Synthesis, Structure, and Polymerization Activity of Neutral Halide, Alkyl, and Hydrido Yttrium Complexes of Isopropylidene-Bridged Cyclopentadienyl-Fluorenyl Ligands

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Reactions of the anionic complex $[(Cp\text{-}CMe_2\text{-}Flu)YCl_2]^-[Li(ether)_4]^+$ (**1**) ($Cp = C_5H_4$, $Flu = 9\text{-}C_{13}H_8$), prepared in situ from $YCl_3(THF)_{3.5}$ and 1 molar equiv of the dilithium salt $[Cp\text{-}CMe_2\text{-}Flu]Li_2$, with equimolar amounts of RLi give alkyl mono-THF complexes $[(Cp\text{-}CMe_2\text{-}Flu)]Y(R)(THF)$ ($R = CH(SiMe_3)_2$, **3**; CH_2SiMe_3, **4**) in high yields. The solid-state structure of **3** was established by X-ray diffraction, showing the fluorenyl moiety symmetrically coordinated to yttrium in an intermediary η^3-η^5 mode. Hydrogenolysis of **3** and **4** with H_2 or $PhSiH_3$ gives the hydride $\{[(\mu{:}\eta^5,\eta^5\text{-}Cp\text{-}CMe_2\text{-}Flu)]Y(\mu\text{-}H)(THF)\}_2$ (**5**). The solid-state structure of **5** was determined by X-ray diffraction, revealing a dimeric structure with both bridging $Cp\text{-}CMe_2\text{-}Flu$ and hydride ligands (Y−H = 1.99(4)−2.01(4) Å). Complex **5** is the first structurally characterized example of a group 3 metal hydride stabilized by a fluorenyl ligand. Reaction of **1** with $PhCH_2MgBr$ gives, instead of a benzyl derivative, the neutral base-free bromo complex $\{[(\eta^5,\eta^5\text{-}Cp\text{-}CMe_2\text{-}Flu)]Y(\mu\text{-}Br)\}_2$ (**6**), which shows a dimeric structure in the solid state with chelating $Cp\text{-}CMe_2\text{-}Flu$ and bridging bromide ligands. Introduction of the bulky *tert*-butyl substituent on the Cp ring of the ligand system enabled the preparation of the neutral chloro complex $[(3\text{-}^t\text{BuCp})\text{-}CMe_2\text{-}Flu]YCl(THF)$ (**7**), using a salt elimination between the dilithium salt of the ligand and $YCl_3(THF)_{3.5}$. Reaction of **7** with $LiCH(SiMe_3)_2$ gives the alkyl complex $\{[(3\text{-}^t\text{BuCp})\text{-}CMe_2\text{-}Flu)]Y(CH(SiMe_3)_2)$ (**8**), which contains no THF molecule in its coordination sphere in contrast to unsubstituted analogues **3** and **4**. Preliminary studies of the catalytic activity of these new complexes for ethylene and MMA polymerization are reported.

Introduction

Single-carbon-bridged fluorenyl/cyclopentadienyl ligands $[Cp\text{-}CR_2\text{-}Flu]^{2-}$ ($Cp = 1,3\text{-}C_5H_3R'$ with $R' = H$, ^{t}Bu, $SiMe_3$; R = Me, Ph; $Flu = 9\text{-}C_{13}H_8$) are of high interest for the elaboration of early transition metal catalysts for stereospecific polymerization of α-olefins. A large variety of group 4 *ansa*-metallocenes bearing this type of ligands have been developed, and some of them were shown to produce highly syndiotactic polypropylene with remarkable catalytic performance of industrial relevance.[1] The preparation of related complexes based on group 3 metals is often hampered by synthetic difficulties in accessing potentially useful species, i.e., neutral alkyls, amides, or even halogeno derivatives.[2] Qian et al. have described salt elimination reactions between alkali metal salts of the diphenylcarbon-bridged ligand $[Cp\text{-}CPh_2\text{-}Flu]M_2$ (M = Li, K) and $LnCl_3(THF)_n$ (Ln = Y, Lu) precursors that give ionic complexes $[(\eta^5,\eta^5\text{-}Cp\text{-}CPh_2\text{-}Flu)LnCl_2]^-[Li(THF)_4]^+$.[3] The latter are converted to the corresponding neutral amido complexes by subsequent reaction with $LiN(SiMe_3)_2$.[4] The chemistry of isopropylene-bridged ligands turned out to be more delicate. We have shown that amine elimination reactions of homoleptic amides $Ln[N(SiMe_3)_2]_3$ (Ln = Y, La, Nd) with the diprotio ligand $CpH\text{-}CMe_2\text{-}FluH$ lead to the formation of the *ansa*-

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(1) (a) Alt, H.; Kopple, A. *Chem. Rev.* **2000**, *100*, 1205, and references therein. (b) Even, J. A.; Jones, L. R.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6256. (c) Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **2001**, *621*, 267. (d) Razavi, A.; Ferrara, J. *J. Organomet. Chem.* **1992**, *435*, 299.

(2) For lanthanide complexes supported by silylene-bridged fluorenyl/cyclopentadienyl ligands, see: (a) Lee, M. H.; Hwang, J.-W.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 5124. (b) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080. (c) Qian, C.; Nie, W.; Sun, J. *Organometallics* **2000**, *19*, 4134. (d) Nie, W.; Qian, C.; Chen, Y.; Sun, J. *J. Organomet. Chem.* **2002**, *21*, 3238.

(3) Qian, C.; Nie, W.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1999**, 3283.

(4) Qian, C.; Nie, W.; Chen, Y.; Sun, J. *J. Organomet. Chem.* **2002**, *645*, 82.

(5) Dash, A. K.; Razavi, A.; Mortreux, A.; Lehmann, C. W.; Carpentier, J.-F. *Organometallics* **2002**, *21*, 3238.

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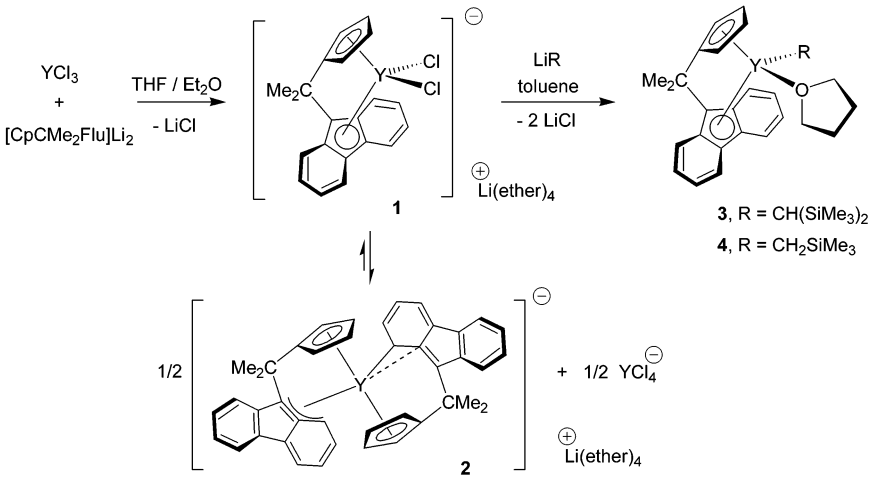
Scheme 1



