s, 1H, CO*H*); $^{13}C\{^1H\}$ δ 148.40 (*ipso*-aryl*C*), 139.77 (Cp-*C1*), 134.82 (Cp-*C3*), 134.19 (Cp-*C4*), 133.04 (Cp-*C2*), 132.01 (q, aryl*C*CF_3, $^2J_{CF} = 33$ Hz), 126.47 (*o*-aryl*C*H), 123.67 (q, *C*F_3, $^1J_{CF} = 273$ Hz), 121.66 (*p*-aryl*C*), 76.02 (*C*OH), 41.85 (Cp-*C5*), 41.54 (*C*H_2CO); $^{19}F\{^1H\}$ δ −62.81 (CF_3). Minor isomer **3b** (2-alkylCp): NMR (benzene-d_6) ^1H δ 7.79 (m, 4H, *o*-aryl*H*), 7.58 (m, 2H, *p*-aryl*H*), 6.14 (dq, 1H, Cp-*H3*, $J = 5.4$, 1.7 Hz), 5.98 (m, 1H, Cp-*H4*), 5.82 (m, 1H, Cp-*H1*), 2.58 (br s, 2H, CH_2CO, overlaps major isomer), 2.17 (q, 2H, Cp-*H5*), 1.96 (s, 1H, CO*H*); $^{13}C\{^1H\}$ δ 148.52 (*ipso*-aryl*C*), 140.13 (Cp-*C2*), 134.15 (Cp-*C1*), 133.54 (Cp-*C4*), 132.12 (q, aryl*C*CF_3, $^2J_{CF} =$

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33 Hz), 131.92 (Cp-*C3*), 126.24 (*o*-aryl*C*H), 123.64 (q, *C*F$_3$, $^1J_{CF}$ = 273 Hz), 121.66 (*p*-aryl*C*, overlaps major isomer), 76.13 (*C*OH), 44.58 (Cp-*C5*), 42.64 (*C*H$_2$CO); ^{19}F{^{1}H} δ −62.92 (C*F*$_3$). MS (EI): 533 (M$^+$ − H, 20%), 455 (M$^+$ − CpCH$_2$, 70%), 241 (3,5-C$_6$H$_3$(CF$_3$)$_2$CO, 100%) amu.

{η^5:η^1-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}$_2$Y$^-$Li$^+${THF}$_n$ (4a, *n* = 2; 4b, *n* = 1): Method A. A 50 mL Erlenmeyer was charged with Y[O-2,6-*t*-Bu$_2$C$_6$H$_3$]$_3$[THF] (0.105 g, 0.14 mmol) in the glovebox, and 10 mL toluene was added. A solution of LiCH$_2$SiMe$_3$ (0.026 g, 0.28 mmol) in 5 mL of toluene was added to the colorless phenoxide solution at room temperature, and the mixture was stirred for 30 min. At the end of this period, a white precipitate of Li$^+$[O-2,6-*t*-Bu$_2$C$_6$H$_3$]$^-$ was evident. A 5 mL toluene solution of **3** (0.075 g, 0.14 mmol) was added dropwise, and the white suspension was stirred for a further 30 min. The reaction mixture was filtered through Celite on a fine sintered glass frit, and the solvent was removed from the filtrate to yield a white powder. Recrystallization from a minimum of toluene at −30 °C afforded colorless prisms of the bis(THF) adduct (**4a**). Exposure of this material to vacuum resulted in partial solvent loss to afford the mono(THF) adduct **4b**. Yield: 40% (based on yttrium).

Method B. A solution of **3** (0.255 g, 0.48 mmol) in 30 mL of THF was prepared under argon in a 250 mL Schlenk tube. The flask was cooled to −78 °C, and *n*-BuLi (0.48 mL of 2 M solution in hexane, 0.96 mmol) was added via syringe. The solution was stirred for 5 min and then transferred by cannula into a stirred suspension of YCl$_3$ (0.093 g, 0.48 mmol) in 50 mL of THF, also cooled to −78 °C. The reaction mixture was allowed to warm to room temperature, and stirring was continued for a further 3 h. At the end of this period, the solvent was removed under vacuum and 30 mL of diethyl ether was added. Precipitated LiCl was removed by Schlenk filtration through a Celite pad, and the solvent was removed to leave a white powder. Recrystallization from hot toluene afforded **4a**. Yield: 75%. Mp: 184−185 °C. NMR (benzene-*d*$_6$): ^{1}H δ 8.16 (br s, 4H, *o*-aryl*H*$_A$), 7.70 (br s, 4H, *o*-aryl*H*$_B$), 7.66 (br s, 2H, *p*-aryl*H*$_A$), 7.41 (br s, 2H, *p*-aryl*H*$_B$), 6.19 (dd, 2H, Cp-*H5*, *J* = 5.0, 2.5 Hz), 5.94 (dd, 2H, Cp-*H4*, *J* = 5.8, 3.1 Hz), 5.65 (dd, 2H, Cp-*H3*, *J* = 5.4, 2.6 Hz), 4.79 (dd, 2H, Cp-*H2*, *J* = 5.5, 2.3 Hz), 3.71 (d, 2H, C*H$_a$*H$_b$CO, $^2J_{HH}$ = 14.1 Hz), 2.81 (d, 2H, CH$_a$*H$_b$*CO, $^2J_{HH}$ = 14.1 Hz), 2.41 (m, 8H, α-THF *H*), 0.72 (m, 8H, *β*-THF *H*); ^{13}C{^{1}H} δ 155.27 (*ipso*-aryl*C*), 153.49 (*ipso*-aryl*C*), 132.42 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 128.91 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 127.32 (Cp-*C1* alkyl substituted), 126.44 (*o*-aryl*C*$_A$), 125.15 (*o*-aryl*C*$_B$), 123.85 (q, *C*F$_3$, $^1J_{CF}$ = 273 Hz), 123.46 (q, *C*F$_3$, $^1J_{CF}$ = 273 Hz), 121.61 (*p*-aryl*C*$_A$), 120.85 (*p*-aryl*C*$_B$), 115.05 (Cp-*C4*), 113.09 (Cp-*C3*), 108.03 (Cp-*C2*), 107.19 (Cp-*C5*), 88.45 (CH$_2$*C*O), 67.68 (α-THF *C*), 42.19 (*C*H$_2$-CO), 24.43 (*β*-THF *C*); ^{19}F{^{1}H} δ −62.49 (*C*F$_3$), −62.96 (*C*F$_3$). Exposure of **4a** to vacuum for several hours afforded the *mono*(THF) adduct **4b**. NMR (benzene-*d*$_6$): ^{1}H δ 8.15 (br s, 4H, *o*-aryl*H*$_A$), 7.69 (br s, 4H, *o*-aryl*H*$_B$), 7.68 (br s, 2H, *p*-aryl*H*$_A$), 7.43 (br s, 2H, *p*-aryl*H*$_B$), 6.18 (dd, 2H, Cp-*H5*, *J* = 5.0, 2.5 Hz), 5.95 (dd, 2H, Cp-*H4*, *J* = 5.8, 3.1 Hz), 5.63 (dd, 2H, Cp-*H3*, *J* = 5.4, 2.6 Hz), 4.80 (dd, 2H, Cp-*H2*, *J* = 5.5, 2.3 Hz), 3.70 (d, 2H, C*H$_a$*H$_b$CO, $^2J_{HH}$ = 14.1 Hz), 2.81 (d, 2H, CH$_a$*H$_b$*CO, $^2J_{HH}$ = 14.1 Hz), 2.36 (m, 4H, α-THF *H*), 0.70 (m, 4H, *β*-THF *H*); ^{13}C{^{1}H} δ 155.26 (*ipso*-aryl*C*), 153.28 (*ipso*-aryl*C*), 132.44 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 132.39 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 126.47 (Cp-*C1* alkyl substituted, overlaps *o*-aryl resonance), 126.46 (*o*-aryl*C*$_A$), 125.11 (*o*-aryl*C*$_B$), 121.64 (*p*-aryl*C*$_A$), 120.88 (*p*-aryl*C*$_B$), 115.04 (Cp-*C4*), 113.05 (Cp-*C3*), 108.02 (Cp-*C2*), 107.20 (Cp-*C5*), 88.44 (CH$_2$*C*O), 67.64 (α-THF *C*), 42.32 (*C*H$_2$CO), 24.36 (*β*-THF *C*), the *C*F$_3$ resonances were not located; ^{19}F{^{1}H} δ −62.50 (*C*F$_3$), −63.00 (*C*F$_3$). Anal. Calcd for C$_{57}$H$_{40}$F$_{24}$LiO$_3$Y (**4b** as a mono(toluene) solvate): C, 51.68; H, 3.04. Found: C, 51.82; H, 3.38.

