Alkoxide-functionalized cyclopentadienyl complexes of yttrium containing a two-carbon tether

Roland A.L. Gendron, David J. Berg, and Tosha Barclay

Abstract: The ligand $C_5H_4(CH_2CH_2CAr^F{}_2OH)$ (**3**) (Ar^F = 3,5-$C_6H_3(CF_3)_2$) was prepared in two steps, from the iodo ester $ICH_2CH_2CO_2Me$ by way of the cyclopentadienyl ester $C_5H_5CH_2CH_2CO_2Me$ (**2**), in 55% overall yield. Thermal reaction of **3** with $\{Y[N(SiMe_3)_2]_2(THF)_2(\mu\text{-}Cl)\}_2$ afforded the neutral chloride complex $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}YCl\{THF\}_n$ (**5a**: n = 2, **5b**: n = 1). Metathesis reactions of **5** with 1 equiv of $NaN(SiMe_3)_2$, LiO-2,6-*t*-$Bu_2C_6H_3$, and $LiCH(SiMe_3)_2$ afforded $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{N(SiMe_3)_2\}\{THF\}_n$ (**6**), $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3\}\{THF\}_n$ (**7**), and $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{CH(SiMe_3)_2\}\{THF\}_n$ (**8**), respectively, (**a**: n = 2, **b**: n = 1). Exposure of the *bis*(THF) solvates to reduced pressure resulted in desolvation to the *mono*(THF) adducts for **5**–**8**. The solid state structure of **6b** was established by X-ray crystallography. In addition, formation of a spirocyclic ether ($C_4H_6CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2$ **4**), obtained by the intramolecular cyclization of ligand **3**, was confirmed by X-ray crystallography.

Key words: yttrium, organometallic, cyclopentadienyl, X-ray, alkoxide, chelate, alkyl, hybrid ligand, NMR, cyclization.

Résumé : On a préparé le ligand $C_5H_4(CH_2CH_2CAr^F{}_2OH)$ (**3**) (Ar^F = 3,5-$C_6H_3(CF_3)_2$) en deux étapes à partir de l'ester iodé $ICH_2CH_2CO_2Me$, par le biais de l'ester cyclopentadiényle, $C_5H_5CH_2CH_2CO_2Me$ (**2**), avec un rendement global de 55%. La réaction thermique du composé **3** avec $\{Y[N(SiMe_3)_2]_2(THF)_2(\mu\text{-}Cl)\}_2$ conduit à la formation du complexe chloré neutre $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)]\}YCl\{THF\}_n$ (**5a**: n = 2, **5b**: n = 1). Les réactions de métathèse des composés **5** avec un équivalent de $NaN(SiMe_3)_2$, LiO-2,6-*t*-$Bu_2C_6H_3$ et $LiCH(SiMe_3)_2$ conduisent respectivement au $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)]\}Y\{N(SiMe_3)_2\}\{THF\}_n$ (**6**), $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)]\}Y\{O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3\}\{THF\}_n$ (**7**) et $\{\eta^5{:}\eta^1\text{-}C_5H_4[CH_2CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)]\}Y\{CH(SiMe_3)_2\}\{THF\}_n$ (**8**) (**a**: n = 2, **b**: n = 1). Si l'on soumet les produits *bis*(THF) solvatés **5**–**8** à une pression réduite, il en résulte une désolvatation conduisant aux adduits *mono*(THF). On a déterminé la structure du composé **6b** par diffraction des rayons X. De plus on a confirmé par diffraction des rayons X que la cyclisation intramoléculaire du ligand **3** conduit à la formation d'un éther spirocyclique, $C_4H_6CH_2CH_2(CO)(3,5\text{-}C_6H_5(CF_3)_2)_2$ (**4**).

Mots clés : yttrium, organométallique, cyclopentadiényle, rayons X, alcoolate, chélate, alkyle, ligand hybride, RMN, cyclisation.

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Introduction

The development of *hybrid* ligands that contain both Cp and a pendant anionic group has been an important trend in organometallic chemistry of the lanthanides and group 4 elements during the past decade (1–3). The introduction of new Cp-alkoxide and Cp-amide mixed ligands has been especially successful 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). It is particularly surprising, then, that Cp-alkoxides have not been widely investigated as ligands in yttrium or lanthanide chemistry (2(*c*), 4, 5).[2] Ligands of this type developed for use in group 4 chemistry, however, are often poorly suited to group 3 and lanthanide chemistry because they do not possess sufficient steric bulk to satisfy the coordination sphere of the larger metals. In particular, many of the existing ligands bear no substituents on the alkoxide carbon.

In earlier work, we reported the preparation of a Cp-alkoxide ligand (**1**) with a single carbon bridge between the Cp unit and the alkoxide carbon (6). The preparation of simple

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R.A.L. Gendron and D.J. Berg.[1] Department of Chemistry, University of Victoria, P.O. Box 3060, Victoria, BC V8W 3V6, Canada.
T. Barclay. Department of Chemistry, North Harris College, 2700 W. W. Thorne Drive, Houston, TX 77073, U.S.A.

[1]Corresponding author (e-mail: djberg@uvic.ca).

[2]Cyclopentadienyl ligands bearing *neutral* pendant donors are well known in yttrium and lanthanide chemistry. Literature prior to 1994 has been reviewed (5*a*). Several complexes of this type have been reported more recently (5(*b*)–5(*l*)).

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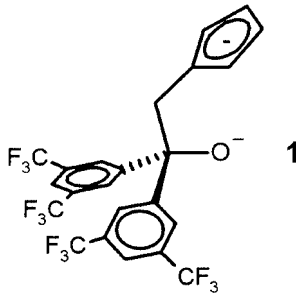
yttrium complexes of the type (CpO)YX (CpO = **1**; X = Cl, Cp, $N(SiMe_3)_2$, 2,6-*t*-$Bu_2C_6H_3O$, $CH(SiMe_3)_2$) was generally complicated by the tenacious retention of additional anionic groups to form "*ate*" complexes of the type $(CpO)YX_2^-$, suggesting that ligand **1** lacks sufficient steric bulk to stabilize the neutral (CpO)YX species. Indeed, one of the most persistent problems encountered in previous work was rapid redistribution of the anionic *mono*(ligand) "ate" complexes to the *bis*(ligand) species $(CpO)_2Y^-$, clearly demonstrating the small effective size of **1**.