metallocenes ($\eta,^5\eta^5$-Cp-CMe_2-Flu)Ln(η^5-Cp-CMe_2-FluH), instead of the desired amido complexes (η,η-Cp-CMe_2-Flu)Ln[$N(SiMe_3)_2$].[5] Also, we have recently reported that the salt elimination reaction between $YCl_3(THF)_{3.5}$ and 1 equiv of the dilithium salt [Cp-CMe_2-Flu]Li_2 gives a product, of which the elemental analysis is consistent with the formula "[(η,η-Cp-CMe_2-Flu)YCl_2]$^-$[Li(ether)$_4$]$^+$" (**1**) (ether = THF, Et_2O). However, crystallization of this product gives eventually the ionic, halogen-free bis(*ansa*)-metallocene complex [(η^5,η^3-Cp-CMe_2-Flu)(η^5,η^1-Cp-CMe_2-Flu)Y]$^-$[Li(Et_2O)$(THF)_3$]$^+$ (**2**), which features, in the solid state, unusual bonding modes for the fluorenyl moieties.[6] A similar chemistry was also observed for lanthanum. In this contribution, we describe efficient salt elimination routes toward various neutral yttrium alkyl and halogeno complexes of general formula [(3-RCp)-CMe_2-Flu]Y(Z)$(THF)_x$ (Z = Br, Cl, CH$(SiMe_3)_2$, CH_2SiMe_3; R = H, ^{t}Bu; x = 0, 1). The results give evidence of the striking influence of the R substituent on the Cp ring of the ligand system to control the ionic/neutral nature of the complexes and their coordination sphere, to attain solvent-free or solvated complexes. The first structurally characterized example of a hydride of a group 3 metal supported by a fluorenyl ligand is also reported.

Results and Discussion

Alkylation Reactions of [(Cp-CMe_2-Flu)YCl_2]$^-$[Li(ether)$_4$]$^+$ (1). Synthesis of [η^5,η^5-Cp-CMe_2-Flu]Y(CH$(SiMe_3)_2$)(THF) (3) and [η^5,η^5-Cp-CMe_2-Flu]Y(CH_2SiMe_3)(THF) (4). Salt metathesis of **1** with 1 equiv (vs Y) of LiCH$(SiMe_3)_2$ and $LiCH_2SiMe_3$ proceeds at room temperature in toluene solution to afford the neutral alkyl *ansa*-metallocenes [Cp-CMe_2-Flu]Y(R)(THF) (R = CH$(SiMe_3)_2$, **3**; CH_2SiMe_3, **4**) in 84 and 65% yields, respectively, with concomitant elimination of LiCl (Scheme 1).[7] Complex **3** was more conveniently prepared in a one-pot procedure by the reaction of $YCl_3(THF)_{3.5}$ with [Cp-CMe_2-Flu]Li_2 in diethyl ether, followed by treatment with LiCH$(SiMe_3)_2$ in toluene. These results indicate that, despite the disproportionation via ligand redistribution observed in the solid state upon crystallization of complex **1**,[6] the latter reacts in solution as a single Y−Cl species (Scheme 1). Both complexes **3** and **4** were found to be readily soluble in aromatic hydrocarbons (benzene, toluene), where they are thermally stable up to 60 °C for hours, and sparingly soluble in aliphatic ones (pentane, hexane). Their identity was formally established by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and an X-ray diffraction study for **3**.

Bright yellow crystals of **3** suitable for X-ray diffraction were obtained from a toluene/pentane mixture upon cooling at −30 °C. The crystallographic data are summarized in Table 1. The molecular structure of **3** (Figure 1) comprises a chiral yttrium atom coordinated in a pseudo-tetrahedral fashion by the fluorenyl and cyclopentadienyl groups of the ansa ligand, the bis(trimethylsilyl)methyl group, and a THF molecule. Overall, the geometry is similar to that described for (η^5,η^1-C_5Me_4-$SiMe_2$-NMe_2Et)Y(CH_2SiMe_3)(THF)[8] and (η^5:η^1-C_5Me_4-CH_2-$SiMe_2$-NMe_2Et)Y(CH_2SiMe_3)(THF).[9] The value of 2.448(2) Å for the Y(1)−C(30) bond length falls in the range of 2.36−2.49 Å observed for nonsolvated Y−CH$(SiMe_3)_2$ complexes.[10] Similarly, the Y(1)−O(21) bond of 2.323(1) Å is in the usual range of 2.32−2.46 Å found for similar THF-containing complexes.[11] The Cp ligand is η^5-bonded with an average Y(1)−C(11−15) bond distance of 2.629(2) Å, identical to that observed in complex **2**.[12] The coordinating mode of the fluorenyl

(6) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Kahlal, S.; Saillard, J.-Y.; Carpentier, J.-F. *Organometallics* **2003**, *22*, 4038.

(7) Alkane elimination between $Y(CH_2SiMe_3)_3(THF)_2$ and 1 equiv of CpH-CMe_2-FluH failed to give **4** but led instead to the formation of the bis(cyclopentadienyl) complex (η^5-Cp-CMe_2-FluH)$_2$Y(CH_2SiMe_3)-$(THF)_2$, with pendant fluorenyl moieties (see Experimental Section). The much lower acidity of the FluH moiety (pK_a = ca. 23) vs that of CpH (pK_a = ca. 16) likely accounts for this result.

(8) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228.

(9) Trifonov, A. A.; Spaniol, T.; Okuda, J. *Organometallics* **2001**, *20*, 4869.

(10) Y−C(alkyl) bond distances (Å): (a) {$Me_2Si(\eta^5$-$C_5Me_4)_2$}Y(CH$(SiMe_3)_2$): 2.418(6); Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *Inorg. Chim. Acta* **1996**, *242*, 205. (b) (*R*)-$Me_2(\eta^5$-$C_5Me_4)$[(+)-neomenthylCp]Y(CH$(SiMe_3)_2$): 2.49(1), (*S*)-$Me_2Si(\eta^5$-$C_5Me_4)$[(+)-neomenthylCp]Y(CH$(SiMe_3)_2$): 2.36(1); Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.

(11) Y−O(THF) bond distance (Å): (a) (η^5,η^1-C_5Me_4-$SiMe_2$-NMe_2-Et)Y(CH_2SiMe_3)(THF): 2.319(5), see ref 8. (b) (η^5,η^1-$C_5Me_4CH_2$-$SiMe_2$-NMe_2Et)Y(CH_2SiMe_3)(THF): 2.327(1), see ref 9.

(12) Average Y−C(Cp) bond distances (Å) in [(Cp-CMe_2-Flu)$_2$Y]$^-$[Li(Et_2O)$(THF)_3$]$^+$, monoclinic polymorph: 2.601(45), 2.645(8); triclinic polymorph: 2.611(45), 2.606(8); orthorhombic polymorph: 2.624(11), 2.629(12); see ref 6.