{η^5:η^1-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}YCl{THF}$_2$ (5). A 50 mL Erlenmeyer flask was charged with {Y[N(SiMe$_3$)$_2$]$_2$-(THF)$_2$(μ-Cl)}$_2$ (0.181 g, 0.155 mmol) and 10 mL of toluene in the glovebox. A solution of **3** (0.165 g, 0.31 mmol) in 20 mL was added dropwise to the rapidly stirred solution. The solution slowly became turbid as **5** precipitated from solution. After 2 h, the solvent was removed under vacuum and the white solid was recrystallized from hot hexane to afford pure **5** as a white microcrystalline powder. Yield: 90%. Mp: 196−197 °C. NMR (THF-*d*$_8$): ^{1}H δ 8.34 (s, 4H, *o*-aryl*H*), 7.68 (s, 2H, *p*-aryl*H*), 5.77 (br s, 2H, Cp*H*), 5.40 (br s, 2H, Cp*H*), 3.65 (s, 2H, C*H$_2$*CO), 3.58 (m, 8H, α-THF *H*), 1.73 (m, 8H, *β*-THF *H*); ^{13}C{^{1}H} δ 158.06 (*ipso*-aryl*C*), 131.44 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 127.53 (*o*-aryl*C*), 126.73 (Cp-*C1*), 124.94 (q, *C*F$_3$, $^1J_{CF}$ = 272 Hz), 120.19 (*p*-aryl*C*), 111.84 (Cp*C*), 110.18 (Cp*C*), 91.07 (*C*OY), 68.21 (α-THF *C*), 44.59 (*C*H$_2$CO), 26.37 (*β*-THF *C*); ^{19}F-{^{1}H} δ −63.28 (*C*F$_3$). Anal. Calcd for C$_{31}$H$_{28}$ClF$_{12}$O$_3$Y: C, 46.49; H, 3.52. Found: C, 45.98; H, 3.36.

{η^5:η^1-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}Y{N(SiMe$_3$)$_2$}-{THF}$_n$ (6a, *n* = 2; 6b, *n* = 1). An Erlenmeyer flask was charged with **5** (0.131 g, 0.17 mmol) and 20 mL of toluene in the glovebox. To the rapidly stirred white suspension was added a 10 mL toluene solution of NaN(SiMe$_3$)$_2$ (0.032 g, 0.17 mmol). The suspension was stirred for 1 h at room temperature and filtered through Celite on a glass frit, and the solvent was removed from the filtrate to give a white powder. Recrystallization of this product from a toluene−hexane mixture gave pure **6a** as small white crystals. Yield: 0.092 g (58%). Mp: 148−149 °C. NMR (benzene-*d*$_6$): ^{1}H δ 8.14 (*o*-aryl*H*), 7.59 (*p*-aryl*H*), 5.99 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.9 Hz), 5.80 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.9 Hz), 3.39 (m, 10H, α-THF *H* and C*H$_2$*CO), 1.18 (m, 8H, *β*-THF *H*), 0.25 (s, 18H, Si*Me$_3$*); ^{13}C{^{1}H} δ 155.37 (*ipso*-aryl*C*), 131.69 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 130.80 (Cp-*C1*), 126.16 (*o*-aryl*C*), 124.01 (q, *C*F$_3$, $^1J_{CF}$ = 273 Hz), 120.41 (*p*-aryl*C*), 113.96 (Cp*C*), 110.17 (Cp*C*), 92.90 (*C*OY), 70.69 (α-THF *C*), 42.15 (*C*H$_2$CO), 24.99 (*β*-THF *C*), 4.87 (Si*Me$_3$*); ^{19}F{^{1}H} δ −62.49 (C*F$_3$*); ^{29}Si{^{1}H} δ −10.20 (*Si*Me$_3$).

Exposure of **6a** to vacuum for extended periods of time resulted in the loss of one THF molecule to give **6b**. The NMR data for **6b** were essentially identical to those for **6a** with the exception that the THF resonances integrated to only 4H each rather than 8H. Anal. Calcd for C$_{33}$H$_{38}$F$_{12}$NO$_2$Si$_2$Y: C, 46.42; H, 4.49; N, 1.64. Found: C, 46.41; H, 4.66; N, 1.32.

