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Super-size Cp! Tetrabenzo[a,c,g,i]fluorenyl Complexes of Yttrium.

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Abstract

The synthesis of the tetrabenzo[a,c,g,i]fluorenyl (Tbf) yttrium dialkyl complexes, (Tbf)Y(CH₂SiMe₃)₂(L) (L = THF, **1**; L = bipy, **2**) by direct protonolysis of the *tris*(alkyl) complex, Y(CH₂SiMe₃)₃(THF)₂, are reported. The X-ray crystal structures of **1** and **2** display the helical twisting typically observed for the Tbf ligand. Dynamic NMR studies on **1** show a barrier to Tbf helical inversion (epimerization or ‘wagging’) of 38.1 ± 0.5 kJ mol⁻¹. Reaction of **1** with acidic hydrocarbons such as 1,3-*bis*(trimethylsilyl)cyclopentadiene or trimethylsilylacetylene results in protonolysis to form the mixed Cp derivative [(Tbf){C₅H₃(SiMe₃)₂}Y(CH₂SiMe₃)(THF)] (**3**) or [(Tbf)Y(CCSiMe₃)₂(THF)]_n (**4**), respectively. In the case of **4**, a small amount of the trinuclear cluster (Tbf)Y₃(μ³-CCSiMe₃)₂(μ²-CCSiMe₃)₃(CCSiMe₃)₃(THF)₂ (**5**) was isolated and characterized by X-ray crystallography. Dialkyl **1** undergoes smooth insertion of trimethylsilyl isocyanate to afford [(Tbf)Y{κ²-(N,O)-Me₃SiN(Me₃SiCH₂)CO}₂(THF)] (**6**) but it does not react with alkenes. Treating **1** with [Ph₃C]⁺[B(C₆F₅)₄]⁻ in bromobenzene generates a moderately active ethylene polymerization catalyst (36 kg mol⁻¹ h⁻¹ bar⁻¹).

Keywords: yttrium, bulky cyclopentadienyl ligand, fluorenyl, X-ray, alkyl, insertion, organometallic, synthesis

Dedication

This contribution is dedicated to Professor Reginal H. Mitchell, an inspirational teacher, gifted researcher and exceptional colleague: I feel exceptionally fortunate to have known you in all these roles.

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Introduction

Cyclopentadienyl (Cp) ligands have long been the dominant ancillary ligand in lanthanide organometallic chemistry with those bearing additional alkyl, silyl or phenyl substituents being especially prominent.¹ Substituted Cp ligands are widely used because their larger size helps to prevent extensive bridging interactions and ligand redistribution reactions resulting in monomeric or dimeric complexes that are easier to characterize and generally more reactive. However, simply adding bulk to the Cp ligand, while effective at producing monomeric complexes, can also render the metal center in those same complexes so crowded that reactivity is hindered. This is mainly caused by the fact that the substituents can project into the metallocene wedge in complexes such as $\text{Cp}'_2\text{LnR}$ (Cp' = substituted Cp; Ln = Y or a lanthanide), rendering access to the metal center difficult.² To solve this problem, the effective steric bulk of the Cp ligand can be increased by fusing aromatic rings to the Cp core. This makes dimer formation difficult without blocking access to the metal center by small molecules, effectively creating a pocket of reactivity. This approach has been widely explored using indenyl and fluorenyl ligands in yttrium and lanthanide chemistry but even in these cases, bridging interactions can still occur.³ Surprisingly, fusing additional benzene rings to the Cp core has not been widely explored despite the potential benefits this might offer.⁴ This may be due to the perception that larger fused-aromatic systems would reduce the charge on the Cp core by delocalization, resulting in weaker binding to the lanthanide center. While there are some examples of ligand loss in larger π -systems, calculations have shown that the charge on the Cp core carbons is not substantially diminished by fusion of additional benzene rings to a fluorenyl anion.^{4a,5}

We have been exploring yttrium and lanthanide chemistry of large aromatic anions including the phenanthrene-fused Cp derivatives, PCp^{R} , and the large non-Cp aromatic phenalenide anion, Pn^{R} (Fig. 1).^{6,7} Only the PCp^* ligand (Fig. 1b) always forms monomeric, *mono*(ligand) complexes but

ligand loss is only a feature of the chemistry of the Pn^{R} supported complexes.⁷ These observations suggested that the larger tetrabenzo[a,c,g,i]fluorenyl anion (Tbf, Fig. 2) might be an ideal ligand candidate for yttrium chemistry. This ligand system has been used successfully in titanium chemistry and recently it has been shown that ammonium salts of the Tbf⁻ anion are stable in water.^{8,9} In this contribution we show that this is indeed the case: the Tbf ligand system allows formation of highly stable complexes of the type, $(\text{Tbf})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{L})$ ($\text{L} = \text{THF}$, bipy) that do not undergo redistribution. The synthesis, solid state and solution structure, and reactivity of this complex are discussed.