Table 1. Summary of Crystallographic Data

	3	**5**·0.5benzene	**6**·toluene
formula	$C_{32}H_{45}OSi_2Y$	$C_{53}H_{57}O_2Y_2$	$C_{49}H_{44}Br_2Y_2$
cryst size, mm	0.14 × 0.14 × 0.13	0.14 × 0.09 × 0.06	0.09 × 0.07 × 0.05
M, g mol^{-1}	590.77	903.81	970.48
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	16.4868(3)	9.74370(10)	9.2140(4)
b, Å	12.5071(2)	13.8585(2)	12.6316(6)
c, Å	14.4568(2)	15.8020(2)	17.4376(9)
α, deg	90	91.3700(10)	91.405(3)
β, deg	91.5030(10)	106.6200(10)	104.014(3)
γ, deg	90	92.7240(10)	90.455(2)
V, Å^3	2980.00(8)	2040.77(4)	1968.32(16)
Z	4	2	2
D_{calc}, g.cm^{-3}	1.317	1.471	1.637
T, K	100	100	100
θ range, deg	4.09−33.16	2.94−31.05	4.08−27.49
μ, mm^{-1}	2.0600	2.872	4.998
no. of measd reflns	45 456	51 442	17 479
no. of indep reflns	11 258	13 012	7840
no. of reflns with $I>2\sigma(I)$	8439	9681	4332
no. of params	333	533	483
goodness of fit	1.034	1.013	1.007
R [$I>2\sigma(I)$]	0.0469	0.0542	0.0722
wR^2	0.0887	0.1125	0.1302
lgst diff peak, hole, e Å^{-3}	−0.412/1.002	−1.177/1.173	−0.742/0.937

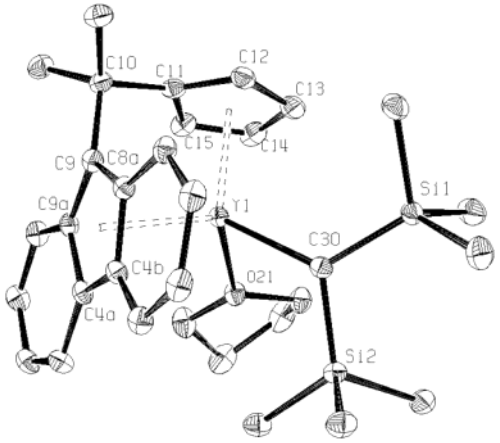


Figure 1. Molecular structure of [Flu-CMe$_2$-Cp]Y(CH(SiMe$_3$)$_2$)(THF) (**3**). Ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−O(21), 2.3233(13); Y(1)−Cp$_{cent}$, 2.339(2); Y(1)−Flu$_{cent}$, 2.478(2); Y(1)−C(30), 2.4478(19); Y(1)−C(12), 2.578(2); Y(1)−C(11), 2.5865(19); Y(1)−C(13), 2.661(2); Y(1)−C(14), 2.690(2); Y(1)−C(15), 2.6265(19); Y(1)−C(9), 2.6092(19); Y(1)−C(8A), 2.6572(18); Y(1)−C(9A), 2.7560(19); Y(1)−C(4B), 2.8729(18); Y(1)−C(4A), 2.9191(18); O(21)−Y(1)−C(30), 96.18(5); Flu$_{cent}$−Y(1)−Cp$_{cent}$, 110.85(6) (cent = centroids of C(11−15) and C(9−8A−4B−4A−9A)).

moiety is more obscure. A formal 16-electron count for those complexes of a general ML$_8$ type would rather point out the preferable η^5-coordination mode of the fluorenyl ligand. On the other hand, the bond distances between the Y(1) atom and the bridgehead C(9) atom and the two adjacent atoms C(8a) and C(9a) (2.609(2), 2.657(2), and 2.756(2) Å, respectively) are shorter than the two other bond distances Y(1)−C(4a) and Y(1)−C(4b) (2.919(2) and 2.873(2) Å), although the latter are still within the range of bonding interactions. A similar situation has been reported for the fluorenyl fragment in [η^5,η-Cp-SiMe$_2$-Flu)]YCl$_2$Li(Et$_2$O)$_2$ (Y−C(Flu) = 2.56(2), 2.66(2), 2.74(2), 2.95(2), and 2.96(2) Å)[2a] and, to a lesser extent, in [η^5,η-Cp-SiMe$_2$-Flu]Y(N(SiMe$_3$)$_2$) (Y−C(Flu) = 2.602(3), 2.707(3), 2.715(3), 2.787(4), and 2.788(4) Å).[2a] For both these complexes, a slipped coordination from a η^5 mode toward a η^3 hapticity was suggested.[2a] The issue of the fluorenyl hapticity for **3** in solution can be addressed also by ^{13}C NMR spectroscopy (vide infra). The constraint in the structure is illustrated by the narrow bite angle Flu$_{cent}$−Y(1)−Cp$_{cent}$ of 110.85°, a value that is similar to the corresponding ones observed in related single carbon-bridged cyclopentadienyl/fluorenyl *ansa*-metallocenes of small ionic radius metals.[13]

The ^{1}H NMR of **3** in toluene-d_8 at 25 °C features an unusually shielded alkyl resonance (δ −4.07, d, $^2J_{H-Y}$ = 2.4 Hz). This shielding is likely induced by the magnetic anisotropy of the fluorenyl group. The coordinated THF molecule in **3** is labile on the NMR time scale, as indicated by the temperature dependence of the chemical shifts of the THF methylene protons, which undergo substantial high-field shifts upon cooling over the temperature range −80 to 60 °C. The ^{1}H NMR signals of the THF methylene protons decoalesce at −10 °C (α-CH$_2$) and −30 °C (β-CH$_2$). These observations are in agreement with the existence of a THF-free species and a THF adduct, which interconvert via a dissociation equilibrium, fast on both the chemical and NMR time scales.[8] The temperature dependence of the equilibrium constant was obtained from the chemical shifts of α- and β-methylene protons (Figure 2).[14] An Eyring analysis gave Δ_rH = 28 ± 2 kJ mol^{-1} and Δ_rS = 58 ± 10 J K^{-1} mol^{-1} for **3** (Figure 3). The positive reaction entropy and enthalpy are in accordance with a dissociative process. The thermodynamic parameters for the "constrained geometry" complex described by Okuda et al. (C$_5$Me$_4$-SiMe$_2$-N^{t}Bu)Y(CH$_2$SiMe$_3$)(THF) are on the same order

(13) Cp$_{cent}$−M−Flu$_{cent}$ bite angles (deg): (a) [(η^5,η^5-Cp-CPh$_2$-Flu)-LuCl$_2$]$^-$[Li(THF)$_4$]$^+$, 112.25; [(η^5,η^5-Cp-CPh$_2$-Flu)Ln(BH$_4$)$_2$]$^-$[Li(THF)$_4$]$^+$, Ln = La, 103.83; Ln = Nd, 105.90; see ref 3. (b) (η^5,η^5-Cp-CMe$_2$-Flu)-Ln(η^5-Cp-CMe$_2$-FluH), Ln = La, 103.67; Ln = Nd, 105.08; see ref 5. (c) (η^5,η^5-Cp-CMe$_2$-Flu)MCl$_2$, M = Zr, 118.6; M = Hf, 119.4. (η^5,η^5-Cp-CPh$_2$-Flu)ZrCl$_2$, 117.6; see ref 1d.

(14) (a) Slejko, F. L.; Drago, R. S.; Brown D. G. *J. Am. Chem. Soc.* **1972**, *94*, 9210. (b) See also ref 8.

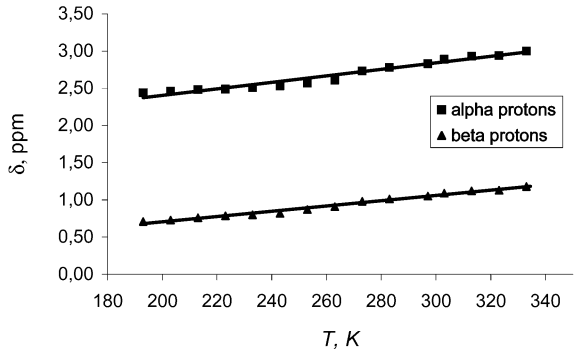


Figure 2. Temperature dependence of chemical shifts of the α- and β-CH_2 protons of the coordinated THF molecule in (Cp-CMe_2-Flu)Y($CH(SiMe_3)_2$)(THF) (**3**) in toluene-d_8.