{η^5:η^1-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}{N(SiMe$_3$)$_2$}$_2$Y$^-$-Na$^+${THF}$_2$ (7). An Erlenmeyer flask was charged with **6** (0.100 g, 0.108 mmol) and 10 mL of toluene in the glovebox. To the rapidly stirred clear solution was added a 10 mL toluene solution of NaN(SiMe$_3$)$_2$ (0.018 g, 0.108 mmol). The suspension was stirred 4 h at room temperature and filtered through Celite on a glass frit, and the solvent was removed from the filtrate to give a white powder. Recrystallization of this product from a toluene−hexane mixture gave pure **7** as small colorless needles. Yield: 0.070 g (60%). NMR (benzene-*d*$_6$): ^{1}H δ 8.36 (*o*-aryl*H*), 7.65 (*p*-aryl*H*), 5.97 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.9 Hz), 5.84 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.9 Hz), 3.52 (m, 2H, C*H$_2$*CO), 3.39 (m, 10H, α-THF *H*), 1.18 (m, 8H, *β*-THF *H*), 0.44 (s, 36H, Si*Me$_3$*); ^{13}C{^{1}H} δ 156.17 (*ipso*-aryl*C*), 131.87 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 129.25 (Cp-*C1*), 126.59 (*o*-aryl*C*), 123.77 (q, *C*F$_3$, $^1J_{CF}$ = 273 Hz), 120.64 (*p*-aryl*C*), 110.58 (Cp*C*), 108.25 (Cp*C*), 90.05 (*C*OY), 68.87 (α-THF *C*), 42.41 (*C*H$_2$CO), 25.06 (*β*-THF *C*), 6.15 (Si*Me$_3$*); ^{19}F{^{1}H} δ −62.32 (C*F$_3$*); ^{29}Si{^{1}H} δ −11.36 (*Si*Me$_3$).

{η^5:η^1-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}Y{η^5-C$_5$H$_5$}-{THF}$_n$ (8a, *n* = 2; 8b, *n* = 1). The cyclopentadienyl derivative **8** was prepared from **5** and NaCp using the procedure outlined for **6**. The crude product was isolated as a waxy yellow solid; recrystallization from hexane at −30 °C initially afforded the bis(THF) adduct **8a** as colorless plates. However on removal of the mother liquor, these crystals rapidly lost solvent to form the mono(THF) adduct **8b** as a white powder. Yield: 65%. Mp: 168−170 °C. NMR (benzene-*d*$_6$): ^{1}H δ 8.37 (s, 2H, *o*-aryl*H*), 8.11 (s, 2H, *o*-aryl*H*), 7.68 (s, 1H, *p*-aryl*H*), 7.60 (s, 1H, *p*-aryl*H*), 6.10 (s, 5H, C$_5$*H$_5$*), 6.07 (br s, 1H, Cp*H*), 5.40 (br s, 2H, Cp*H*), 5.29 (br s, 1H, Cp*H*), 3.48 (d, 1H, C*H$_a$*H$_b$CO, $^2J_{HH}$ = 13.6 Hz), 3.05 (m, 4H, α-THF *H*), 2.95 (d, 1H, CH$_a$*H$_b$*CO,

$^2J_{HH}$ = 13.6 Hz), 1.02 (m, 4H, *β*-THF *H*); $^{13}C\{^1H\}$ *δ* 156.0 (*ipso*-aryl*C*), 155.5 (*ipso*-aryl*C*), 131.61 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 128.65 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 128.49 (Cp-*C1*), 127.60 (q, *C*F$_3$, $^1J_{CF}$ = 275 Hz), 125.96 (*o*-aryl*C*), 126.63 (*o*-aryl*C*), 124.15 (q, *C*F$_3$, $^1J_{CF}$ = 274 Hz), 120.40 (*p*-aryl*C*), 120.20 (*p*-aryl*C*), 113.4 (Cp*C*), 110.88 (*C*$_5$H$_5$), 110.2 (Cp*C*), 108.4 (Cp*C*), 105.9 (Cp*C*), 92.60 (d, *C*OY, $^2J_{YC}$ = 2.3 Hz), 71.25 (α-THF *C*), 43.77 (*C*H$_2$-CO), 24.99 (*β*-THF *C*); $^{19}F\{^1H\}$ *δ* −62.53, −62.61 (C*F*$_3$). Anal. Calcd for $C_{32}H_{25}F_{12}O_2Y$: C, 50.68; H, 3.32. Found: C, 50.45; H, 3.31.

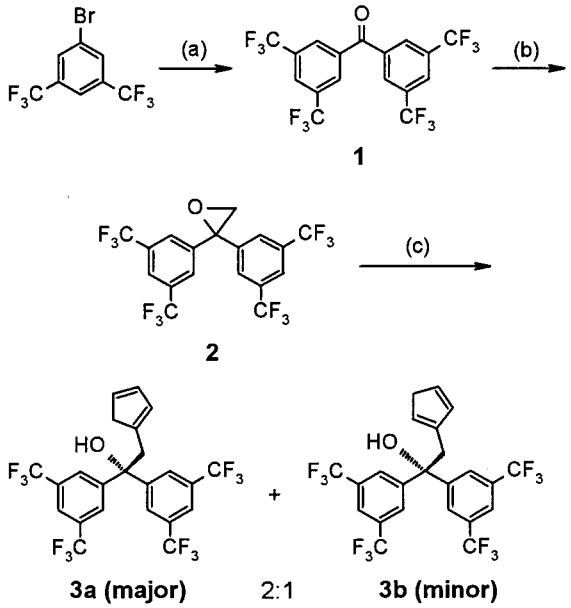
{*η*^{5}:*η*^{1}-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}Y{CH(SiMe$_3$)$_2$}-{THF}$_2$ (9). Crude **9** was isolated as a yellow oil using a procedure analogous to **6** starting from **5** and LiCH(SiMe$_3$)$_2$ (1 equiv). Repeated recrystallization from hexane at −30 °C produced **9** as an impure solid. Yield: 20%. NMR (benzene-d_6): ^1H *δ* 8.13 (s, 4H, *o*-aryl*H*), 7.67 (s, 2H, *p*-aryl*H*), 6.31 (br s, 2H, Cp*H*), 6.11 (br s, 2H, Cp*H*), 3.38 (s, 2H, C*H*$_2$CO), 2.93 (m, 8H, α-THF *H*), 1.07 (m, 8H, *β*-THF *H*), 0.28 (s, 18H, Si*Me*$_3$), −1.08 (d, 1H, C*H*(SiMe$_3$)$_2$, $^2J_{YH}$ = 2.4 Hz); $^{19}F\{^1H\}$ *δ* −62.33; $^{29}Si\{^1H\}$ *δ* −7.10 ppm.