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To *close down* the coordination sphere somewhat, **1** can be modified by adding bulk at the Cp or by extending the length of the tether by one carbon (7, 8). So far, our attempts to modify the ligand by using a substituted Cp (C_5Me_4, fluorenyl, indenyl) have not met with success, primarily because chelate coordination of the substituted Cp group does not occur (bridging interactions predominate, leading to insoluble materials). While work is still continuing in that direction, the second option may prove to be a better choice. This is a particularly attractive option because we have observed a tendency for ligand cleavage to occur between the alkoxide carbon and the lone CH_2 group in **1** (6). Presumably, addition of another CH_2 between the alkoxide and the Cp ring will help stabilize the ligand by removing any resonance effects involved in the ligand cleavage mechanism.

A two-atom backbone has been applied in organolanthanide chemistry for several neutral pendant donors (9) and one recently reported pendant alkoxide donor (10). The latter was found to stabilize larger iodide complexes, but no hydrocarbyl chemistry was reported. In the related yttrium hydride ($[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}H)(THF)]_2$) (4(*e*)), extension of the backbone by a single carbon, to give $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(\mu\text{-}H)(THF)]_2$ (11), showed distinct changes in geometry and reactivity. The observed bite angles opened from 97.8(2)° and 97.4(2)° to 104.9(2)° and 104.3(2)°, respectively, and catalytic activity toward hydrosilation of styrene was higher in the yttrium complex with the longer "-CH_2SiMe_2-" link ($PhSiH_3$: 100% conversion, 1 h, vs. 80% conversion, 7 h) (11). This effect has been ascribed to an increased contribution of monomer in the monomer–dimer equilibrium for complexes containing the ligand with an extended backbone. VT-NMR studies on the monomer–dimer dissociation kinetics of $(Cp^*_2YH)_2$ indicated that the terminal hydride Cp^*_2YH is much more active toward olefin insertion than the dimeric form (12). This finding supports the theory of a dissociative mechanism as the rate-determining step in olefin insertion and, consequently, polymerization. Bulky ligands can only enhance dimer dissociation (i.e., backbone extension), so reactivity should increase with larger ligand size; however, excessive bulk leads to oversaturation of the metal and inhibits the approach of the inserting species. The solution is to use a synthesis that allows the adjustment of bulk in small increments, so as to approach, but not overshoot, the desired ligand size. The extension of the backbone by sequential addition of CH_2 units seems the most logical approach. In this contribution we report the synthesis of a new Cp-alkoxide ligand with an extended two-carbon backbone between the Cp and alkoxide carbons and the formation of several neutral yttrium complexes derived from it.

Experimental

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 and methyl 3-chloropropionate were purchased commercially (Aldrich) and used as received. $Li[3,5\text{-}C_6H_3(CF_3)_2]$ was prepared from *n*-butyl lithium and $3,5\text{-}C_6H_3(CF_3)_2Br$ in hexane at –78°C. The precipitated fluorinated aryl lithium salt was washed with cold hexane and redissolved in diethyl ether before use. Care must be taken to keep $Li[3,5\text{-}C_6H_3(CF_3)_2]$ cold during all operations, since it is unstable above –20°C. The iodo ester ($ICH_2CH_2CO_2CH_3$) was prepared using conventional halogen exchange between methyl 3-chloropropionate and NaI in acetone (13). Yttrium tris(2,6-di-*t*-butylphenoxide) (14) and $\{Y[N(SiMe_3)_2]_2(THF)_2(\mu\text{-}Cl)\}_2$ (6) 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) NMR 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. Canadian Microanalytical (Delta, B.C) performed elemental analyses. Despite the use of co-oxidants such as V_2O_5 and PbO_2, the analytical data for most metal complexes were consistently 1 to 2% 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), electron impact (70 eV), or liquid secondary ion mass spectroscopy (LSIMS).

Methyl 3-cyclopentadienylpropionate (2)

To a dry 500 mL Schlenk flask was added $ICH_2CH_2C(O)OCH_3$ (1.61 g, 7.5 mmol), 10 mL diethyl ether, and a Teflon-coated stir-bar. The light yellow solution was stirred under argon and cooled to –78°C. In a separate 100 mL Schlenk flask, sodium cyclopentadienide (0.660 g, 7.5 mmol) was dissolved in 10 mL THF and added slowly via canula. The mixture was allowed to reach room temperature and stirred overnight under argon. The resulting white suspension was quenched with 1 M NH_4Cl (100 mL), and

the organic phase was extracted with 3 × 20 mL of diethyl ether and dried over anhyd $MgSO_4$. Removal of the solvent gave a mixture of the 1-alkylCp (**2a**) and 2-alkylCp (**2b**) isomers as yellow liquids in a 1.2:1 ratio. The 5-alkyl isomer was not observed. Yield: 0.751 g (66%). Major isomer **2a** (1-alkylCp): ^{1}H NMR (*d*-chloroform) δ: 6.40 (m, 1H, Cp-*H*3), 6.26 (dq, 1H, Cp-*H*4, *J* = 5.1, 1.5 Hz), 6.03 (m, 1H, Cp-*H*2), 3.67 (s, 3H, C(O)OCH_3)), 2.95 (dd, 2H, Cp-*H*5), 2.72 (t, 2H, CH_2C(O)OCH$_3$, $^3J_{HH}$ = 8.1 Hz), 2.57 (m, 2H, CH_2CH$_2$C(O)OCH$_3$, *J* = 8.1 Hz). ^{13}C NMR δ: 173.69 (*C*(O)OCH$_3$), 145.29 (Cp-*C*1), 134.12 (Cp-*C*3), 131.04 (Cp-*C*4), 126.90 (Cp-*C*2), 41.35 (C(O)O*C*H$_3$), 41.34 (Cp-*C*5), 33.98 (CpCH$_2$*C*H$_2$C(O)), 25.09 (Cp*C*H$_2$CH$_2$C(O)). Minor isomer **2b** (2-alkylCp): ^{1}H NMR (*d*-chloroform) δ: 6.41 (m, 1H, Cp-*H*3, overlaps **2a**), 6.39 (dq,1H, Cp-*H*4, *J* = 5.1, 1.5 Hz), 6.17 (m, 1H, Cp-*H*1), 3.67 (s, 3H, C(O)OCH_3)), 2.89 (dd, 2H, Cp-*H*5), 2.72 (t, 2H, CH_2C(O)OCH$_3$, overlaps **2a**, $^3J_{HH}$ = 8.1 Hz), 2.57 (m, 2H, CH_2CH$_2$C(O)OCH$_3$, overlaps **2a**, *J* = 8.1 Hz). ^{13}C NMR δ: 173.69 (*C*(O)OCH$_3$, overlaps **2a**), 147.47 (Cp-*C*2), 132.32 (Cp-*C*1), 132.13 (Cp-*C*4, overlaps **2a**), 129.67 (Cp-*C*3), 43.28 (C(O)O*C*H$_3$), 41.34 (Cp-*C*5), 33.98 (CpCH$_2$*C*H$_2$C(O), overlaps **2a**), 25.88 (Cp*C*H$_2$CH$_2$C(O)).