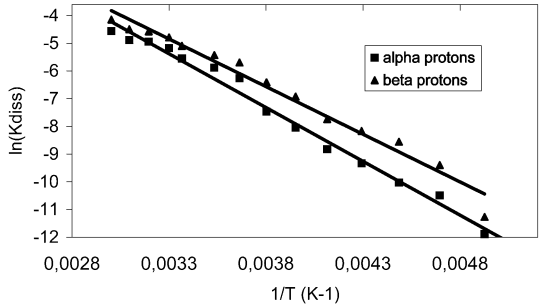


Figure 3. Plot of ln K_{diss} versus $1/T$ for hydrocarbyl complex **3**.

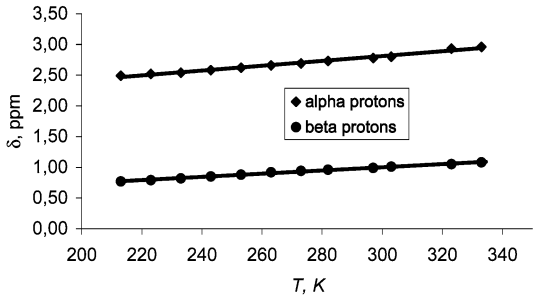


Figure 4. Temperature dependence of chemical shifts of the α- and β-CH_2 protons of the coordinated THF molecule in (Cp-CMe_2-Flu)Y(CH_2SiMe_3)(THF) (**4**) in toluene-d_8.

($\Delta_r H = 24 \pm 3$ kJ mol^{-1} and $\Delta_r S = 61 \pm 12$ J K^{-1} mol^{-1}).[8] The stronger binding of the THF molecule in **3** can be evaluated from the equilibrium constants ratio $K_{diss}{}^{Cp-N}/K_{diss}{}^{3}$, which is 14 at 300 K.

The ^{1}H NMR spectrum of **4** in toluene indicated a fluxional behavior similar to that of **3**, with broad resonances observed at room temperature. At −40 °C, the complex appears dissymmetric on the NMR time scale, featuring eight sharp resonances for the Flu moiety, four resonances for the Cp, two singlets for the methyl groups of the isopropylidene bridge, and two doublets of doublets ($J_{H-H} = 11.9$ Hz, $J_{Y-H} = 3.4$ Hz) for the C*HH*$SiMe_3$ moiety. Upon heating, those signals broaden and coalesce, and at 60 °C, two (broadened) singlets are observed for the C(CH_3)$_2$ and CH_2SiMe_3 units. Also, substantial temperature dependence of the THF methylene protons is observed (Figure 4). All of these dynamic phenomena are reversible and also best explained considering THF dissociation, with the existence of a stable THF adduct **4** (dissymmetric on the NMR time scale) at low temperature and the coexistence of a THF-free complex and the THF adduct **4** (symmetric on the NMR time scale) at relatively higher temperatures. The thermodynamic parameters measured for this process ($\Delta_r H = 31 \pm 2$ kJ mol^{-1} and $\Delta_r S = 50 \pm 10$ J K^{-1} mol^{-1}) (Figure 5) are on the same order than those determined for **3** ($K_{diss}{}^{4} = 0.002$ at 300 K).

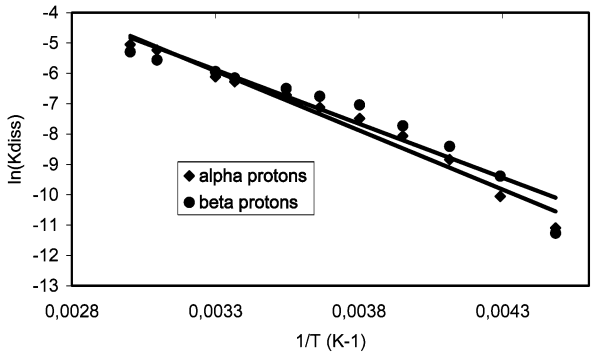


Figure 5. Plot of ln K_{diss} versus $1/T$ for hydrocarbyl complex **4**.

{[(μ:η^5,η^5-Cp-CMe_2-Flu)]Y(μ-H)(THF)}$_2$, the First Hydrido Group 3 Metal Complex Supported by a Fluorenyl Moiety. Although quite numerous hydrido group 3 metal complexes are described in the literature,[15] unambiguous examples of hydrides supported by fluorenyl ligands are still missing. Very recently, we reported on the putative "constrained geometry" hydrido complex {[(3,6-^{t}Bu$_2$Flu)-$SiMe_2$-N^{t}Bu]Y(H)(THF)}$_2$.[16] This product was, however, characterized only by elemental analysis, due to its insolubility in most common organic solvents hampering recrystallization and informative NMR spectroscopy. The isolation of a 1,4-hydride addition product to pyridine brought later indirect evidence for the hydrido identity of this complex.[17] We therefore explored the possibility of obtaining and characterizing such hydrido species with the present fluorenyl ligand system. In fact, the alkyl complexes **3** and **4** were found to react slowly with H_2 (1 atm), at room temperature, in benzene or toluene solutions, to give the hydrido complex **5** in 75 and 89% yield, respectively. Complex **5** can also be prepared in 75% yield using $PhSiH_3$ as the reducing agent[18] (Scheme 2). Alternatively, we found that the reduction of the anionic dichloro complex **1** with sodium triethylborohydride in toluene solution provides another effective (77% yield), more direct route to **5** (Scheme 2).

Hydride **5** is a yellow microcrystalline solid that is almost insoluble in all common organic solvents (pentane, benzene, toluene, THF, CH_2Cl_2), even at high temperature, also hampering NMR characterization and recrystallization. The reason for such insolubility remains unclear.[19] Crystals of **5** suitable for X-ray analysis

(15) (a) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193. (b) Edelmann, F. T. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1995; Vol. 4, p 11. (c) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (d) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (e) Bochkarev, M. N.; Zakharov, L. N.; Kalinina, G. S. *Organoderivatives of Rare Earth Elements*; Kluwer Academic Publishers: London, 1995.

(16) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Organometallics* **2003**, *22*, 4467.

(17) Kirillov, E.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, 943.

(18) (a) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543. (b) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157.