{*η*^{5}:*η*^{1}-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]} {CH(SiMe$_3$)$_2$}$_2$-Y$^-$Li$^+${THF}$_2$ (10). Crude **10** was isolated as a yellow oily solid using a procedure analogous to **6** starting from **5** and LiCH-(SiMe$_3$)$_2$ (2 equiv), but instead using hexane as solvent. Repeated recrystallization from hexane at −30 °C produced white crystals of **10** containing trace amounts of **9**. Yield: 60%. Mp: 97−98 °C. NMR (benzene-d_6): ^1H *δ* 8.32 (s, 4H, *o*-aryl*H*), 7.65 (s, 2H, *p*-aryl*H*), 6.32 (br s, 2H, Cp*H*), 6.10 (br s, 2H, Cp*H*), 3.52 (s, 2H, C*H*$_2$CO), 2.98 (m, 8H, α-THF *H*), 1.07 (m, 8H, *β*-THF *H*), 0.49 (s, 18H, Si*Me*$_{3a}$), 0.36 (s, 18H, Si*Me*$_{3b}$), −1.22 (br d, 2H, C*H*$_{a,b}$(SiMe$_3$)$_2$); $^{13}C\{^1H\}$ *δ* 154.73 (*ipso*-aryl*C*), 132.06 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 126.59 (*o*-aryl*C*), 123.99 (q, *C*F$_3$, $^1J_{CF}$ = 272 Hz), 120.95 (*p*-aryl*C*), 111.75 (Cp*C*), 108.19 (Cp*C*), 90.50 (*C*OY), 68.43 (α-THF *C*), 40.33 (*C*H$_2$CO), 34.62 (d, *C*H(SiMe$_3$)$_2$, $^1J_{C-Y}$ = 35 Hz), 25.07 (*β*-THF *C*), 5.99 (Si*Me*$_{3a}$), 5.69 (Si*Me*$_{3b}$); $^{19}F\{^1H\}$ *δ* −62.42; $^{29}Si\{^1H\}$ *δ* −6.56, −7.05. Anal. Calcd for $C_{37}H_{48}F_{12}OSi_4YLi$: C, 47.01; H, 5.12. Found: C, 46.46; H, 5.20.

{*η*^{5}:*η*^{1}-C$_5$H$_4$[CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}Y{O-2,6-*t*-Bu$_2$-C$_6$H$_3$}{THF}$_2$ (11). A solution of Y[O-2,6-*t*-Bu$_2$C$_6$H$_3$][CH-(SiMe$_3$)$_2$]$_2$[THF]$_2$[12] (0.27 g, 0.36 mmol) in 10 mL of toluene was prepared in an Erlenmeyer flask in the glovebox. To this solution, solid **3** (0.21 g, 0.36 mmol) was added and the clear solution was stirred for 10 min. Removal of the solvent under vacuum and recrystallization of the crude white powder from hexanes at −30 °C afforded **11** as colorless crystals. Yield: 0.248 g (71%). Mp: 146−147 °C. NMR (benzene-d_6): ^1H *δ* 8.25 (s, 4H, *o*-aryl*H*), 7.59 (s, 2H, *p*-aryl*H*), 7.33 (d, 2H, *m*-phenoxide *H*, $^3J_{HH}$ = 8.1 Hz), 6.81 (t, 1H, *p*-phenoxide *H*, $^3J_{HH}$ = 8.1 Hz), 6.06 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.6 Hz), 5.84 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.6 Hz), 3.54 (s, 2H, C*H*$_2$CO), 3.32 (m, 8H, α-THF *H*), 1.54 (2, 18H, C*Me*$_3$), 1.07 (m, 8H, *β*-THF *H*); $^{13}C\{^1H\}$ *δ* 162.16 (d, *ipso*-phenoxide *C*, $^2J_{YC}$ = 4.5 Hz), 156.27 (*ipso*-aryl*C*), 137.25 (*o*-phenoxide *C*), 131.73 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 131.08 (Cp-*C1*), 126.24 (*m*-phenoxide *C*), 125.84 (*o*-aryl*C*), 124.04 (q, *C*F$_3$, $^1J_{CF}$ = 271 Hz), 120.31 (*p*-aryl*C*), 116.67 (*p*-phenoxide *C*), 113.34 (Cp*C*), 109.89 (Cp*C*), 92.29 (*C*OY), 71.14 (α-THF *C*), 42.00 (*C*H$_2$CO), 35.20 (*C*Me$_3$), 31.57 (C*Me*$_3$), 24.98 (*β*-THF *C*); $^{19}F\{^1H\}$ *δ* −62.38 (*CF*$_3$). Anal. Calcd for $C_{45}H_{49}F_{12}O_4Y$: C, 55.68; H, 5.09. Found: C, 54.93; H, 4.80.

X-ray Crystallography. Crystals of **4a** and **11** were isolated from toluene solution and a toluene−hexane mixture, respectively. The crystals were placed in mineral oil under an atmosphere of argon and sealed in a glass capillary. Data were collected on a Siemens Smart 1000 CCD diffractomter equipped with graphite-monochromated Mo *K*α radiation (*λ* = 0.71073 Å) at 293 K. Structure solutions were carried out using SHELXS-97[13] and refinement was done on F^2. An absorption correction was applied in both cases (abs range: **4a** 0.60−1.00; **11** 0.68−1.00). The final Fourier difference maps showed maximum and minimum peaks of −0.38/+0.60 (**4a**) and −0.44/+0.67 (**11**) e Å^{-3}. Thermal ellipsoid plots were drawn with ORTEP3.[14]

Scheme 1 [a]



[a] Reaction conditions: (a) (i) *n*-BuLi (1 equiv), −78 °C, (ii) (EtO)$_2$CO (0.5 equiv), −78 °C, (iii) H$_2$O quench; (b) (i) Na$^+$[CH$_2$SO(CH$_3$)$_2$]$^-$ (1 equiv), −10 °C, (ii) H$_2$O; (c) (i) NaCp (1.5 equiv), −78 °C, (ii) H$_2$O quench.