Fig. 1 Large aromatic anions

Fig. 2 The tetrabenzo[a,c,g,i]fluorenyl anion including numbering for NMR assignments

2. Experimental

General Procedures. All manipulations were carried out under a nitrogen atmosphere using Schlenk or glovebox (Braun MB150-GII) techniques. Tetrahydrofuran (THF) and diethyl ether

were dried by distillation from sodium benzophenone ketyl under nitrogen immediately prior to use. Hexane and toluene were dried and degassed using a Braun solvent purification system. $[Y(CH_2SiMe_3)_3(THF)_2]$ and the Tbf-H parent hydrocarbon were prepared according to literature procedures.^{10,11} 2,2'-Bipyridine, trimethylsilylisocyanate, trimethylsilylacetylene and trityl tetrakis(pentafluorophenyl)borate were purchased commercially and purified by recrystallization or distillation prior to use. All ^1H and ^{13}C NMR spectra were recorded on Bruker 300, 360 or 500 MHz spectrometers referenced to residual solvent resonances. ^{19}F , ^{11}B , and ^{29}Si NMR spectra were recorded on a Bruker AMX500 spectrometer referenced to external standards (CCl_3F , $BF_3(OEt_2)$ and $SiMe_4$ set to 0 ppm). All deuterated solvents were dried over activated 4Å molecular sieves and spectra were recorded using 5 mm tubes fitted with a Teflon valve (Brunfeldt). Melting points were recorded using a Büchi melting point apparatus and are not corrected.

$[(Tbf)Y(CH_2SiMe_3)_2(THF)]$ (1) A solution of Tbf-H (0.123 g, 0.34 mmol) in 5 mL toluene was added to a solution of $[Y(CH_2SiMe_3)_3(THF)_2]$ (0.170 g, 0.34 mmol) in 5 mL toluene at 0 °C. The reaction mixture was allowed to warm to room temperature overnight with rapid stirring followed by removal of solvent under vacuum. The Schlenk flask was transferred to the glovebox, 40 mL hexanes was added and the resulting solution was filtered through Celite. Evaporation of the filtrate under reduced pressure gave crude **1** as a yellow powder. Recrystallization of this solid from hexanes produced pale yellow crystals of **1** at -35 °C. Yield: 0.188 g (88%). Mp 134°C (dec). ^1H NMR (500 MHz, C_6D_6): δ 9.03 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, *8-arylH*), 8.40 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, *1-arylH*), 8.37 (m, 4H, *4,5-arylH*), 8.00 (s, 1H, *9-CpH*), 7.48 (m, 2H, *2-arylH*), 7.38-7.34 (m, 4H, *3,6-arylH*), 7.30 (m, 2H, *7-arylH*), 2.54 (br m, 4H, α - CH_2 THF), 0.59 (br m, 4H, β - CH_2 THF), 0.02 (s, 18H, $SiMe_3$), -0.98 (d, $^2J_{YH} = 3.1$ Hz, 4H, $Y-CH_2$); $^{13}C\{^1H\}$ NMR

(125MHz, C₆D₆): δ 131.11, 130.69, 130.06, 129.16, 128.11, 127.26, 126.88, 126.52, 125.90, 125.64, 125.11, 125.07, 124.21, 115.53 (*arylC*), 92.41 (CpCH), 70.40, 24.66 (THF), 37.92 (d, $^1J_{YC}$ = 45Hz, Y-CH₂), 4.34 (SiMe₃). Anal. Calcd. for C₄₁H₄₇OSi₂Y: C 70.26, H 6.76; found: C 70.31, H 6.67.

[(Tbf)Y(CH₂SiMe₃)₂(bipy)] (2) Addition of 0.030 g 2,2'-bipyridine (0.2 mmol) to 0.14 g **1** (0.2 mmol) in 10 mL toluene produced a dark red solution. Removal of the solvent under reduced pressure gave **2** as a red powder. Recrystallization of the powder from a hot mixture of toluene and hexanes afforded deep red crystals of pure **2**. Yield: 0.152 g (97%). Mp. 220 °C (dec.). ¹H NMR (500 MHz, C₆D₆): δ 8.60 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *8-arylH*), 8.28 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *1-arylH*), 8.28 (s, 1H, *9-CpH*), 8.18 (d, $^3J_{HH}$ = 8.4 Hz, 4H, *4,5-arylH*), 7.63 (d, $^3J_{HH}$ = 5.2 Hz, 2H, *6-bipyH*), 7.55 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *7-arylH*), 7.37 (m, 2H, *2-arylH*), 7.09 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *6-arylH*), 6.89 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *3-arylH*), 6.57 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, *4-bipyH*), 6.36 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *3-bipyH*), 6.11 (t, 2H, $^3J_{HH}$ = 6.3 Hz, *5-bipyH*), 0.06 (s, 18H, SiMe₃), -0.82 (dd, $^2J_{YH}$ = 3.0 Hz, $^2J_{HH}$ = 11.5 Hz, 2H, YCH₂), -0.88 (dd, $^2J_{YH}$ = 3.0 Hz, $^2J_{HH}$ = 11.0 Hz, 2H, YCH₂). The ¹³C{¹H} NMR was not obtained due to the low solubility of this compound. Anal. Calcd. for C₄₇H₄₇N₂Si₂Y: C 71.92, H 6.04, N 3.57; found: C 70.55, H 6.00, N 3.71.