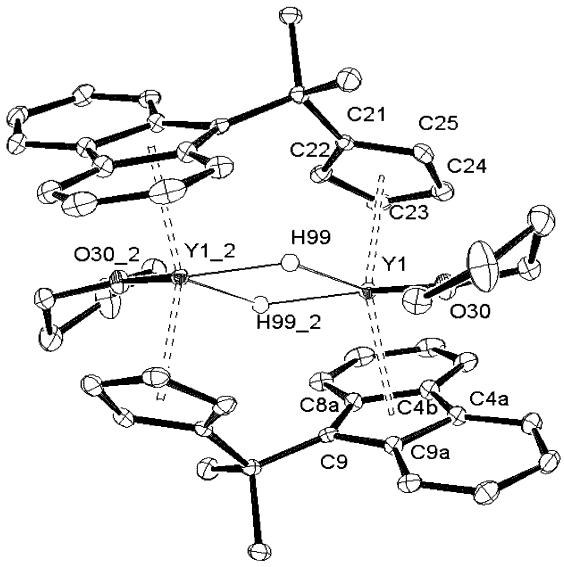
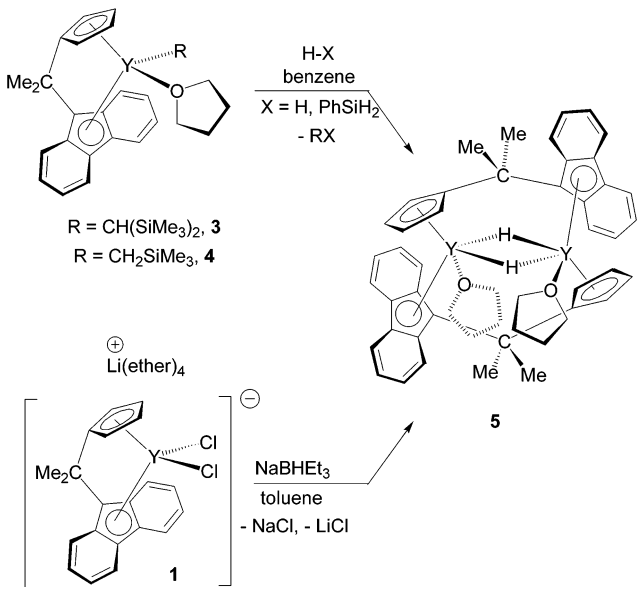


Figure 6. ORTEP view of the molecular structure of [(μ:η^5,η^5-Cp-CMe$_2$-Flu)Y(μ-H)(THF)]$_2$·1/2C$_6$H$_6$ (**5**·0.5benzene). Ellipsoids drawn at the 50% probability level. Hydrogen atoms (except H99 and H99_2) omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−Y(1_2), 3.4731(5); Y(1)−H(99), 1.99(4); Y(1)−H(99_22), 2.01(4); Y(1)−O(30), 2.419(2); Y(1)−Cp$_{cent}$, 2.364; Y(1)−C(21), 2.707(3); Y(1)−C(22), 2.671(3); Y(1)−C(23), 2.611(3); Y(1)−C(24), 2.608(3); Y(1)−C(25), 2.668(3); Y(1)−Flu$_{cent}$, 2.471; Y(1)−C(9a), 2.832(3); Y(1)−C(9), 2.751(3); Y(1)−C(8a), 2.688(3); Y(1)−C(4b), 2.716(3); Y(1)−C(4a), 2.806(3); Cp$_{cent}$−Y(1)−Flu$_{cent}$, 137.61.

Scheme 2



were obtained by the slow (2−4 days) hydrogenolysis reaction between **4** and PhSiH$_3$ in a very diluted benzene solution at room temperature.

Complex **5** features in the solid state a dimeric molecular structure with both bridging hydride and Cp-CMe$_2$-Flu ligands (Figure 6), a "spanned coordination" that has been previously described for some halogeno and hydrido *ansa*-lanthanidocenes.[20] The overall geometry of the yttrium centers in **5** is best described as a distorted trigonal bipyramid with the two hydrogen atoms and one THF oxygen atom lying in the equatorial plane and the Cp$_{cent}$ and Flu$_{cent}$ posed in the apical positions. The Y(1)−Y(1_2) distance of 3.4731(6) Å in **5** is ca. 0.15−0.2 Å shorter than the values observed in related yttrium hydrides.[21] The yttrium−hydride bonds must be discussed cautiously due to usual problematic localization of hydrogen atoms close to metal centers. The Y(1)−H(99) and Y(1)−H(99_22) bond lengths (1.99(4) and 2.01(4) Å) appear also in the bottom range of distances (1.98(6)−2.48(4) Å) found in those other yttrium hydrides.[21] The Y(1)−O(30) bond distance of 2.419(2) Å falls within the range of values (2.361−2.460 Å) found for related THF-containing complexes.[21] The η^5-ligation of the central five-membered ring of both fluorenyl moieties in **5** is more obvious as compared to **3**, considering the limited dispersion of the Y(1)−C(9,9a,8a,4a,4b) bond distances (2.688(3)−2.832(3) Å). The Y(1)−Flu$_{cent}$ bond distance (2.471 Å) is almost equal to the corresponding value in **3** (2.478 Å). Also, the η^5-coordinated Cp ring in **5** is insignificantly moved aside from the yttrium atom as compared to **3**, judging by the values of the average Y(1)−C(21−25) bond distances (2.653(3) Å) and Y(1)−Cp$_{cent}$ bond distance (2.364 Å).

Reaction of [(Cp-CMe$_2$-Flu)YCl$_2$]$^-$[Li(ether)$_4$]$^+$ (1) with PhCH$_2$MgBr; Preparation of [(Cp-CMe$_2$-Flu)Y(μ-Br)]$_2$ (6). Reactions of lanthanide halogeno derivatives with benzyl Grignard reagents, PhCH$_2$MgX, are known to produce most usually the corresponding neutral benzyl complexes. For instance, the yttrocene complex (C$_5$Me$_5$)$_2$Y(CH$_2$Ph)[MgCl$_2$(THF)$_2$][22] and the β-diketiminato scandium complex {(2,6-^{i}Pr-C$_6$H$_3$)NC(^{t}Bu)CHC(^{t}Bu)N(2,6-^{i}Pr-C$_6$H$_3$)}Sc(CH$_2$Ph)$_2$[23] were prepared in good yields using this procedure. Unexpectedly, the reaction of the chloro complex **1** with PhCH$_2$MgBr proceeded in a different way. The addition of 1 equiv (vs Y) of the Grignard reagent to a suspension of **1** in toluene at room temperature resulted in a change of the coloration from deep red to yellow and concomitant precipitation of LiCl. After workup, the pale yellow microcrystalline dibromo complex [(Cp-CMe$_2$-Flu)Y-

(19) Mixtures of hydride **5** with equimolar amounts of pyridine or 2,4-^{t}Bu$_2$C$_6$H$_3$OH in toluene at room temperature have been found intact after several weeks.

(20) (a) [{Me$_2$Si(C$_5$H$_4$)$_2$}Yb(μ-Cl)]$_2$: Qiao, K.; Fischer, R. D.; Paolucci, G.; Traldi, P.; Celon, E. *Organometallics* **1990**, *9*, 1361. (b) [{Me$_2$Si(C$_5$H$_4$)$_2$}Yb(μ-Br)]$_2$: Akhnoukh, T.; Muller, J.; Qiao, K.; Li, X.-F.; Fischer, R. D. *J. Organomet. Chem.* **1991**, *408*, 47. (c) [{Me$_2$Si(Flu)(C$_5$H$_3$R)}Ln(μ-Cl)]$_2$ (Ln = Y, Dy; R = H, ^{t}Bu): Qian, C.; Nie, W.; Sun, J. *Organometallics* **2000**, *19*, 4134. (d) [{Et$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)}Lu(μ-H)]$_2$: Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (e) {[Me$_2$Si(C$_5$Me$_4$)$_2$}Y(μ-H)]$_2$: Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *Inorg. Chim. Acta* **1996**, *242*, 205. (f) [{Me$_2$Si(3-Me$_3$Si-C$_5$H$_2$)$_2$}-Sm(μ-H)(THF)]$_2$: Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811. (g) [{Me$_2$Si(C$_5$H$_4$)$_2$}Ln(μ-H)(μ-Cl)(THF)]$_2$: Qiao, K.; Paolucci, G.; Fischer, R. D. *J. Organomet. Chem.* **1993**, *456*, 185.