3-Cyclopentadienyl-1,1-di(3,5-bis(trifluoromethyl)phenyl)propanol (3)

A 5 mL ethereal solution of **2** (1.76 g, 11.6 mmol) was added dropwise to a cold solution of Li[3,5-C$_6$H$_3$(CF$_3$)$_2$] (37.1 mmol) in 30 mL of diethyl ether (–78°C) with vigorous stirring. The resulting deep red solution was stirred for an additional 30 min at –78°C before quenching with 100 mL of aqueous NH_4Cl (1 M). The organic phase was extracted with 3 × 20 mL diethyl ether and dried over anhyd $MgSO_4$. Filtration and removal of solvent under vacuum afforded **3** as a yellow oil that contained the 1-alkyl and 2-alkyl isomers in a 1.2:1 ratio. The product was further dried for 1 day over 4 Å molecular sieves and stored as a 0.46 M toluene solution to avoid intermolecular Diels-Alder dimerization. Yield: 5.02 g (79%). Major isomer **3a** (1-alkylCp): ^{1}H NMR (d_6-benzene) δ: 7.79 (s, 4H, *o*-arylC*H*), 7.59 (s, 2H, *p*-arylC*H*), 6.16 (m, 1H, Cp-*H*3), 6.17 (dq, 1H, Cp-*H*4, *J* = 5.2, 1.4 Hz), 5.69 (m, 1H, Cp-*H*2), 2.67 (m, 2H, Cp-*H*5), 2.00 (m, 2H, CpCH$_2$CH_2CO), 1.92 (m, 2H, CpCH_2CH$_2$CO), 1.45 (s, 1H, CO*H*). ^{13}C NMR δ: 147.77 (*ipso*-aryl*C*), 146.98 (Cp-*C*1), 135.04 (Cp-*C*3), 132.15 (q, aryl*C*CF$_3$, $^2J_{CF}$ = 34 Hz), 131.84 (Cp-*C*4), 131.56 (Cp-*C*2), 125.88 (*o*-aryl*C*), 125.82 (q, *C*F$_3$, $^1J_{CF}$ = 236 Hz), 125.87 (*p*-aryl*C*, overlaps *o*-aryl*C*), 65.65 (*C*OH), 43.19 (Cp-*C*5), 41.37 (CH$_2$*C*H$_2$CO), 24.57 (*C*H$_2$CH$_2$CO). ^{19}F NMR δ: –63.09 (C*F*$_3$). Minor isomer **3b** (2-alkylCp): ^{1}H NMR (d_6-benzene) δ: 7.79 (s, 4H, *o*-arylC*H*, overlaps **3a**), 7.59 (s, 2H, *p*-arylC*H*, overlaps **3a**), 6.25 (m, 1H, Cp-*H*3, overlaps **3a**), 6.34 (dq, 1H, Cp-*H*4, *J* = 5.3, 1.5 Hz), 5.91 (m, 1H, Cp-*H*1), 2.44 (q, 2H, Cp-*H*5), 2.00 (m, 2H, CpCH$_2$CH_2CO, overlaps **3a**), 1.92 (m, 2H, CpCH_2CH$_2$CO, overlaps **3a**), 1.37 (s, 1H, CO*H*). ^{13}C NMR δ: 148.83 (*ipso*-aryl*C*), 146.98 (Cp-*C*2, overlaps **3a**), 133.60 (Cp-*C*1), 132.14 (q, *C*CF$_3$, $^2J_{CF}$ = 34 Hz, overlaps **3a**), 131.80 (Cp-*C*4), 131.56 (Cp-*C*3, overlaps **3a**), 125.88 (*o*-aryl*C*), 125.82 (q, *C*F$_3$, $^1J_{CF}$ = 236 Hz, overlaps **3a**), 125.87 (*p*-aryl*C*, overlaps *o*-aryl*C*), 65.65 (*C*OH, overlaps **3a**), 41.08 (Cp-*C*5), 40.26 (CH$_2$*C*H$_2$CO), 24.57 (*C*H$_2$CH$_2$CO, overlaps **3a**). ^{19}F NMR δ: –63.09 (C*F*$_3$, **3a** and **3b**). LSI-MS *m/z* (%): 548 ([M]$^+$, 22), 530 ([M$^+$ – H$_2$O], 60), 240 (C$_6$H$_3$(CF$_3$)$_2$CO, 100), 213 (C$_6$H$_3$(CF$_3$)$_2$C, 50).