[(Tbf){(C₅H₃(SiMe₃)₂)₂Y(CH₂SiMe₃)(THF)] (3) Addition of a solution of H[C₅H₃(SiMe₃)₂] (0.120 g, 0.57 mmol) in 20 mL toluene was added to a solution of **1** (0.390 g, 0.556 mmol) in 10 mL toluene. The reaction mixture was allowed to stir at room temperature overnight followed by removal of solvent under vacuum. The residue was washed repeatedly with hexane and recrystallized from hot toluene to yield the mixed ligand complex **3** as a pale yellow powder (0.28 g, 61%). Mp 158 °C (dec). ¹H NMR (500 MHz, C₆D₆): δ 9.19 (d, 1H, *8-arylH*), 9.13 (d, 1H, *8'-arylH*), 8.41 (m, 2H, overlapping *1- and 1'-arylH*), 8.34 (~d, 2H, *arylH*), 8.32 (d, 1H,

arylH), 8.23 (d, 1H, *aryl H*), 7.77 (s, 1H, *9-CpH*), 7.51 (t, 1H, *arylH*), 7.44 (m, 2H, *arylH*), 7.29-7.39 (m, 5H, *arylH*), 6.19 (m, 1H, $J = 2.5$ Hz, $C_5H_3(SiMe_3)_2$), 5.70 (m, 1H, $J = 1.5$ Hz, $C_5H_3(SiMe_3)_2$), 4.61 (m, 1H, $J = 2.5$ Hz, $C_5H_3(SiMe_3)_2$), 2.25 (m, 2H, $\alpha-CH_2$ THF), 2.16 (m, 2H, $\alpha-CH_2$ THF), 0.50 (br m, 4H, $\beta-CH_2$ THF), 0.41 (s, 6H, $SiMe_3$), 0.35 (s, 3H, $SiMe_3$), 0.32 (s, 3H, $SiMe_3$), 0.07 (s, 9H, CH_2SiMe_3), 0.03 (s, 3H, $SiMe_3$), -0.02 (s, 3H, $SiMe_3$), -1.82 (dd, 1H, $^2J_{YH} = 3.7$ Hz, $^2J_{HH} = 10$ HZ, Y- CH_2SiMe_3), -2.16 (dd, 1H, $^2J_{YH} = 3.7$ Hz, $^2J_{HH} = 10$ HZ, Y- CH_2SiMe_3); $^{13}C\{^1H\}$ NMR (125MHz, C_6D_6): δ 131.87, 131.73, 130.50, 130.39, 130.08, 129.99, 129.90, 129.80, 129.66, 128.89, 127.86, 127.76, 127.70, 126.62, 126.55, 126.35, 126.28, 126.22, 125.57, 125.52, 125.28, 125.14, 124.94, 124.75, 124.56, 124.14, 121.89, 121.87, 121.70, 121.40, 121.06, 116.43, 114.57 (*arylC*), 91.65, (P^2CpCH), 70.97 ($\alpha-C$ THF), 25.82 (d, $^1J_{YC} = 40$ Hz, Y- CH_2), 24.48 ($\beta-C$ THF), 2.48, 1.58, 0.81, 0.36, -0.10, -0.30 ($C_5H_3(SiMe_3)_2$), 1.29 (CH_2SiMe_3). Anal. Calcd. for $C_{48}H_{57}OSi_3Y$: C 70.04, H 6.98; found: C 69.35, H 6.92.

[(Tbf)Y(CCSiMe₃)₂(THF)]_n (4) A solution of trimethylsilylacetylene (0.030 g, 0.31 mmol) in 1 mL hexane was added dropwise to a vigorously stirred solution of **1** (0.043 g, 0.061 mmol) in 5 mL hexane. The mixture immediately became cloudy and after stirring overnight, the solution was filtered through Celite and the solvent removed under reduced pressure to afford a pale yellow powder, **4**. Yield: 0.030 g (68%). Mp 125-8 °C (dec). ^1H NMR (500 MHz, C_6D_6): δ 9.86 (d, $^3J_{HH} = 8.3$ Hz, 2H, *8-arylH*), 8.72 (dd, $^3J_{HH} = 7.9$ Hz, 2H, *1-arylH*), 8.59 (s, 1H, *9-CpH*), 8.46 (d, 2H, $^3J_{HH} = 7.6$ Hz, *5-arylH*), 8.41 (d, $^3J_{HH} = 8.0$ Hz, 2H, *4-arylH*), 7.58 (m, 2H, *7-arylH*), 7.45 (m, 2H, *2-arylH*), 7.40 (m, 2H, *6-arylH*), 7.33 (m, 2H, *3-arylH*), 3.55 (br m, 4H, $\alpha-CH_2$ THF), 1.46 (br m, 4H, $\beta-CH_2$ THF), 0.21 (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 172.46 (d, $^1J_{YC} = 47.8$ Hz, Y-CCSiMe₃), 132.92, 131.16, 130.62, 129.88, 129.09, 127.03, 125.93, 125.86, 125.75, 125.54, 124.76, 123.71, 123.53, 116.87 (*arylC*), 111.95 (d, $^2J_{YC} = 8.8$ Hz, Y-CCSiMe₃), 98.99 (*9-CpCH*),

1.69 (SiMe₃). THF resonances in this complex overlap with the residual solvent resonances of d₈-THF at 68 and 25 ppm. Anal. Calcd. for C₄₃H₄₃OSi₂Y: C 71.64, H 6.01; found: C 71.18, H 5.89. Recrystallization of **3** from hot toluene resulted in formation of a small amount of well-formed crystals that proved, by X-ray crystallography (*vide infra*) to be the alkynide cluster compound, (Tbf)Y₃(μ³-CCSiMe₃)(μ²-CCSiMe₃)₃(CCSiMe₃)₄(THF)₂, **5**.