(21) (a) [(η^5,η^1-C$_5$Me$_4$-SiMe$_2$-N^{t}Bu)Y(μ-H)(THF)]$_2$: Y(1)···Y(1_2), 3.672(1) Å; Y−O, 2.361(5), 2.378(5) Å; Y−H, 2.48(4), 1.98(6) Å: Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227. (b) [(η^5,η^1-C$_5$Me$_4$CH$_2$-SiMe$_2$-N^{t}Bu)Y(μ-H)(THF)]$_2$: Y(1)···Y(1_2), 3.7085(8) Å; Y−O, 2.440(4), 2.413(4) Å; Y−H, 2.30(4), 2.07(6) Å: Trifonov, A. A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2001**, *20*, 4869. (c) [(η^5,η^1-C$_5$Me$_4$CH$_2$-SiMe$_2$-NCH$_2$CH$_2$NMe$_2$)Y(μ-H)]$_2$: Y(1)···Y(1_2), 3.5995(4) Å; Y−H, 2.28(3), 2.19(3) Å: Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 3921. (d) [(C$_5$Me$_4$Me)$_2$Y(μ-H)(THF)]$_2$: Y(1)···Y(1_2), 3.664(1) Å, Y−O, 2.460(8) Å; Y−H, 2.17(8), 2.19(8) Å: Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008.

(22) Den Haan, K. H.; Wielstra, Y.; Johan, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181.

(23) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533.

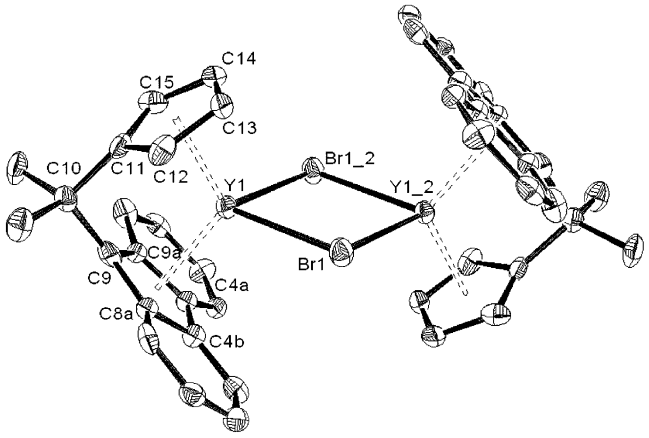
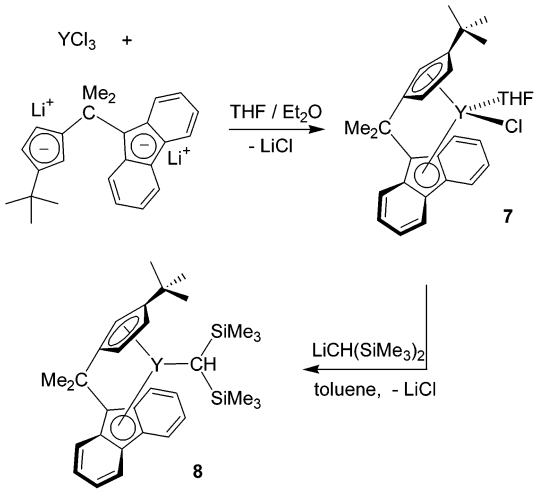


Figure 7. ORTEP view of the molecular structure of $[(\eta^5,\eta^5\text{-Cp-CMe}_2\text{-Flu})\text{Y}(\mu\text{-Br})]_2\cdot C_7H_8$ (**6**·toluene). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Y(1)−Y(1_2), 4.062(8); Y(1)−Br(1), 2.8065(12); Y(1)−Br(1_22), 2.8055(13); Y(1)−Cp_{cent}, 2.288; Y(1)−C(11), 2.536(8); Y(1)−C(12), 2.570(9); Y(1)−C(13), 2.625(9); Y(1)−C(14), 2.639(9); Y(1)−C(15), 2.554(9); Y(1)−Flu_{cent}, 2.342; Y(1)−C(9a), 2.615(8); Y(1)−C(9), 2.530(9); Y(1)−C(8a), 2.585(8); Y(1)−C(4b), 2.738(9); Y(1)−C(4a), 2.752(8); Cp_{cent}−Y(1)−Flu_{cent}, 114.81.

(μ-Br)]$_2$ (**6**), that is, the trans-halogenation product,[24,25] was recovered in 47% yield. Complex **6** is sparingly soluble in aromatic hydrocarbons (benzene, toluene), even at 80 °C, which hampered its authentication by NMR spectroscopy. It dissolves rapidly in THF-d_8 at room temperature, but the ^{1}H NMR spectrum featured numerous resonances, casting doubt on the innocuousness of this solvent. The nature of **6**, in particular the absence of coordinated solvent and magnesium salt molecules, was established on the basis of microanalysis and an X-ray diffraction study.

In the solid state, complex **6** has a dimeric structure formed by bridging bromine atoms (Figure 7). The molecule is quite symmetric: it has a (noncrystallographic) C_{2v} plane comprising the C(9), C(10), Y(1), Y(1_2), C(10_2), and C(9_2) atoms and a (noncrystallographic) C_2-axis passing through the Br(1) and Br(1_2) atoms. The central Y_2Br_2 square core is minimally distorted with each of the angles close to 90° (Y(1)−Br(1)−Y(1_2), 92.73(4)°; Br(1)−Y(1)−Br(1_2), 87.27(4)°). The Y−Br bond lengths are almost equal to each other (2.8065(12), 2.8055(13) Å) and very close to that found in the bromo yttrium complex $\{[(\eta^5\text{-}C_5H_4)(CH_2)_2P(CH_3)_2]_2\text{-YBr}\}_2$ (2.7939(5) Å).[26] The Cp-CMe$_2$-Flu moiety is chelated to the metal center, in contrast with the bridging mode observed in the silylene−bridged parent complex $[(\mu{:}\eta^5,\eta^5\text{-Cp-SiMe}_2\text{-Flu})\text{Y}(\mu\text{-Br})]_2$.[20c] Both the fluorenyl and cyclopentadienyl fragments in **6** are unambiguously η^5-coordinated, and the yttrium atom features significantly short distances (Y(1)−Cp_{cent}, 2.288 Å; Y(1)−Flu_{cent}, 2.342 Å) as compared with the corresponding ones in **3** and **5**. In particular, the bond distances between the five-membered ring of the fluorenyl fragment and the metal center (Y(1)−C(8a,9,9a,4b,4a) = 2.530(9)−2.752(8) Å) are the shortest so far reported for fluorenyl complexes of yttrium.[2−6,12] The value of the bite angle Cp_{cent}−Y(1)−Flu_{cent} (114.81°) is slightly larger than that observed in the alkyl complex **3**.