C$_4$H$_6$CH$_2$CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$ (4)

A 10 mL toluene solution of **3** (1.02 g) became turbid after storage for 3 days at room temperature. Removal of toluene and recrystallization from hexane at room temperature produced long colorless prisms of the intramolecularly cyclized product **4**. Monitoring this reaction by ^{1}H NMR showed that cyclization was detectable after 2 days and essentially complete after 3 days for a dilute solution (0.03 M) in d_6-benzene at 22°C. Cyclization can be minimized by storage of dilute solutions of **3** in toluene at –30°C. Yield: 0.66 g (60%). ^{1}H NMR (d_6-benzene) δ: 7.94 (s, 2H, *o*-arylCH_a), 7.91 (s, 2H, *o*-arylCH_b), 7.57 (s, 2H, *p*-arylC$H_{a,b}$), 5.61 (m, 1H, C2-*H*, *J* = 5.5, 2.4 Hz), 5.38 (m, 1H, C3-*H*, *J* = 5.5, 2.4 Hz), 2.20 (m, 1H, C4-H_a, *J* = 5.5 Hz), 1.93 (t, 2H, C1-CH$_2$CH_2CO, $^3J_{HH}$ = 6.6 Hz), 1.92 (m, 1H, C4-H_b), 1.92 (m, 1H, C5-H_a), 1.47 (m, 1H, C5-H_b, *J* = 2.4 Hz), 1.33 (t, 2H, C1-CH_2CH$_2$CO, $^3J_{HH}$ = 6.6 Hz). ^{13}C NMR δ: 149.51 (*ipso*-arylC_a), 149.44 (*ipso*-arylC_b), 134.74 (*C*1), 134.17 (*C*2), 132.20 (q, *C*CF$_3$, $^2J_{CF}$ = 33 Hz), 125.83 (*o*-aryl*C*), 125.20 (q, *C*F$_3$, $^1J_{CF}$ = 273 Hz), 121.48 (*p*-aryl*C*), 97.03 (*C*OH), 86.127 (*C*3), 39.63 (CH$_2$*C*H$_2$CO), 37.57 (*C*4), 36.48 (*C*5), 30.89 (*C*H$_2$CH$_2$CO). ^{19}F NMR δ: –62.85 (C$F_{3a,b}$). EI-MS *m/z* (%): 548 ([M]$^+$, 100), 455 ([M$^+$ – F], 42), 241 (3,5-C$_6$H$_3$(CF$_3$)$_2$CO, 40).

{η^5:η^1-C$_5$H$_4$[CH$_2$CH$_2$C(O)(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$]}YCl{THF}$_n$ (5a: *n* = 2, 5b: *n* = 1)

A 60 mL thick-walled Schlenk flask with a Teflon stopcock was charged with Y[N(SiMe$_3$)$_2$]$_3$ (0.352 g, 0.618 mmol), YCl_3 (0.060 g, 0.309 mmol), and 10 mL THF under an argon atmosphere. The flask was sealed and stirred at 80°C for 2 h. The colourless solution of {Y[N(SiMe$_3$)$_2$]$_2$(THF)$_2$(μ-Cl)}$_2$, formed in situ, was then cooled to –20°C and a 10 mL toluene solution of **3** (0.508 g, 0.927 mmol) was added slowly via syringe. The solution was once again sealed and heated at 80°C for 2 h, becoming more yellow in colour. Solvent was then removed in vacuo, and the off-white solid recrystallized from hot toluene in the glovebox, yielding the chloride (**5**) as small white nodules. Yield: 0.549 g (80%); mp 189 to 190°C. ^{1}H NMR (d_6-benzene – d_8-THF, 5:1) δ: 8.18 (s, 4H, *o*-aryl*H*), 7.67 (s, 2H, *p*-aryl*H*), 6.28 (br s, 2H, Cp*H*), 5.87 (br s, 2H, Cp*H*), 3.55 (m, 8H, α-THF *H*), 2.54 (br s, 2H, CH$_2$CH_2CO), 2.45 (br s, 2H, CH_2CH$_2$CO), 1.43 (m, 8H, β-THF *H*). ^{13}C NMR δ: 154.39 (*ipso*-aryl*C*), 131.30 (q, *C*CF$_3$, $^2J_{CF}$ = 32 Hz), 127.13 (*o*-aryl*C*), 126.30 (Cp-*C*1), 124.00 (q, *C*F$_3$, $^1J_{CF}$ = 283 Hz), 120.35 (*p*-aryl*C*), 111.01 (Cp*C*), 110.45 (Cp*C*), 79.49 (*C*OY), 67.48 (α-THF *C*), 42.55 (CH$_2$*C*H$_2$CO), 25.63 (*C*H$_2$CH$_2$CO), 24.57 (β-THF *C*). ^{19}F NMR δ: –62.58 (C*F*$_3$). Anal. calcd for (*mono*(THF) adduct **5b**) C$_{28}$H$_{22}$ClF$_{12}$O$_2$Y (%): C 45.26, H 2.98; found: C 43.98, H 3.24.

{η^5:η^1-C$_5$H$_4$[CH$_2$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** (0.122 g, 0.160 mmol) and 20 mL of toluene in the glovebox. To the rapidly stirred sticky suspension was added a 10 mL toluene

solution of $NaN(SiMe_3)_2$ (0.030 g, 0.16 mmol). The suspension was stirred at 70°C for 2 h, during which time the solids became white and free-flowing. Filtration through Celite on a glass frit and removal of solvent in vacuo gave the product as a crude yellow solid. Recrystallization of this solid from a toluene–hexane mixture gave pure **6** as a white powder. Yield: 0.090 g (65%); mp 135 to 136°C. **6a** (*bis*(THF) adduct): ^{1}H NMR (d_6-benzene) δ: 7.88 (s, 4H, *o*-aryl*H*), 7.63 (s, 2H, *p*-aryl*H*), 6.24 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.5 Hz), 5.82 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.5 Hz), 3.58 (m, 8H, α-THF *H*), 2.32 (br s, 4H, CH_2CH_2CO, CH_2CH_2CO), 1.27 (m, 8H, β-THF *H*), 0.09 (s, 18H, SiMe_3). ^{13}C NMR δ: 153.40 (*ipso*-aryl*C*), 131.17 (q, CCF_3, $^2J_{CF}$ = 33 Hz), 129.73 (Cp-*C*1), 126.28 (*o*-aryl*C*), 123.90 (q, CF_3, $^1J_{CF}$ = 273 Hz), 120.23 (*p*-aryl*C*), 110.91 (Cp*C*), 110.82 (Cp*C*), 78.89 (*C*OY), 70.46 (α-THF *C*), 43.04 (CH_2CH_2CO), 24.85 (β-THF *C*), 23.40 (CH_2CH_2CO), 4.50 (SiMe_3). ^{19}F NMR δ: –62.54 (CF_3). ^{29}Si NMR δ: –10.22 (*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 (**6b**) $C_{34}H_{40}F_{12}NO_2Si_2Y$ (%): C 47.06, H 4.65, N 1.61; found: C 46.12, H 4.55, N 1.55.