[(Tbf)Y{κ²-(N,O)-Me₃SiN(Me₃SiCH₂)CO₂(THF)}] (**6**) Me₃SiNCO (0.060 g, 0.50 mmol) was added to 0.070 g of **1** (0.10 mmol) in 10 mL toluene and the solution was allowed to stir at room temperature overnight. Evaporation of the solvent under vacuum afforded a pale yellow solid. Yield: 0.090 g (96%). ¹H NMR (300 MHz, C₆D₆): δ 9.22 (d, ³J_{HH} = 7.9 Hz, 2H, 8-arylH), 8.42-8.47 (m, 6H, 1,4,5-arylH), 7.90 (s, 1H, 9-CpH), 7.35-7.52 (m, 8H, 2,3,6,7-arylH), 2.99 (br m, 4H, α-CH₂ THF), 1.37 (s, 4H, CH₂SiMe₃), 1.01 (br m, 4H, β-CH₂ THF), 0.02 (s, 18H, CH₂SiMe₃), -0.22 (s, 18H, NSiMe₃); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 188.78 (NCO), 130.09, 128.70, 128.38, 127.57, 127.24, 126.11, 125.28, 125.07, 124.58, 124.25, 115.60 (arylC), 94.89 (CpCH), 69.53, 25.51 (THF), 30.89 (CH₂SiMe₃), 1.53 (CH₂SiMe₃), -0.22 (NSiMe₃). Anal. Calcd. for C₄₉H₆₅N₂O₃Si₄Y: C 63.19, H 7.03, N 3.01; found: C 63.33, H 7.08, N 2.78.

Alkyl abstraction product, 7 A solution of [Ph₃C]⁺[B(C₆F₅)₄]⁻ (0.030 g, 0.033 mmol) in 1 mL toluene was added to **1** (0.023 g, 0.033 mmol) in 3 mL toluene with vigorous stirring. The solution turned deep red immediately but the colour faded to pale peach within 30 minutes indicating complete formation of the cationic complex. The solvent was removed from the reaction mixture under reduced pressure and the oily solid was characterized by NMR. The ¹H NMR of this material was quite broad and consisted of many overlapping resonances and we were unable to remove these impurities by washing or recrystallization. ¹⁹F NMR (470.4 MHz, C₆D₅Br): δ -131.7 (br s, *ortho*-arylF), -161.8 (t, ³J_{FF} = 30 Hz, *para*-arylF), -165.7 (v br t, ³J_{FF} = 30 Hz, *meta*-arylF);

^{11}B NMR (160.4 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ -16.2; ^{29}Si NMR (99.3 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ -0.09, -1.33. On standing for several days, a few colourless crystals deposited in the NMR tube that proved by X-ray crystallography to be the $[\text{Tbf}]_2$ dimer **8** (*vide infra*).

Ethylene polymerization with 7. A solution of the alkyl abstraction product **7**, generated as described above in a Kontes flask, was frozen in liquid nitrogen and the headspace of the flask was evacuated for several minutes followed by introduction of ethylene gas (1 bar). The flask was removed from liquid nitrogen and the flask sealed and placed in a water bath at 20 °C. The reaction mixture turned yellow and a white precipitate formed. After 30 minutes, methanol was introduced resulting in a colour change to colourless. The precipitate was washed with 1M HCl and methanol before drying to constant weight at 60 °C under reduced pressure. The activity of **7** was calculated to be 36 kg polyethene $\text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$ (assuming the active species was $[(\text{Tbf})\text{Y}(\text{CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$).

X-ray crystallographic studies. Crystals of the compound to be examined were removed from a sealed glass ampoule under a nitrogen atmosphere and covered with a layer of Paratone oil. A suitable crystal was selected, attached to a MiTeGen fiber and placed in the low-temperature nitrogen stream.¹² Data for **1**, **2**, **5** and **8** were collected at low temperature (87(2)K for **1**, **5** and **8**; 185(2)K for **2**) using a Bruker/Siemens SMART APEX instrument (Mo $K\alpha$ radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 (**1**), 20 (**2**), 30 (**5**) or 60 (**8**) seconds, and a full sphere of data was collected. A total of 2450 (**1**, **5**, **8**) or 2400 (**2**) frames were collected with a final resolution of 0.77 (**1**), 0.83 (**2** and **8**) or 0.93 (**5**) Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software and refined using SAINTPlus¹³ on all observed reflections. Data reduction and correction for Lp and

decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.¹⁴ The structures were solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.¹⁵ The structures were solved in the space group $P2_1/n$ (No. 14) for **1**, **2** and **8** and in $P2_1/c$ (No. 14) for **5** by analysis of systematic absences. All atoms were refined anisotropically for **1**, **2** and **8**. For **5**, all non-hydrogen atoms were refined anisotropically except for the atoms of both THF molecules, C42 and C75 and the partially occupied ligand (HCCSiMe_3). The disordered THF groups in **5** were refined at 65% for the major moiety. No decomposition was observed during data collection. A summary of the basic crystallographic data is given in Table 1.