Scheme 3



Preparation of Solvent-Free Complexes with Cp-Substituted Ligands. In general, bidentate *ansa*-bis(cyclopentadienyl) systems are known to form stable solvent-free, electron-poor alkyl complexes with rare earth metals.[27] In addition to the examples reported herein (i.e., **3** and **4**), the *ansa*-samarocene [Me$_2$Si(3-Me$_3$Si-C_5H_2)$_2$]Sm(CH(SiMe$_3$)$_2$)(THF)[15b] constitutes another unusual example of a mono-THF adduct. To explore the influence of the introduction of bulky substituents on the coordination sphere of the metal center, the modified ligand system [(3-^{t}Bu-C_5H_3)-CMe$_2$-Flu]$^{2-}$ was used to prepare the corresponding yttrium alkyl complex (**8**) (Scheme 3). The salt elimination reaction of the dilithium salt of this ligand with $YCl_3(THF)_{3.5}$ gave [(3-^{t}Bu-C_5H_3)-CMe$_2$-Flu]YCl(THF) (**7**) in 87% yield. This complex is readily soluble both in ethers (THF, Et_2O) and in aromatic hydrocarbons (toluene, benzene), and its consistency was confirmed by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. Thus, in contrast to the nonsubstituted ligand system [Cp-CMe$_2$-Flu] that leads essentially to *ionic* chloro complexes,[6] a *neutral* salt-free chloro complex is here obtained. Subsequent treatment of **7** with 1 equiv of LiCH(SiMe$_3$)$_2$ led to the THF-free alkyl complex **8** in 70% yield (Scheme 3).

(24) The formation of a bromo derivative instead of desired alkyls upon reaction of bis(amidophosphine)yttrium chloride with different aromatic Grignard reagents has been reported: Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1387.

(25) For similar *trans*-halogenation reactions mediated by Grignard reagents in group 3−8 metal complexes, see: (a) Larson, E. J.; Van Dort, P. C.; Dailey, J. S.; Lakanen, J. R.; Pederson, L. M.; Silver, M. E.; Huffman, J. C.; Russo, S. O. *Organometallics* **1987**, *6*, 2141. (b) Larson, E. J.; Van Dort, P. C.; Dailey, J. S.; Lakanen, J. R.; O'Neil, J. R.; Pederson, L. M.; Lori, M.; McCandless, J. J.; Silver, M. E.; Russo, S. O.; Huffman, J. C. *Organometallics* **1988**, *7*, 1183. (c) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4860. (d) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (e) Forschner, T. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7420. (f) Hermann, W. A.; Floel, M.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *358*, 321. (g) Lindsay, C.; Cesarotti, E.; Adams, H.; Bailey, N. A.; White, C. *Organometallics* **1990**, *9*, 2594. (h) Neumueller, B.; Gahlmann, F. *Z. Anorg. Allg. Chem.* **1992**, *612*, 123. (i) Chernega, A. N.; Green, M. L.; Suarez, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, *20*, 3031. (j) Werner, B.; Kraeuter, T.; Neumueller, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 346.

(26) Karsch, H. H.; Graf, V.; Reisky, M.; Witt, E. *Eur. J. Inorg. Chem.* **1998**, 1403.

(27) (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Anwander, R. *Top. Organomet. Chem.* **1999**, *2*, 1.

Table 2. Polymerization of MMA Initiated by 3 and 4[a]

complex	temp (°C)	time (h)	yield (%)	M_n (10^3)	M_w/M_n	tacticity *rr*	*mr*	*mm*
3	20	1	75	271	1.87	60	35	5
3	−5	1	53	297	1.80	66	30	4
4	−15	1	25	376	1.43	63	31	6

[a] [MMA]/[Y] = 300−500, [MMA] = 1.0−1.5 M in toluene; total volume = 20 mL.

The ^{1}H and ^{13}C NMR spectra of both the chloro complex **7** and alkyl complex **8** in toluene-d_8 and benzene solutions revealed a dissymmetric structure on the NMR time scale in the temperature range −70 to +25 °C. This dissymmetry is obviously inherent to the substitution of the Cp ring. For instance, the ^{1}H NMR spectrum of **8** (benzene-d_6, 25 °C) features eight sharp resonances for the fluorenyl moiety, three resonances for the Cp hydrogens, two singlets for both the methyl groups of the isopropylidene bridge and the Me_3Si moieties from the hydrocarbyl group, and a singlet for the ^{t}Bu group. The ^{1}H resonance for the alkyl in **8** (δ −2.66, d, $^2J_{H-Y}$ = 1.8 Hz) appears also unusually shielded, presumably due to the anisotropic shielding from the fluorenyl moieties.

The ^{13}C chemical shift for the bridgehead (C-9) fluorenyl carbon atom in (η^5,η-Cp-CMe_2-Flu) complexes of early transition metals has been recently proposed to be diagnostic of the hapticity of the fluorenyl moiety in solution.[28] In particular, the value of δ 95.4 ppm reported for the corresponding carbon in [(η^5,η^3-Cp-CMe_2-Flu)Zr(μ-H)(Cl)]$_2$[29] has been suggested to give evidence for a reduced hapticity tending toward η^3.[28] The ^{13}C resonance for the bridgehead (C-9) fluorenyl carbon atom was found at δ 93.3 ppm in **7** (toluene-d_8) and δ 91.9 ppm in **8** (benzene-d_6). These values are to be compared to those observed for **3** and **4** (δ 94.2 and 93.9 ppm, respectively, toluene-d_8). Despite the minimal upfield shielding for **8**, these values are all quite similar and suggest that the fluorenyl moiety in all of these complexes adopts the same hapticity. Although a reduced η^3 hapticity is conceivable for complexes **3**, **4**, and **7**, which bear a coordinated THF molecule, resulting in a formal 14-electron count, this would appear unreasonable for the THF-free complex **8** since it would lead to a quite electron-deficient (12-e) species. One can, therefore, cast doubt on the appropriateness of such analysis, at least for this series of fluorenyl yttrium complexes.

Ethylene and MMA Polymerization Abilities of Complexes 3, 4, and 6−8. The complexes obtained were preliminarily explored as catalysts/initiators for ethylene and MMA polymerization. Complexes **3** and **4** initiate the rapid polymerization of MMA in toluene to give high molecular weight PMMA with relatively narrow polydispersity (Table 2). The polymers formed are syndiotactic-rich, with *rr* triad relative intensity values (60−66%) characteristic of chain-end control.

On the other hand, no activity for ethylene polymerization was detected with alkyl complexes **3** and **4** (20−80 °C, 1−10 atm C_2H_4, toluene solution). Such inactivity of **3** and **4** toward ethylene suggests that, despite their tendency to dissociate rather fast above room temperature, the THF molecule remains within the coordination sphere of the complex and blocks the "active-site". Noteworthy, Okuda's "constrained geometry" complex (C_5Me_4-$SiMe_2$-N^{t}Bu)Y(CH_2SiMe_3)(THF), from which THF dissociates to a greater extent than in **3** and **4** (vide supra), is active (though moderately) for ethylene polymerization under ambient conditions.[8] No evidence for coordination of ethylene onto yttrium in **3** and **4** was observed by ^{1}H NMR spectroscopy. Only traces of polyethylene were obtained using the THF-free bromo complex **6** activated with [HAl(*i*-Bu)$_2$(*n*-Bu)]$^-$Li$^+$ (HAl(*i*-Bu)$_2$/*n*-BuLi/Y = 40:40:1; cyclohexane, 80 °C, 8 atm).[30] Using the same activator and polymerization conditions with the *tert*-butyl-substituted mono-THF precursor **7** gave a moderately active catalyst (76 kg mol^{-1} h^{-1}), offering low molecular weight polyethylene (M_n = 900, M_w/M_n = 2.02, T_m = 124 °C). The THF-free yttrium alkyl complex **8** was found also to be ineffective for ethylene polymerization under the same conditions than those used for **3** and **4**, likely in part because of the bulkiness of the bis(trimethylsilyl)methyl group.