{η^5:η^1-C_5H_4[CH_2CH_2C(O)(3,5-$C_6H_3(CF_3)_2)_2$]}Y{O-2,6-*t*-$Bu_2C_6H_3$}{THF}$_n$ (7a: *n* = 2, 7b: *n* = 1)

Crude **7** was isolated as a white solid using a procedure analogous to **6** (0.300 g, 0.368 mmol), starting from **5** and Li(O-2,6-*t*-$Bu_2C_6H_3$) (0.088 g, 0.368 mmol). Repeated recrystallization from hexane at –30°C produced **7a** as small colourless crystals. Exposure to vacuum overnight produced the *mono*(THF) adduct (**7b**) with the same NMR data, suggesting fast exchange of the remaining THF. Yield: 0.271 g (75%); mp 110 to 111°C. ^{1}H NMR (d_6-benzene) δ: 7.80 (s, 4H, *o*-aryl*H*), 7.61 (s, 2H, *p*-aryl*H*), 7.32 (d, 2H, *m*-phenoxide *H*, $^3J_{HH}$ = 8.1 Hz), 6.83 (t, 1H, *p*-phenoxide *H*, $^3J_{HH}$ = 8.1 Hz), 6.22 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.9 Hz), 5.82 (t, 2H, Cp*H*, $^3J_{HH}$ = 2.9 Hz), 3.34 (m, 8H, α-THF *H*), 2.52 (br t, 2H, CH_2CH_2CO), 2.37 (t, 2H, CH_2CH_2CO, $^3J_{HH}$ = 5.1 Hz), 1.47 (s, 18H, CMe_3), 1.08 (m, 8H, β-THF *H*). ^{13}C NMR δ: 162.22 (d, *ipso*-phenoxide *C*, $^2J_{YC}$ = 5.0 Hz), 154.24 (*ipso*-aryl*C*), 137.60 (*o*-phenoxide *C*), 131.64 (q, CCF_3, $^2J_{CF}$ = 32 Hz), 129.25 (Cp-*C*1), 126.62 (*m*-phenoxide *C*), 125.47 (*o*-aryl*C*), 123.71 (q, CF_3, $^1J_{CF}$ = 273 Hz), 121.82 (*p*-aryl*C*), 116.95 (*p*-phenoxide *C*), 111.42 (Cp*C*), 110.97 (Cp*C*), 79.18 (d, *C*OY, $^2J_{YC}$ = 3.8 Hz), 71.60 (α-THF *C*), 42.58 (CH_2CH_2CO), 34.89 (*C*Me_3), 31.22 (CMe_3), 24.80 (β-THF *C*), 23.96 (CH_2CH_2CO). ^{19}F NMR δ: –62.47 (CF_3). Anal. calcd for (*mono*(THF) adduct **7b**) $C_{42}H_{43}F_{12}O_3Y$ (%): C 55.27, H 4.75; found: C 54.03, H 4.90.

{η^5:η^1-C_5H_4[CH_2CH_2C(O)(3,5-$C_6H_3(CF_3)_2)_2$]}Y{CH-$(SiMe_3)_2$}{THF}$_n$ (8a: *n* = 2, 8b: *n* = 1)

Crude **8a** was isolated as a white solid using a procedure analogous to that used for **6**, starting from **5** (0.100 g, 0.122 mmol) and $LiCH(SiMe_3)_2$ (0.0203 g, 0.122 mmol). Repeated recrystallization from hexane at –30°C produced **8a** as a white microcrystalline solid. Exposure to vacuum overnight produced the *mono*(THF) adduct (**8b**). In solution, **8b** shows fluxional behavior, as evidenced by broadened resonances observed in the ^{1}H NMR spectrum. These broadened lines sharpen at higher temperatures (+80°C). Yield: 0.069 g (60%); mp 102 to 103°C. ^{1}H NMR (d_6-benzene) δ: 7.90 (br s, 4H, *o*-aryl*H*), 7.63 (br s, 2H, *p*-aryl*H*), 6.20 (br m, 2H, Cp*H*), 5.79 (br s, 2H, Cp*H*), 3.35 (m, 8H, α-THF *H*), 2.25 (br s, 2H, CH_2CH_2CO), 2.24 (br s, 2H, CH_2CH_2CO, overlaps preceding CH_2), 1.11 (m, 8H, β-THF *H*), 0.15 (s, 18H, SiMe_3), –1.11 (d, 1H, C*H*$(SiMe_3)_2$, $^2J_{YH}$ = 4.3 Hz). ^{13}C NMR δ: 152.81 (*ipso*-aryl*C*), 131.26 (q, CCF_3, $^2J_{CF}$ = 33 Hz), 126.20 (*o*-aryl*C*), 123.63 (q, CF_3, $^1J_{CF}$ = 273 Hz), 120.39 (*p*-aryl*C*), 111.39 (Cp*C*), 111.39 (overlapping Cp*C*), 78.92 (*C*OY, $^2J_{YC}$ = 3.7 Hz), 70.78 (α-THF *C*), 43.77 (CH_2CH_2CO), 24.50 (β-THF *C*), 23.27 (CH_2CH_2CO), 32.37 (d, *C*H$(SiMe_3)_2$, $^1J_{CY}$ = 39 Hz), 25.07 (β-THF *C*), 4.54 (SiMe_3). ^{19}F NMR δ: –62.53. ^{29}Si NMR δ: –7.56 (*Si*Me_3, $^2J_{YSi}$ = 1.6 Hz). Anal. calcd for (*mono*(THF) adduct **8b**) $C_{35}H_{41}F_{12}O_2Si_2Y$ (%): C 48.49, H 4.77; found: C 45.88, H 4.43.