Results

The synthesis of the ligand is outlined in Scheme 1. The formation of ketone **1** and epoxide **2** proceeded in good yield. However, ring opening of epoxide **2** with NaCp did not proceed in very high yield, even when Lewis acids such as AlCl$_3$, BF$_3$·Et$_2$O, or B(C$_6$F$_5$)$_3$ were added. Nevertheless the desired alcohol **3** could be obtained, in marked contrast to the reaction of NaCp with the nonfluorinated diphenyl analogue of **2**. In the latter case ring opening does not occur even under forcing conditions, demonstrating that the trifluoromethyl substituents activate the epoxide toward nucleophilic attack, as might be expected. Although **3** is thermally stable to at least 100 °C for days in pure form, it decomposed to ketone **2** when the reaction mixture was heated in attempts to increase the yield. Similarly, we have found that **3** decomposes to ketone **2** over a period of days when heated at 70 °C in the presence of yttrium complexes.

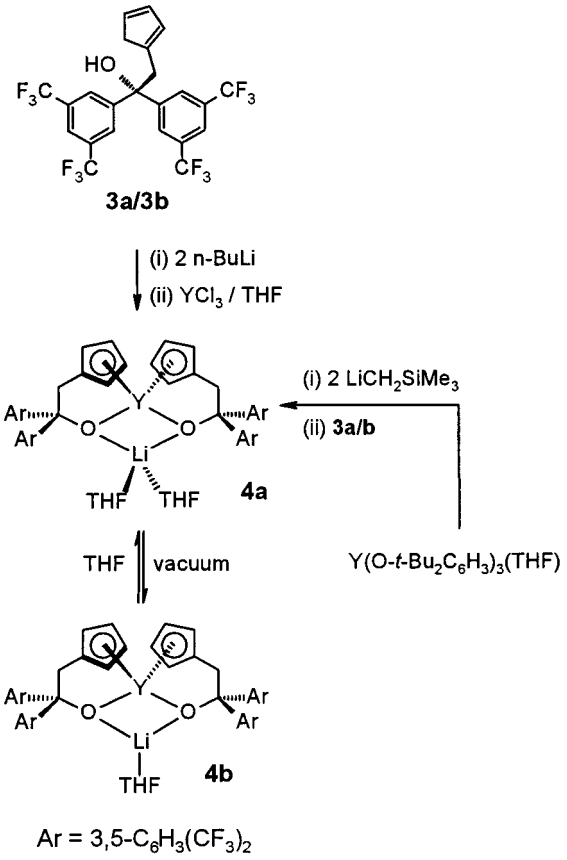
Reaction of the dianion of **3**, formed in situ, with YCl$_3$ in THF did not lead to the expected yttrium chloride complex (Scheme 2). Instead, the bis(ligand) *ate* complex **4** was obtained as the only isolable yttrium species. Initially, this complex was isolated from the reaction mixture as the crystalline bis(THF) adduct **4a**, and a crystal structure was obtained, confirming this (vide

(12) This compound was prepared by reaction of 2 equiv of LiCH-(SiMe$_3$)$_2$ with Y(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$ in hexane. Lee, L.; Berg, D. J.; Gendron, R. A. L. Unpublished results.

(13) Sheldrick, G. *SHELX-97: Programs for Crystal Structure Determination*; University of Göttingen: Germany, 1997.

(14) Farrugia, L. J. ORTEP3 for Windows. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Scheme 2



infra).[15] Complex **4a** loses one THF molecule, slowly on standing and rapidly under vacuum, to give the mono(THF) adduct **4b** as a white powder. The NMR data for **4b** are consistent with C_2 molecular symmetry whereby the two ligands are related by symmetry to one another, but all protons of the backbone and Cp unit within the same ligand are inequivalent.

It is possible to isolate the chloride complex **5** in good yield by protonolysis of the silylamido groups in dimeric $\{Y[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)_2\}_2$ using **3** (Scheme 3).[16] In this case, the complex appears to bind THF tightly as recrystallization from hot toluene and exposure to vacuum does not result in solvent loss. It is necessary to use THF-d_8 to dissolve **5** sufficiently to obtain NMR data. The NMR spectra in this solvent are consistent with mirror plane symmetry for the coordinated ligand. Distinct C_4H_8O resonances are observable, well resolved from the C_4HD_7O residual solvent resonances. While this could be taken as evidence that coordinated THF does not exchange with bulk solvent, it seems more likely that rapid exchange is occurring and that *H*/*D* isotopic effects are responsible for the small chemical shift difference observed.[17]

Substitution of the remaining chloride in **5** can be accomplished cleanly in some, but not all, cases. Reaction of **5** with $NaN[(SiMe_3)_2]_2$ affords the silylamido complex **6a** in moderate yield (Scheme 3). The NMR spectra of this complex are again consistent with mirror plane symmetry for the ligand. Prolonged exposure of **6a** to vacuum results in loss of one THF ligand and formation of the less soluble mono(thf) adduct **6b**. Excess coordinating solvents such as THF must be avoided in order to prevent redistribution to the *ate* complex **4**. Attempts to prepare **6a** by the direct protonolysis of $Y[N(SiMe_3)_2]_3$ with **3** fail to give any of the desired product. Presumably this is due to the high degree of bulk in the tris(amido) yttrium precursor since the less crowded dimer $\{Y[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)_2\}_2$ reacts smoothly with **3** under the same conditions to give **5**. Marks et al. have reported that it is necessary to alternately reflux and then remove the toluene solvent during the reaction of $Ln[N(SiMe_3)_2]_3$ with $C_5Me_4H(SiMe_2NH\text{-}t\text{-}Bu)$ (Ln = Nd, Sm, Lu) in order to deprotonate the Cp ring and prevent competitive protonolysis by $HN(SiMe_3)_2$.[18] The latter reaction does not appear to be of major concern here, judging by the results with the bis(amido) dimer, and we cannot heat the reaction mixture without significant ligand redistribution to give **4a**. It is also interesting that the addition of another equivalent of $NaN[(SiMe_3)_2]_2$ forms the anionic species **7** in moderate yield, showing that the metal coordination sphere in **6a** and **6b** is still quite open.

Reaction of **5** with NaCp proceeds smoothly in toluene to give the Cp derivative as the bis(THF) adduct **8a** (Scheme 3). This complex readily loses THF to form the mono(THF) adduct **8b** on standing. The ^1H NMR spectrum of **8b** in benzene reveals a low-symmetry environment where all ligand C_5H_4 and backbone protons are inequivalent, indicating that the remaining THF is not labile on the NMR time scale. Interestingly, $^{89}Y-^{13}C$ coupling ($^2J_{YC}$ = 2.3 Hz) is resolved for the alkoxide carbon of the ligand in this case.