[Table 1]

3. Results and Discussion

Synthesis and Characterization. One equivalent of the parent ligand, Tbf-H, reacted smoothly with one equivalent of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ in toluene to produce the mono ligand complex $(\text{Tbf})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$, **1**, in good yield (Scheme 1). Attempts to generate the *bis* ligand complex using two equivalents of Tbf-H failed even under forcing conditions (heating at 80 °C for extended times), presumably indicating that the *mono* Tbf complex is the steric limit with yttrium as the metal. Adding 1 equivalent of 2,2'-bipyridine results in similar formation of the bipy adduct, $(\text{Tbf})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{bipy})$, **2**, in excellent yield. Complex **2** is considerably less soluble in toluene than **1**.

Scheme 1

Crystals of **1**, grown from hot toluene solution, were examined by X-ray crystallography. This complex was found to adopt a three-legged piano stool geometry in the solid state (Fig. 3, Table 2). The Y-C bond distances to the CH_2SiMe_3 groups (2.353(3), 2.360(3) Å) are slightly shorter than those previously reported for pseudo-tetrahedral $Cp^*Y(CH_2SiMe_3)_2(THF)$ complexes (median: 2.381 Å; range: 2.370-2.390 Å).^{6b,16} There is slight Tbf ring slippage towards η^3 (Δ_{slip} = average of 2 longest Y-C distances – average of 3 shortest Y-C distances = 0.08 Å) observable but the complex is best characterized as possessing an η^5 - Tbf ligand. In contrast, the bipy complex **2** adopts a distorted square pyramidal geometry with the Tbf ligand in the axial position (Fig. 4, Table 2). As expected, the Y-C bond distances to the CH_2SiMe_3 group (2.396(2), 2.423(2) Å) are longer than

Figure 3. ORTEP3¹⁹ diagram (50% probability level) for **1**

Figure 4 ORTEP3¹⁹ diagram (40% probability level) for **2**

[**Table 2.** Selected Bond Distances and Angles for **1** and **2**]

The Tbf ligand is clearly distorted in both **1** and **2** with the two ‘back’ benzene rings (those furthest from the unsubstituted Cp ring carbon: C12-C17 and C24-C29 in **1**; C9-C14 and C17-C22 in **2**) of each phenanthrene twisted relative to one another by 38.8° and 30.9°, respectively. The ‘front’ benzene rings, in contrast, are only twisted 6.1° (**1**) and 3.9° (**2**) relative to one another. Thus the twisting occurs between the ‘back’ benzene rings to minimize steric interactions between the 8 and 8’ hydrogens. This has been observed before in the free ligand and Cp-alkylated derivatives (range: 16.4-45.8°; median: 37.6°) and in lithium salts of the deprotonated Tbf ligand (29.8, 43.7°).^{8c,9,20} This makes the ligand chiral in the solid state but both enantiomers are present in the unit cells of these complexes by symmetry.

Interestingly, the ¹H NMR of **1** in benzene-*d*₆ or toluene-*d*₈ at room temperature shows only one resonance for the CH₂SiMe₃ methylene protons. This is not consistent with the structure observed

for **1** in the solid state because the highest possible symmetry (C_s) still leaves the methylene H of a given CH_2SiMe_3 group inequivalent. The most logical explanation for this is that THF exchange occurs rapidly in solution resulting in effective inversion at the yttrium centre. Indeed, cooling a sample of **1** to 225K in toluene- d_8 results in germinal inequivalence of the two CH_2 resonances indicating THF exchange is slow at this temperature (Fig. 5c). The fact that the complex retains C_s symmetry at 225K also clearly indicates that Tbf ‘wagging’ (helical inversion = epimerization) is still rapid at this temperature (Fig. 5a). However on further cooling, this motion slows and by 195K becomes slow on the NMR timescale. This can be seen in Fig. 5 for the CH_2 , SiMe_3 and the 8-aryl protons of the phenanthrene groups. Using the coalescence temperature for the 8 and 8'-protons or the SiMe_3 groups (Fig. 5a and 5b, respectively), a $\Delta G^\ddagger$ for the helical inversion of **1** can be calculated to be $38.1 \pm 0.5 \text{ kJ mol}^{-1}$.²¹

Figure 5 Variable temperature ^1H NMR spectra (500 MHz, toluene- d_8) for selected resonances of **1**: (a) 8,8'-Tbf; (b) $\alpha\text{-CH}_2$ resonances of THF (black arrow), SiMe_3 resonances (gray arrows); (c) Y- CH_2 resonances (black arrows, onset of geminal inequivalence CH_aH_b ; gray dashed arrows, decoalescence of pairwise related resonances, CH_a and CH_a').