X-ray crystallography

Crystals of **4** and **6b** were isolated from hexane 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 (**4**) or a Nonius CAD 4F diffractometer (**6b**) equipped with graphite monochromated Mo Kα or Cu Kα radiation at 293 K, respectively. Structure solutions were carried out using teXsan98 (15) and refinement was done on *F*. Refinement of **4** was plagued by severe disorder problems and was only sufficient to establish the connectivity of the molecule.[3]

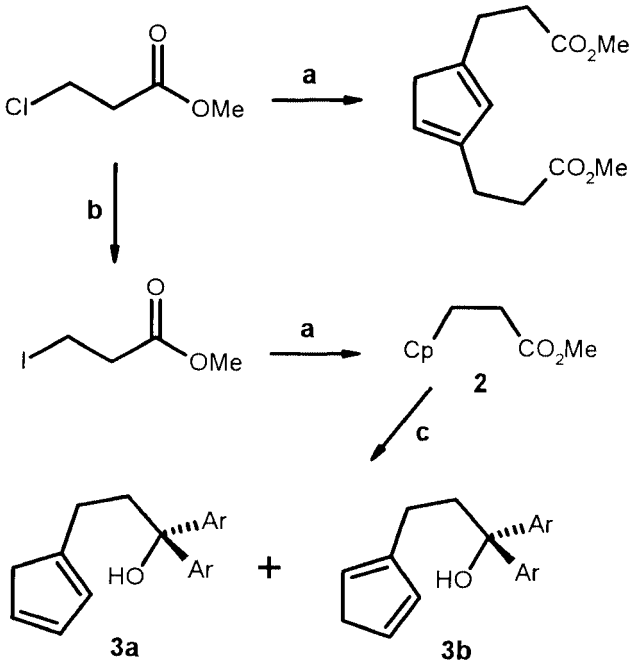
The data for **6b** were corrected for Lorentz and polarization effects, and a correction for secondary extinction was applied (coefficient = $2.91(4) \times 10^{-6}$). An empirical absorption correction was applied (absorption range: 0.92 – 1.00). Refinement proceeded normally although, as usual, rotational disorder of the CF_3 groups was observed. This was modeled successfully by allowing the six 0.5 occupancy fluorine atoms and the carbon of each CF_3 group to refine isotropically. The weak data set obtained for this crystal prevented anisotropic refinement of these atoms owing to the low data-to-parameter ratio. Hydrogen atoms were included in idealized positions and were not refined. The final Fourier difference maps showed maximum and minimum peaks of +0.66 and –0.52 e Å^{-3}, respectively, all in the vicinity of the disordered CF_3 groups. Thermal ellipsoid plots were drawn with ORTEP3 (16).

Results

Since the epoxide ring-opening route used to prepare **1** could not be used to prepare Cp-alkoxides with an extended

[3] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC contains the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

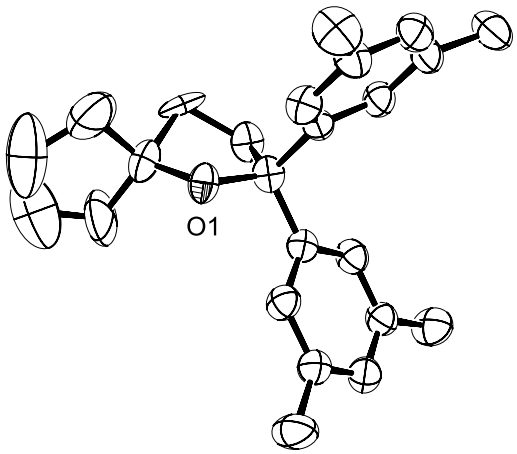
Scheme 1. (*a*) NaCp, THF–Et_2O, –78°C; (*b*) NaI, acetone, 24 h; (*c*) 3.2 equiv Li(3,5-$C_6H_3(CF_3)_2$), THF–Et_2O, –78°C.



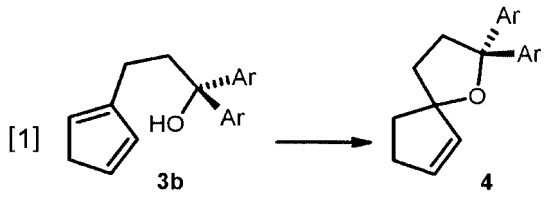
backbone, a new ligand synthesis was developed (Scheme 1). Although the three-step synthesis gives an overall yield of 55%, highly specific conditions are required in each step to achieve these results. The use of the iodo-ester and sodium cyclopentadienide appears to be critical in obtaining the desired cyclopentadienyl ester (**2**). We found that if the commercially available chloroester or the bromoester was not converted to the iodide, the diester $C_5H_4(CH_2CH_2C(O)OMe)_2$ was produced as the major product, rather than **2**. This was observed regardless of the addition rate or reaction temperatures. Similar disubstituted products have been observed by Peters (17) when RC(O)Cl was treated with NaCp. Selective substitution at the CH_2I group occurred with NaCp; use of LiCp resulted in a mixture of products. The crude ester was distilled under static vacuum (ca. 1 torr (1 torr = 133.322 Pa)) to give **2** as a yellow liquid containing a 1.2:1 mixture of the 1-alkyl and 2-alkyl isomers. The two fluorinated phenyl groups were incorporated at the ester carbon by the addition of 3,5-*bis*(trifluoromethyl)phenyl lithium to **2**. Three equiv of the lithium salt must be used because deprotonation of the cyclopentadienyl group occurs readily. Following hydrolysis of the reaction mixture, **3** was isolated as a pure yellow oil, again containing the 1-alkyl and 2-alkyl substituted isomers in 1.2:1 ratio.

The protonated ligand **3** must be stored at –30°C as a dilute toluene solution (<0.5 M) to avoid irreversible transformation products. As a neat oil, **3** undergoes the expected Diels-Alder cyclization in a period of about 1 week at room temperature. Even in dilute solution (0.5 M), however, the 2-alkyl substituted isomer (**3b**) undergoes alcohol addition across one double bond of the diene in Markovnikov fashion, to give the spirocyclic ether **4** (eq. [1]). The identity of **4** was initially determined by ^{13}C DEPT, which identified four inequivalent CH_2 carbons, and ^1H-^1H COSY experiments,

Fig. 1. ORTEP3 (16) plot for **4** (30% probability, fluorine atoms omitted for clarity).