Attempts to prepare alkyl complexes by the metathesis reaction of **5** with lithium alkyls rapidly produced *ate* complex **4** via redistribution when smaller alkyls (Me, Et, Ph, CH_2Ph) were employed; the fate of the alkyl-containing product was not established. Reaction with $LiCH_2SiMe_3$ also led to redistribution, but the reaction was noticeably slower in this case. Eventually we were able to isolate the neutral alkyl complex **9** using the lithium salt of the bulky alkyl $^-CH(SiMe_3)_2$, albeit in low yield and moderate purity. Complex **9** was invariably contaminated with the bis(ligand) redistribution product **4a** and what proved to be the bis(alkyl) *ate* complex **10**. Complex **10** was isolated as the major product of **5** with 2 equiv of $LiCH(SiMe_3)_2$ provided the reaction was performed in noncoordinating solvents and the reaction time was kept short (<30 min).

In an effort to avoid some of the problems caused by LiCl elimination, we attempted to prepare a phenoxide complex for use in metathesis reactions.[19] However, the direct reaction between the dilithium salt of **3** and Y[O-

(15) Similarly, reaction of $Li_2[C_5Me_4SiMe_2NCH_2CH_2X]$ (X = OMe or NMe_2) with $LnCl_3$ (Ln = Y, Lu) has been reported to afford the *ate* complex $Li[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)_2]$.[4b]

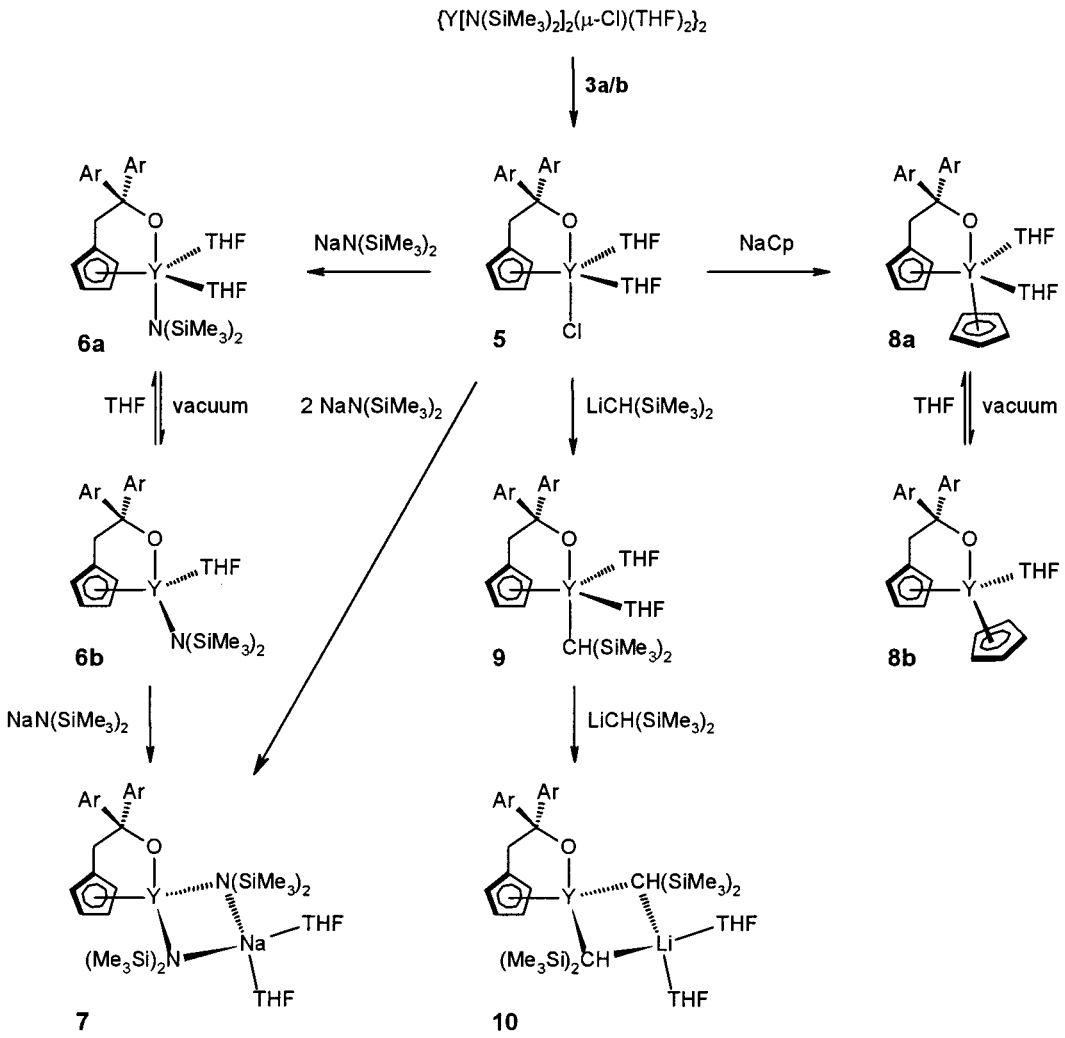
(16) A similar protonolysis strategy has been used to prepare $Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(CH_2SiMe_3)(THF)$ (R = Me, Et) from $C_5Me_4HSiMe_2NHCMe_2R$ and $Y(CH_2SiMe_3)_3(THF)_2$.[2c]

(17) Coordinated THF has been convincingly shown to undergo rapid exchange in solution on the NMR time scale for $Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(CH_2SiMe_3)(THF)$ (R = Me, Et).[2c]

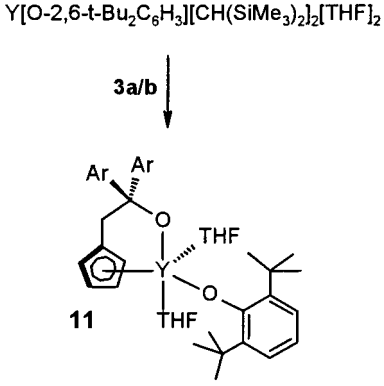
(18) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568.

(19) This strategy has been used successfully in several cases: (a) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637. (b) Schaverien, C. J. *Organometallics* **1994**, *13*, 69. (c) Schaverien, C. J.; Frijn, J. H. G.; Heeres, H. J.; van den Hende, J. R.; Teuben, J. H.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 643.