Although **1** does not react further with additional Tbf-H, it does react overnight with 1,3- $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ in toluene to afford the mixed ligand complex, $[(\text{Tbf})\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})]$, **3**. This complex shows no tendency to undergo ligand redistribution even when heated at 80 °C for several days in benzene- d_6 . The reluctance of this compound to undergo ligand exchange no doubt stems from the inability to form *bis*(Tbf) complexes. However, this complex shows signs of considerable steric congestion in its own right as witnessed by the complete inequivalence of all six methyl groups of the two SiMe_3 groups on the 1,3- $(\text{Me}_3\text{Si})_2\text{Cp}$ ring by ^1H and ^{13}C NMR. Free rotation about the Y-Cp centroid would still leave the SiMe_3 groups different from each other but the observation of six distinct methyl environments indicates that these groups are locked in place and rotation around the Si-Cp_C bond is stopped at room temperature.

The acid-base (protonolysis) reaction of **1** with two equivalents of trimethylsilyl acetylene proceeds very rapidly at room temperature with formation of the alkynide complex, $[(\text{Tbf})\text{Y}(\text{CCSiMe}_3)_2(\text{THF})]_n$, **4**. The product precipitates as a toluene-insoluble powder so we assume that this is an oligomer containing alkynide bridging ligands. This complex does however dissolve readily in excess THF- d_8 and the presence of doublets for both the α - ($^1J_{\text{YC}} = 48$ Hz) and β -alkynide C ($^2J_{\text{YC}} = 9$ Hz) at 172.46 and 111.95 ppm, respectively, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, clearly indicates that **4** contains terminal alkynides in a monomeric structure.

Interestingly, while attempts to recrystallize **4** from hot toluene generally yielded microcrystalline powder, on one occasion, we were able to isolate a small amount of high quality crystals. The X-ray structure of these crystals, however, did not correspond to the bulk product **4** but instead represented a novel trimetallic cluster, **5**, containing one Tbf ligand and eight trimethylsilylacetylide anions, Fig. 6. The structure consists of a triangular arrangement of three

yttrium centres held together by two μ^3 -face bridging acetylides and three μ^2 -edge bridging acetylides. The coordination sphere of Y1 further consists of one Tbf ligand showing distinctive ring slippage towards η^3 -coordination ($\Delta_{\text{slip}} = 0.12 \text{ \AA}$) and a coordinated THF. The remaining coordination sites of the other two metal centres consist of two terminal acetylides (Y2) and one terminal acetylide with one coordinated THF (Y3). Additionally, the two μ^2 -acetylides bridging between Y1 and either Y2 or Y3 are tilted in such a way that the β -C of the acetylides are in close contact with Y2 or Y3, so that the alkyne π -system can interact with the Y centre, effectively increasing the coordination number from 6 to 7 (Y- β C distances: Y2-C36, 2.849(12) $\text{\AA}$; Y3-C45, 2.873(12) $\text{\AA}$). The μ^2 -acetylide bridging between Y2 and Y3 does not show close contact of the π -bond with either yttrium centre. Unlike, **1** and **2**, the cluster **5** shows significant twisting of the ‘front’ benzene rings (27.3° vs. 6.1° and 3.9° in **1** and **2**, respectively) relative to one another, indicating that this complex is more crowded at Y1. This is also evident from the long Y1-O(THF) distance of 2.350(8) $\text{\AA}$ compared to the Y3-O(THF) distance of 2.285(7) $\text{\AA}$. Overall however, the similarity in the Y-C(Tbf) bond lengths for Y1 to those in **1** and **2** suggest that the Y1 metal centre in **5** is not especially crowded.²²

Fig. 6 ORTEP3¹⁹ diagram (30% probability level) for **5**. Trimethylsilyl methyl groups and trimethylsilylacetylene of solvation removed for clarity.

[Table 3]

Reaction of **1** with 2 equivalents of trimethylsilylisocyanate (Me_3SiNCO) affords the double-insertion product $[(\text{Tbf})\text{Y}\{\kappa^2\text{-(N,O)-Me}_3\text{SiN(Me}_3\text{SiCH}_2\text{)CO}\}_2(\text{THF})]$, **6**. The ^1H NMR of **6** is consistent with either C_s or C_2 symmetry (the C_s isomer is depicted in Scheme 1). Other structures, including those with $\kappa^1\text{-O}$ or $\kappa^1\text{-N}$ bound ligands are also possible if rapid interconversion between ligand binding modes is occurring at room temperature. Similar insertion reactions with other isocyanates (xylyl, *i*-Pr) and isonitriles also readily occurred at room temperature but the products obtained were impure oily solids in all cases.

The neutral dialkyl **1** does not react with ethylene gas. In order to generate a more reactive alkyl, **1** was treated with an equivalent of trityl *tetrakis*(pentafluorophenyl)borate. It is presumed

that this leads to formation of a cationic complex such as **7** (Scheme 1), but the broad, uninformative ^1H NMR of the reaction mixture in bromobenzene- d_5 makes it impossible to establish the exact species present. The ^{19}F NMR of the $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion showed considerable broadening of the *o*- and *m*-aryl fluorines which might indicate a significant cation-anion interaction but without further evidence, we cannot say more.²³ In any case, we decided to see whether the reaction mixture formed on treatment with trityl *tetrakis*(pentafluorophenyl)borate would polymerize ethylene. Admission of ethylene gas (1 bar, 20°C) to the reaction mixture in bromobenzene resulted in formation of polyethylene at a very modest rate ($36 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$). The rate of polymerization observed here is substantially lower than observed in other yttrium alkyl systems.^{3a,24}