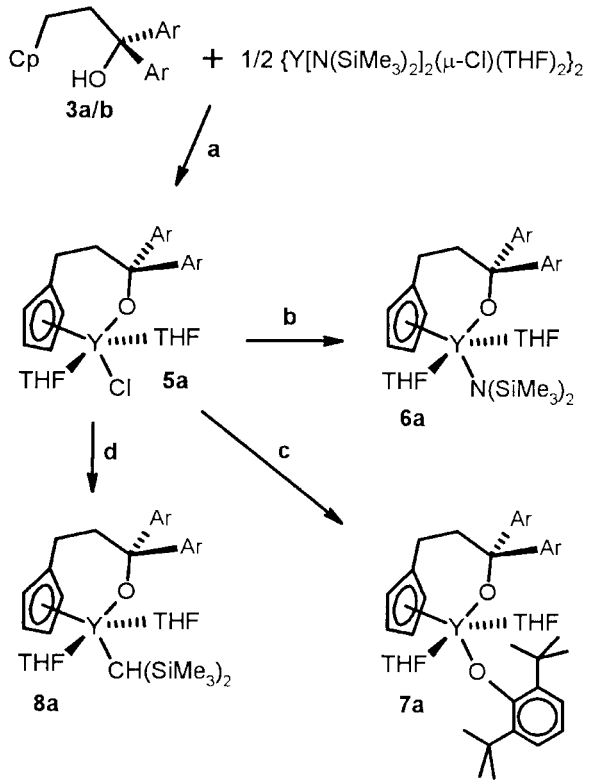
which established connectivity of all protons observed in the ^1H NMR. The structure of **4** was unequivocally established by an X-ray diffraction study, although the quality of the X-ray data was only sufficient to establish connectivity (Fig. 1). This result was unexpected since tertiary alcohols are generally inactive to alkene addition. Some intramolecular additions of primary or secondary alcohols have been observed, but in the presence of palladium or rhenium compounds (18). The electron withdrawing properties of the *meta*-CF_3 groups of the phenyls presumably promote the cyclization of **3**, which occurs spontaneously at room temperature. The Diels-Alder reaction is competitive with the intramolecular cyclization only at higher concentrations (>0.5 M) of ligand.



On a smaller scale, the cleanest and most straightforward way to access yttrium complexes containing the deprotonated form of ligand **3** is to prepare the chloride complex (CpO)YCl(THF)$_n$ (**5a**: n = 2; **5b**: n = 1, HCpOH = **3**) from **3** and $[Y\{N(SiMe_3)_2\}_2(THF)(\mu\text{-}Cl)]_2$, where the latter is prepared in situ from YCl_3 and $Y[N(SiMe_3)_2]_3$ in THF (Scheme 2). Reactions under 1 mmol in scale afford **5** in high yield (70–80%), but larger scale reactions generate oily by-products that must be separated by recrystallization from toluene–hexane mixtures. In general, all yttrium complexes containing the Cp-alkoxide derived from **3** exhibit lower melting points and much higher solubilities in hydrocarbons than their analogues derived from **1** (6). These observations suggest that intermolecular packing interactions or weak bridging interactions have been disrupted by the addition of another CH_2 unit in the ligand backbone.

Reaction of **5** with 1 equiv of $NaN(SiMe_3)_2$ initially forms a silyamide complex as the *bis*(THF) adduct (**6a**) (Scheme 2), which readily loses one coordinated THF to give the *mono*(THF) adduct (**6b**) under vacuum. NMR data

Scheme 2. (*a*) THF, 80°C, 2 h; (*b*) $NaN(SiMe_3)_2$, toluene, 70°C, 2 h; (*c*) $Li(O\text{-}2,6\text{-}C_6H_3(t\text{-}Bu)_2)$, toluene, 20°C, 2 h; (*d*) $LiCH(SiMe_3)_2$, toluene, 20°C, 2 h.



supports mirror plane symmetry for the *bis*(THF) complex (**6a**). Chemical shifts are essentially unchanged between the *bis* and *mono*(THF) adducts, suggesting that exchange of coordinated THF is rapid at room temperature. The two methylene carbons of the backbone show distinct resonances in the ^{13}C NMR, but their respective proton resonances are coincidental and show a broad singlet of integration 4 at δ = 2.32 ppm in the ^1H NMR.

X-ray quality crystals of **6b** were obtained through slow evaporation of a hexane solution of the *bis*(THF) adduct **6a**. The solid-state structure of **6b** is shown in Fig. 2, crystallographic data are summarized in Table 1, and selected bond distances and angles are presented in Table 2. The geometry at yttrium is best described as pseudo-tetrahedral with a single THF occupying the fourth coordination site. The formal coordination number at yttrium is 6, reduced from the 7-coordinate environment found in $\{\eta^5\text{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3\}\{THF\}_2$ (6). The bite angle of the Cp^{cent}-Y-O (105.3(9)°) unit in **6b** is opened significantly compared with the phenoxide above Cp^{cent}-Y-O (93.77(13)°) or $\{\eta^5\text{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}_2Y^-\ Li^+\{THF\}_2$ Cp^{cent}-Y-O (95.69(13)°), as expected for the increased backbone chain length. This change is more dramatic than that seen in the analogous amido systems $[Y(\eta^5\text{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}H)(THF)]_2$ (4(*e*)) and $[Y(\eta^5\text{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(\mu\text{-}H)(THF)]_2$ (11), where the change in bite angle was only 7.0°. The average Y—Cp^{cent} distance is 2.339(14) Å, slightly shorter than that in $\{\eta^5\text{:}\eta^1\text{-}C_5H_4[CH_2C(O)(3,5\text{-}C_6H_3(CF_3)_2)_2]\}Y\{O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3\}\{THF\}_2$ (Y—Cp^{cent} = 2.400(5) Å) as a consequence of the reduced coordination number (CN) of **6b** (Y^{3+}: 1.04 Å, CN 6; 1.10 Å, CN 7). The yttrium nitrogen bond length Y(1)—N(1) of 2.207(8) Å of the *bis*(trimethylsilyl)amido group is comparable to that found in the homoleptic silylamide $Y[N(SiMe_3)_2]_3$ (Y—N 2.224(6) Å) (19).

Fig. 2. ORTEP3 (16) plot for **6b** (40% probability, fluorine atoms omitted for clarity).

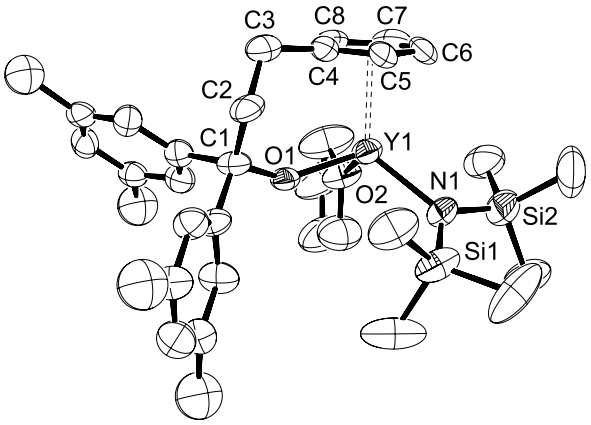


Table 1. Crystallographic data for **6b**.