Scheme 3



Scheme 4



2,6-*t*-$Bu_2C_6H_3]_3$ in THF, ether, or toluene led to formation of *ate* complex **4**. Similarly, in situ formation of Y[O-2,6-*t*-$Bu_2C_6H_3][CH_2SiMe_3]_2$ from Y[O-2,6-*t*-$Bu_2C_6H_3]_3$ and $LiCH_2SiMe_3$ followed by reaction with **3** also produced complex **4** (Scheme 2). We were able to prepare the phenoxide **11** by direct protonolysis of Y[O-2,6-*t*-$Bu_2C_6H_3][CH(SiMe_3)_2]_2[THF]_2$[12] with **3** (Scheme 4). The yield by this route is good provided the mixed alkyl-alkoxide precursor is free of lithium. The phenoxide **11** crystallizes as the bis(THF) adduct according to ^{1}H NMR, elemental analysis, and X-ray crystallography. The ^{1}H NMR spectrum of **11** displays mirror plane symmetry for the ligand in solution. The symmetry in the solid state is lower (vide infra), suggesting that the THF ligands are labile in solution. Not surprisingly, given some of our earlier results, attempts to react **11** with lithium alkyls led to rapid redistribution and formation of **4**.

X-ray Crystal Structures. The crystal structures of the bis(THF) adduct *ate* complex **4a** and the phenoxide **11** were obtained. Crystallographic data are given in Table 1 while significant bond distances and angles are collected in Table 2 for both compounds. Structural plots for **4a** and **11** are given in Figures 1 and 2, respectively. The crystal structure of **4a** shows a bimetallic system in which the ligand alkoxide oxygens bridge between yttrium and lithium. The coordination environment at yttrium is a distorted pseudo-tetrahedral geometry typical of many other Cp_2YX_2 systems.[20] The coordination geometry at the lithium cation in **4a** is quite close to tetrahedral. The closest structural comparisons available in the literature are $(\eta^5\text{-}C_5H_4SiMe_3)_2Y(\mu\text{-O-}t\text{-Bu})_2Li(THF)_2$[21] and the related *ate* complex $Li[Y(\eta^5{:}\eta^1\text{-}Cp^R\text{-}SiMe_2NCH_2CH_2X)_2]$.[22] In the former structure, the $C_5H_4SiMe_3$ centroid−Y distance is longer (2.458 Å) and

(20) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Lappert, M. F., Ed.; Pergamon: London, 1995; Vol. 4, Chapter 2.
(21) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1993**, *12*, 3998.

Table 1. Summary of Crystallographic Data[a]

	4a	11
formula	$YC_{60}H_{46}F_{24}LiO_4$	$YC_{45}H_{49}F_{12}O_4$
fw	1382.82	970.75
cryst size (mm)	0.38 × 0.51 × 0.81	0.09 × 0.27 × 0.65
cryst syst	orthorhombic	monoclinic
space group	*Pbcn* (No. 60)	$P2_1/n$ (No. 14)
a (Å)	17.0844(19)	12.4983(12)
b (Å)	20.056(2)	16.3961(16)
c (Å)	18.066(2)	23.031(2)
α (deg)	90	90
β (deg)	90	101.052(2)
γ (deg)	90	90
V (Å^3)	6190.1(12)	4632.0(8)
Z	4	4
ρ(calcd) (g cm^{-3})	1.48	1.39
μ (mm^{-1})	1.06	1.35
$2\theta_{max}$ (deg)	50	50
no. reflns collected	31228	24351
no. of unique reflns	5452	8182
no. of reflns $I > 2.0\sigma(I)$	3309	4355
F_{000}	2784	1992
R	0.055	0.048
wR2	0.160	0.112
GOF on F^2	0.99	0.88

[a] Data were collected on a Siemens Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4a and 11[a]

4a		11	
	Distances		
Y(1)−Cp	2.372(5)	Y(1)−Cp	2.400(5)
Y(1)−O(1)	2.220(2)	Y(1)−O(1)	2.128(2)
Li(1)−O(1)	1.978(6)	Y(1)−O(2)	2.103(3)
Li(1)−O(S1)	1.979(5)	Y(1)−O(3)	2.505(3)
Y(1)−Li(1)	3.125(6)	Y(1)−O(4)	2.392(3)
	Angles		
Cp−Y(1)−Cp′	128.2(2)	Cp−Y(1)−O(1)	93.77(13)
Cp−Y(1)−O(1)	95.69(14)	Cp−Y(1)−O(2)	137.01(14)
Cp−Y(1)−O(1)′	125.42(12)	Cp−Y(1)−O(3)	104.72(13)
O(1)−Y(1)−O(1)′	78.03(12)	Cp−Y(1)−O(4)	105.35(14)
Y(1)−O(1)−Li(1)	96.1(2)	O(1)−Y(1)−O(2)	94.02(9)
Y(1)−O(1)−C(7)	124.5(2)	O(1)−Y(1)−O(3)	156.19(10)
O(1)−Li(1)−O(1)′	89.9(3)	O(1)−Y(1)−O(4)	85.76(10)
O(1)−Li(1)−O(S1)	114.22(12)	O(2)−Y(1)−O(3)	82.72(9)
O(1)−Li(1)−O(S1)′	114.47(12)	O(2)−Y(1)−O(4)	117.35(10)
O(S1)−Li(1)−O(S1)′	108.8(4)	O(3)−Y(1)−O(4)	75.07(10)
Li(1)−O(1)−C(7)	130.6(2)	Y(1)−O(1)−C(7)	132.7(2)
Y(1)−O(2)−C(24)	174.6(2)[a]		

[a] Estimated standard deviations in parentheses. Primed atoms are symmetry related. Cp refers to the Cp centroid.

the Y−O distance is shorter (2.148(10), 2,157(11) Å) than that found in **4a** (2.372(5) and 2.220(2) Å, respectively), but the basic coordination geometry is otherwise very similar. The differences can be attributed to the fact that the ligand bulk is primarily at the alkoxide carbon in **4a**, whereas it is on the $C_5H_3SiMe_3$ group in the literature complex. The latter family of complexes display very similar Y−Cp^{cent} distances and overall coordination geometry to **4a**.[22]

The geometry at yttrium in **11** is best described as a distorted trigonal bipyramid in which the ligand alkoxide and one THF oxygen reside in axial positions while the Cp centroid, phenoxide, and THF oxygens reside in equatorial positions. Generally, the largest substituents

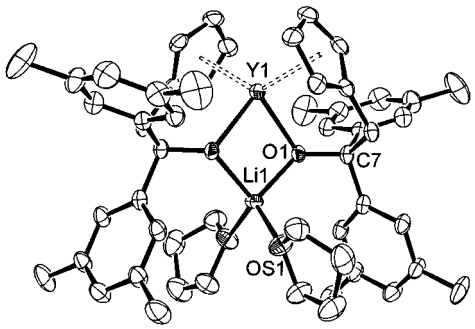


Figure 1. ORTEP3 drawing[14] (thermal ellipsoids 30% probability) of complex **4a**. The fluorine atoms of the ligand CF_3 groups have been omitted for clarity.