Interestingly, the reaction mixture formed from **1** and trityl *tetrakis*(pentafluorophenyl)borate in bromobenzene- d_6 slowly deposited a small amount of yellow plates that on examination by X-ray crystallography turned out to be the σ -dimer, $(\text{Tbf})_2$, **8** (Fig. 7). This dimer has been isolated previously and characterized by X-ray crystallography.^{8c} The C-C bond holding the dimer together (1.614(2) Å) is long indicating considerable steric congestion. As observed in all of the structures above, the ‘back’ benzene rings of both Tbf units are highly twisted (39.2°, 31.2°) while the ‘front’ benzene rings of one unit are twisted substantially and the other is not (17.0°, 3.2°).

Fig. 7 ORTEP3¹⁹ diagram (50% probability level) for **8**. Benzene-*d*₆ of solvation omitted for clarity.

[Table 4]

4. Concluding remarks The Tbf ligand system allows isolation of thermally stable *mono*(ligand) dialkyl complexes that do not undergo ligand redistribution reactions. These complexes do undergo acid-base (protonolysis) reactions with acidic hydrocarbons including smaller Cp derivatives and acetylenes. The dialkyl **1** will undergo insertion reactions with small unsaturated substrates such as isocyanates but it will not react directly with ethylene. Treatment of **1** with modest ethylene polymerization catalyst in bromobenzene. The ability to form *mono*(ligand) complexes that do not undergo extensive coordination polymer formation or ligand redistribution makes the Tbf ligand system a promising scaffold to further explore organolanthanide chemistry.

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

Materials for Depository. X-ray crystallographic data for **1** (CCDC Ref. No. 1487257), **2** (CCDC Ref. No. 1487258), **5** (CCDC Ref. No. 1487259) and **8** (CCDC Ref. No. 1487260) are available (53 pages).

Draft

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Table of Contents Graphic

Table 1. Crystallographic data for [Y(Tbf)(CH₂SiMe₃)₂(THF)] (**1**), [Y(Tbf)(CH₂SiMe₃)₂(bipy)] (**2**), [Y₃(Tbf)(CCSiMe₃)₈(THF)₂]·(0.5 HCCSiMe₃) (**5** · 0.5 HCCSiMe₃) and [Tbf]₂·(0.5 C₆D₆) (**8** · 0.5 C₆D₆)^a

	1	2	5	8
Empirical formula	C ₄₁ H ₄₇ OSi ₂ Y	C ₄₇ H ₄₇ N ₂ Si ₂ Y	C _{79.5} H ₁₁₀ O ₂ Si _{8.5} Y ₃	C ₆₁ H ₃₄ D ₃
Formula weight	700.9	785.0	1603.2	769.9
Temperature (K)	86(2)	185(2)	87(2)	87(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	13.797(3)	11.187(2)	16.685(2)	13.7548(7)
<i>b</i> (Å)	14.840(3)	21.195(3)	14.417(2)	19.4105(10)
<i>c</i> (Å)	18.047(3)	17.318(3)	38.023(5)	15.0190(8)
β (°)	100.77(3)	107.676(15)	98.696(2)	109.039(1)
Volume (Å ³)	3630.0(13)	3912.6(11)	9041.3(19)	3790.5(3)
<i>Z</i>	4	4	4	4
Density (calc., g/cm ³)	1.282	1.333	1.178	1.349
Absorption coeff. μ (mm ⁻¹)	1.703	1.588	2.061	0.076
<i>F</i> (000)	1472	1640	3356	1612
Crystal size (mm)	0.42 x 0.17 x 0.07	0.34 x 0.26 x 0.17	0.29 x 0.08 x 0.04	0.20 x 0.20 x 0.09
Crystal color and habit	colourless plate	orange-red block	colourless needle	yellow needle
Theta range (°)	1.71 to 27.61	1.56 to 25.25	1.51 to 22.50	1.74 to 25.25
Reflections collected	47751	58200	75831	57955
Independent reflections	8414	7080	11808	6864
Max. and min. transmission	0.89 and 0.53	0.77 and 0.61	0.92 and 0.59	0.99 and 0.98
Data / restraints / parameters	8414 / 0 / 412	7080 / 0 / 475	11808 / 72 / 861	6864 / 0 / 562
Goodness-of-fit on <i>F</i> ²	1.011	1.032	1.085	1.024

Final R indices [$I > 2\sigma(I)$]	R1 = 0.046, wR2 = 0.092	R1 = 0.032, wR2 = 0.078	R1 = 0.093, wR2 = 0.21	R1 = 0.040, wR2 = 0.087
R (all data)	R1 = 0.082	R1 = 0.040	R1 = 0.16	R1 = 0.061
Largest diff. peak and hole	0.760 and -0.468 e/Å ³	0.48 and -0.22 e/Å ³	1.68 and -0.98 e/Å ³	0.22 and -0.23 e/Å ³

^a Data was collected on a Bruker / Siemens SMART APEX diffractometer.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for
 $[(\text{Tbf})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ (**1**) and $[(\text{Tbf})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{bipy})]$ (**2**).^a