	6b
Empirical formula	$C_{34}H_{40}F_{12}NO_2Si_2Y$
Formula weight	867.75
Crystal system	Monoclinic
Space group	$P2_1/a$ (No. 14)
a (Å)	10.3467(7)
b (Å)	33.260(3)
c (Å)	12.603(2)
β (°)	108.118(10)
V (Å^3)	4122.1(8)
Z	4
$D_{calcd.}$ (g cm^{-3})	1.40
Absorption coefficient (μ) (cm^{-1})	33.1
Radiation, λ (Å)	Cu Kα, 1.5418
T (K)	293
$2\theta_{max}$ (°)	100.0
Reflections collected	4570
Independent reflections	4330
R^a, $R_w{}^b$	0.074, 0.040

$^aR = \Sigma(|F_o|\text{-}|F_c|)/\Sigma|F_o|$.
$^bR_w = [\Sigma w(|F_o|\text{-}|F_c|^2)/\Sigma w(|F_o|)^2]^{1/2}$.

The phenoxide **7a** was formed cleanly from the reaction of **5** with 1 equiv of $LiO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ (Scheme 2) as the *bis*(THF) adduct, according to ^1H NMR spectroscopy. Coupling to ^{89}Y was observed in the ^{13}C NMR for both the *ipso*-phenoxide ($^2J_{YC}$ = 5.0 Hz) and the ligand YO*C* ($^2J_{YC}$ = 3.8 Hz) carbons. Elemental analysis supports facile loss of THF, as only the *mono*(THF) adduct (**7b**) was observed after exposure to vacuum.

Replacement of the phenoxide with more reactive hydrocarbyls was not successful by metathesis with $LiCH(SiMe_3)_2$ or $LiCH_2SiMe_3$, as the complex would not eliminate lithium phenoxide. Reaction of **5** with 1 equiv of

Table 2. Selected bond distances (Å) and angles (°) for **6b**.

Bond distances			
Y1—O1	2.060(6)	Y1—O2	2.299(7)
Y1—N1	2.207(8)	Y1—C4	2.627(11)
Y1—C5	2.610(10)	Y1—C6	2.603(11)
Y1—C7	2.629(12)	Y1—C8	2.640(11)
Y1—Cp^{cent} [a]	2.339(14)		
Bond angles			
Cp^{cent}-Y1-O1	105.3(9)	Cp^{cent}-Y1-O2	114.0(5)
Cp^{cent}-Y1-N1	122.5(9)	O1-Y1-O2	92.8(3)
O1-Y1-N1	113.3(3)	O2-Y1-N1	104.8(3)
Y1-O1-C1	145.1(6)	Y1-N1-Si1	119.6(4)
Y1-N1-Si2	118.4(5)	Si1-N1-Si2	121.9(5)

[a] Cp^{cent} represents the centroid of the C5 ring (C4-C8).

$LiCH(SiMe_3)_2$, however, readily forms the alkyl complex **8a** (Scheme 2) as a *bis*(THF) adduct, which again loses THF under vacuum to give a *mono*(THF) adduct (**8b**). Complex **8b** was produced in good yield, and both elemental analysis and NMR confirmed the degree of THF solvation. The Cp region of the ^{1}H NMR spectrum of **8b** is broadened somewhat at room temperature, but it sharpens to a pair of multiplets at 80°C, consistent with mirror plane symmetry. Amazingly, no noticeable decomposition of the alkyl complex was observed with repeated heating during the VT analysis. This is an interesting observation, since alkyl complexes of lanthanides are usually thermally unstable. Yttrium coupling was again observed for the alkoxy carbon of the ligand ($^2J_{YC}$ = 3.7 Hz) in the ^{13}C NMR of **8b**.

Discussion

Changing the length of the tether connecting the Cp and alkoxide functionality in the CpO ligand system has profound effects on the type of lanthanide complexes obtained. Extension of the chain by just one CH_2 unit (going from ligands based on **1** (6) to those based on **3**) completely avoids the problems associated with formation of anionic "ate" complexes. In fact, despite repeated attempts, we could not prepare the *bis*(ligand) "ate" complex $(CpO)_2Y^-$ Li^+ for the CpO ligand containing a two-carbon tether, whereas we had great difficulty *avoiding* this complex for the one-carbon tether ligand **1**. The neutral complexes (**5**–**8**) obtained here with the two-carbon tether show no tendency to undergo ligand redistribution reactions.

Despite the success in obtaining neutral, monomeric yttrium complexes, however, silylamide **6b** is not an active catalyst for ε-caprolactone polymerization, and the alkyl **8b** shows very modest oligomerization activity only. Complex **8b** shows no activity as an olefin polymerization catalyst. The reasons for this are not entirely clear, although the presence of coordinated THF may be expected to decrease activity. Related $(CpO)ZrCl_2$ complexes show very high ethylene polymerization activity for complexes containing the shorter tether (ligand **1**) (20),[4] so it seems unlikely that the perfluorophenyl substituted alkoxide is itself detrimental to insertion. Studies to examine the effects of longer chain tethers and replacement of the CF_3 substituents with CH_3 groups are continuing. We hope that these studies will clarify the reasons for the low insertion activity observed here. In addition, we are also investigating the use of complexes like **5** and **7** as Lewis acid catalysts.

Acknowledgements

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[4] $(CpO)ZrCl_2$, 1000 equiv MAO, 50°C, 3 atm ethylene: 4500 kg polyethylene [mol Zr]$^{-1}$ h^{-1} (M_w = 7.5 × 10^5 amu, M_w/M_n = 3.5) for CpO = $C_5H_4(CH_2)C(O)(3,5\text{-}C_6H_3(CF_3)_2)$; 80 kg polyethylene [mol Zr]$^{-1}$ h^{-1} for CpO = $C_5H_4(CH_2CH_2)C(O)(3,5\text{-}C_6H_3(CF_3)_2)$.

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