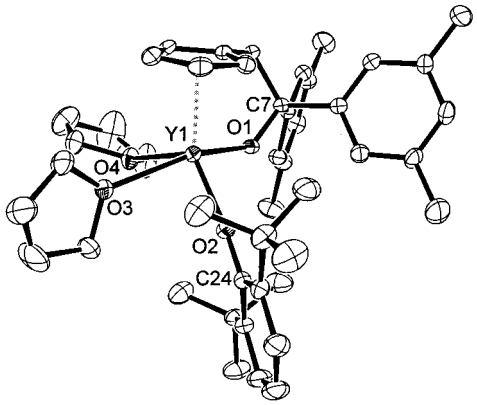


Figure 2. ORTEP3 drawing[14] (thermal ellipsoids 30% probability) of complex **11**. The fluorine atoms of the ligand CF_3 groups have been omitted for clarity.

will occupy equatorial sites in the TBP geometry, but this is not possible in the present case because the CpO ligand can only span an angle of about 95°. The large bulk of the 2,6-di-*tert*-butylphenoxide ligand is accommodated by an opening of the equatorial Cp−phenoxide angle to 137.01(14)° with a corresponding decrease in the Cp−O4 (THF2) angle to 105.35(14)°. As might be expected, the Y−O(aryloxide) distance in **11** (2.103(3) Å), which is formally seven-coordinate, is at the long end of the range reported for five- and six-coordinate yttrium aryloxides (2.046(6)−2.103(10) Å).[19c,23] The angle at the aryloxide oxygen (Y(1)−O(2)−C(24) 174.6(2)°) is similar to that found in Y(O-*t*-$Bu_2C_6H_3)_3$ (171(1)−175(1)°).[9]

The Cp^{cent}−Y−O angle spanned by the ligand is similar for both **4a** (95.69(14)°) and **11** (93.77(13)°). For comparison, the chelating η^5:η^1-Cp-donor ligands found in Zr[η^5:η^1-*t*-$BuC_5H_3(CH_2CH_2O)]_2$,[24] Zr[η^5:η^1-$C_5Me_4(CH_2CH_2S)]_2$,[25] and {Ti[η^5:η^1-$C_5H_4(CH_2CH_2O)]Cl_2\}_2$[26] have bite angles of 99.39° (average), 102.21°, and 100.8°, respectively. The Cp-alkoxide bite angles in **4a** and **11** are closer to the values found in yttrium complexes containing the η^5:η^1-Cp^{R}SiMe$_2$NCH$_2$CH$_2$X series of

(22) Y−Cp^{cent} = 2.392(6), 2.399(6) Å (Cp^R = C_5Me_4, X = OMe); 2.403(3), 2.390(3) Å (Cp^R = *t*-BuC_5H_3, X = OMe); 2.405(3) Å (Cp^R = *t*-BuC_5H_3, X = NMe_2).[4b]

(23) (a) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 3079. (b) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4309. (c) Evans, W. J.; Ansari, M. A.; Ziller, J. W.; Khan, S. I. *J. Organomet. Chem.* **1998**, *553*, 141.

(24) Christoffers, J.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2266.

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(26) Trouvé, G.; Laske, D. A.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.* **1996**, *511*, 255.

ligands (95.6(2)−97.5(2)°).[2c,4b,d] The similarity in bite angle between these ligands can be attributed to the longer Si−C bond lengths, which compensates for the shorter tether in the Cp^RSiMe_2NR series. The angles at C in the ligand backbone are close to tetrahedral in both **4a** and **11**, suggesting that the ligand is not highly strained to achieve the coordination geometry adopted. However, the Y−Cp C distances are not all equal in either complex. In both structures, the Y−Cp C distances fall into a pattern of two short, two medium, and one long distance (**4a**, *C4* 2.634(4), *C5* 2.639(4), *C1* 2.661(4), *C3* 2.663(4), *C2* 2.692(4); **11**, *C1* 2.621(4), *C5* 2.642(4), *C2* 2.693(4), *C4* 2.698(4), *C3* 2.733(4) Å), although the pattern is clearly more pronounced in **11**. Thus it appears the Cp unit is tipped toward yttrium along one edge with the carbon opposite that edge being the furthest away from the metal center. The fact that the alkyl tether is attached in both structures to one of the closer carbons suggests that this effect is due to constraints imposed by the chelate arm. A similar, but less pronounced, effect was previously noted in $\{Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2CH_2O)]Cl_2\}_2$[26] and in other systems.[4b]

Discussion

We were unable to prepare mono(ligand) derivatives by metathesis reactions between the dilithium salt of the ligand and an appropriate yttrium precursor (chloride or alkoxide). Redistribution to the *ate* complex **4** was unavoidable in all cases studied. It is possible to isolate mono(ligand) derivatives by direct protonolysis of a suitable yttrium complex (alkyl or amide derivative) with ligand **3** because no lithium is present during these reactions. Once prepared, it is sometimes possible to convert one mono(ligand) derivative into another by metathesis, but again, smaller alkyls in particular lead to redistribution.

It is quite likely that these problems arise due to the relatively open coordination sphere around yttrium. While an open coordination sphere is desirable from a reactivity viewpoint, the small angle spanned by the CpO ligand is too small to allow isolation of manageable compounds. To c*lose down* the coordination sphere somewhat, the ligand can be modified by adding bulk at the Cp or by extending the length of the tether by one carbon.[26,27] Although the former is a time-honored technique in lanthanide chemistry, our attempts to modify the ligand by using a substituted Cp have not met with success because the ring-opening step fails with anything other than unsubstituted Cp. While work is still continuing in this direction, the second option may prove to be a better choice. This is a particularly interesting option since we have observed some tendency for ligand cleavage to occur between the alkoxide carbon and the lone CH_2 group. Addition of another CH_2 between the alkoxide and the Cp ring should help stabilize the ligand by removing any resonance stabilization effects involved in the ligand cleavage mechanism. Work is underway to assess both of these options.

Acknowledgment. The support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **4a** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0104520

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