Bond Distances			
1		2	
Y(1)—Cp1	2.396	Y(1)—Cp1	2.443
Y(1)—C(1)	2.641(3)	Y(1)—C(1)	2.640(2)
Y(1)—C(2)	2.645(3)	Y(1)—C(2)	2.689(2)
Y(1)—C(3)	2.667(3)	Y(1)—C(15)	2.804(2)
Y(1)—C(4)	2.765(3)	Y(1)—C(16)	2.780(2)
Y(1)—C(5)	2.699(3)	Y(1)—C(29)	2.721(2)
Y(1)—O(1)	2.307(2)	Y(1)—N(30)	2.519(2)
Y(1)—C(30)	2.360(3)	Y(1)—N(41)	2.469(2)
Y(1)—C(34)	2.353(3)	Y(1)—C(42)	2.396(2)
		Y(1)—N(2)	2.423(2)
Bond Angles			
Cp1—Y(1)—O(1)	113.9	Cp1—Y(1)—N(30)	103.6
Cp1—Y(1)—C(30)	119.5	Cp1—Y(1)—N(41)	107.5
Cp1—Y(1)—C(34)	117.9	Cp1—Y(1)—C(42)	117.3
O(1)—Y(1)—C(30)	102.76(9)	Cp1—Y(1)—C(46)	113.0
O(1)—Y(1)—C(34)	95.28(10)	N(30)—Y(1)—N(41)	64.49(6)
C(30)—Y(1)—C(34)	103.93(11)	N(30)—Y(1)—C(42)	136.11(7)
Y(1)—C(30)—Si(1)	135.4(2)	N(30)—Y(1)—C(46)	85.69(7)
Y(1)—C(34)—Si(2)	129.3(2)	N(41)—Y(1)—C(42)	87.48(7)
		N(41)—Y(1)—C(46)	134.28(7)

$$\text{C}(42)\text{—Y}(1)\text{—C}(46) \quad 92.24(8)$$

$$\text{Y}(1)\text{—C}(42)\text{—Si}(1) \quad 150.50(12)$$

$$\text{Y}(1)\text{—C}(46)\text{—Si}(2) \quad 115.24(10)$$

^a estimated standard deviation in parentheses; Cp¹ is the centroid of C(1)-C(5) for **1** and C(1), C(2), C(15), C(16), C(29) for **2**.

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Table 3. Selected Bond Distances (Å) and Angles (deg) for
 $[Y_3(Tbf)(CCSiMe_3)_8(THF)_2] \cdot (0.5 HCCSiMe_3) (5 \cdot 0.5 HCCSiMe_3)^a$

Bond Distances			
Y(1)—Cp1	2.426	Y(2)—C(35)	2.552(12)
Y(1)—C(1)	2.657(11)	Y(2)—C(49)	2.340(14)
Y(1)—C(2)	2.6791(11)	Y(2)—C(54)	2.394(13)
Y(1)—C(15)	2.773(11)	Y(2)—C(59)	2.517(13)
Y(1)—C(16)	2.721(11)	Y(2)—C(64)	2.656(12)
Y(1)—C(29)	2.610(11)	Y(3)—O(2)	2.285(7)
Y(1)—O(1)	2.350(8)	Y(3)—C(30)	2.668(12)
Y(1)—C(30)	2.500(13)	Y(3)—C(44)	2.515(12)
Y(1)—C(35)	2.463(13)	Y(3)—C(59)	2.400(13)
Y(1)—C(44)	2.530(14)	Y(3)—C(64)	2.504(12)
Y(1)—C(64)	2.563(13)	Y(3)—C(69)	2.364(14)
Bond Angles			
Y(1)—C(30)—Y(3)	87.3(4)	Y(1)—C(64)—Y(2)	91.2(4)
Y(1)—C(35)—Y(2)	96.1(4)	Y(1)—C(64)—Y(3)	89.6(4)
Y(1)—C(44)—Y(2)	90.1(4)	Y(2)—C(64)—Y(3)	89.6(4)
Y(2)—C(59)—Y(3)	95.5(4)		
Non-bonding Distances and Angles			
Y(1) ... Y(2)	3.730(2)	Y(1) ... Y(2) ... Y(3)	57.95(3)
Y(1) ... Y(3)	3.570(2)	Y(2) ... Y(3) ... Y(1)	62.33(3)
Y(2) ... Y(3)	3.637(2)	Y(3) ... Y(1) ... Y(2)	59.71(3)

^a estimated standard deviation in parentheses; Cp¹ is the centroid of C(1, 2, 15, 16, 29)

Table 4. Selected Bond Distances (Å) and Dihedral Angle (deg) for [Tbf]₂, 8.^a

Bond Distances			
C(1)—C(1')	1.614(2)	C(2)—C(15)	1.373(2)
C(1)—C(2)	1.524(2)	C(15)—C(16)	1.483(2)
C(1)—C(29)	1.506(2)	C(16)—C(29)	1.369(2)
Dihedral Angle			
Ar1—Ar2		31.2	

^a estimated standard deviation in parentheses; Ar1 is the plane defined by C(9)-C(14) and Ar2 is the plane defined by C(17)-C(22)