Conclusion

Isopropylidene-bridged fluorenyl/cyclopentadienyl ligands appear to be quite flexible systems, demonstrating their ability to stabilize complexes of different nature, both ionic and neutral. Thus, a variety of neutral halogeno and alkyl derivatives of yttrium supported by two (RCp-CMe_2-Flu) ligand systems have been prepared easily using standard salt elimination routes. Ionic chloro and neutral alkyl complexes derived from the nonsubstituted system (R = H) provide an easy entry to the parent hydrido complex. This one constitutes the first unambiguous member of the class of lanthanide hydrides supported by a fluorenyl ligand. The complexes derived from the given ligand (R = H) are mono-THF adducts, unlike most of the *ansa*-metallocene alkyls. This could stem from either the more opened gap around the yttrium atom provided by constrained coordination of the ligand and/or the donor properties of THF to stabilize the electron-deficient metal center. In this regard, the hapticity of the fluorenyl moiety onto yttrium in these complexes, η^5 or tending toward a reduced η^3-mode, remains an open question. Finally, introduction of bulky substituents onto the cyclopentadienyl ring of these ligand systems is clearly the effectual way to control the coordination sphere of the metal center.

Experimental Section

General Procedures. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et_2O) and Na/K alloy (toluene, pentane) under nitrogen, degassed thoroughly, and stored under nitrogen prior to use. Deuterated solvents (benzene-d_6, toluene-d_8, THF-d_8; >99.5% D, Eurisotop) were vacuum-transferred from Na/K alloy into storage tubes. $YCl_3(THF)_{3.5}$ was obtained after repeated extraction of YCl_3 (Strem) from THF or just prior to

(28) Drago, D.; Pregosin, P. S.; Razavi, A. *Organometallics* **2000**, *19*, 1802.
(29) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Mazid, M. *Organometallics* **1993**, *12*, 4718.
(30) Boisson, C.; Barbotin, F.; Spitz, R. In *Progress and Development of Catalytic Olefin Polymerization*; Sano, T., Uozomi, T., Nakatami, H., Terano, M., Eds.; Technology and Education Pub.: Tokyo, 2000; p 75.

use by refluxing anhydrous yttrium chloride in THF for 2 h and subsequent evaporation. Ligands CpH-CMe_2-FluH and (3-^{t}Bu-CpH)-CMe_2-FluH were generously provided by Total Co. Complex $[(Cp\text{-}CMe_2\text{-}Flu)YCl_2]^-[Li(ether)_4]^+$ (ether = THF, Et_2O) (**1**) was prepared according to the published procedure.[6] NMR spectra were recorded on Bruker DPX-200 and AC-300 spectrometers in Teflon-valved NMR tubes at 25 °C unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was made from $^1H-^1H$ COSY, $^1H-^{13}C$ HMQC, and HMBC NMR experiments. Coupling constants are given in hertz. Elemental analyses were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations.

(Cp-CMe_2-Flu)Y($CH(SiMe_3)_2$)(THF) (3). Synthesis from 1. In the glovebox, to a suspension of **1** (0.175 g, 0.181 mmol) in toluene (20 mL) was added $LiCH(SiMe_3)_2$ (0.031 g, 0.186 mmol). The reaction mixture was stirred for 8 h at room temperature. The resulting yellow-orange solution was filtered, and volatiles were removed in vacuo. The residue was washed with pentane (2 × 15 mL) and dried in vacuo to give **3** as a yellow powder (0.094 g, 84%). Yellow crystals of **3** suitable for X-ray diffraction were grown from a toluene/pentane (~3:1) solution at −30 °C. ^1H NMR (300 MHz, toluene-d_8, −40 °C): δ 8.03 (d, 1H, J_{HH} = 8.1, Flu), 8.00 (d, 1H, J_{H-H} = 8.1, Flu), 7.83 (d, 1H, J_{HH} = 8.1, Flu), 7.67 (d, 1H, J_{H-H} = 8.1, Flu), 7.25 (t, 1H, J_{H-H} = 8.1, Flu), 7.17 (t, 1H, J_{H-H} = 8.1, Flu), 6.99 (t, 1H, J_{H-H} = 8.1, Flu), 6.87 (t, 1H, J_{H-H} = 8.1, Flu), 6.61 (br s, 1H, Cp), 6.14 (br s, 1H, Cp), 5.51 (br s, 1H, Cp), 5.47 (br s, 1H, Cp), 2.60 (br m, 2H, α-CH_2, THF), 2.45 (br m, 2H, α-CH_2, THF), 2.28 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 0.81 (br m, 4H, β-CH_2, THF), 0.35 (s, 9H, SiCH_3), 0.10 (s, 9H, SiCH_3), −4.07 (d, 1H, J_{YH} = 2.0, C*H*). ^1H NMR (200 MHz, toluene-d_8, 60 °C): δ 8.03 (d, 2H, J_{H-H} = 8.1, Flu), 7.83 (d, 2H, J_{H-H} = 8.1, Flu), 7.04 (m, 4H, Flu), 6.00 (t, 2H, J_{H-H} = 2.5, Cp), 5.86 (t, 2H, J_{H-H} = 2.5, Cp), 3.00 (br s, 4H, α-CH_2, THF), 2.21 (s, 6H, CH_3), 1.18 (br s, 4H, β-CH_2, THF), 0.02 (s, 18H, SiCH_3), −3.68 (br, 1H, C*H*). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75 MHz, 25 °C): δ 145.4 (Cp), 126.2 (other signals from methyne carbons overlapped with signals from toluene), 124.2, 120.5, 120.1, 117.8 (Flu), 111.1, 103.1 (Cp), 94.2 (C-9, Flu), 70.1 (α-CH_2, THF), 40.5 (CCH_3), 29.9 (CCH_3), 27.3 (d, $^1J_{Y-C}$ = 39.7, Y−*C*H), 24.7 (β-CH_2, THF), 5.9 ($SiCH_3$). Anal. Calcd for $C_{32}H_{45}OSi_2Y$: C, 65.06; H, 7.68. Found: C, 66.01; H, 7.65.

"One-Pot" Synthesis from YCl_3. To a solution of CpH-CMe_2-FluH (1.00 g, 3.67 mmol) in diethyl ether (50 mL) at −10 °C was added under vigorous stirring 2 equiv of *n*-BuLi (4.6 mL of a 1.6 M solution in hexane, 7.34 mmol). The reaction mixture was allowed to warm to room temperature. The solution turned dark yellow, and after 3 h, a yellow crystalline powder precipitated. To this suspension of the dilithium salt in ether cooled to −20 °C was added a suspension of $YCl_3(THF)_n$ (prepared from 0.72 g, 3.68 mmol of YCl_3) in Et_2O (50 mL). Upon vigorous stirring and warming to room temperature, the reaction mixture turned deep red. The red solution was decanted from precipitate and evaporated in vacuo to give 0.80 g of a deep red powder. The latter was placed into a Schlenk vessel, and a solution of $LiCH(SiMe_3)_2$ (0.11 g, 0.662 mmol) in toluene (30 mL) was added. The reaction mixture was stirred overnight at room temperature. The resulting yellow-orange solution obtained was filtered, and volatiles were removed in vacuo. The residue was washed with pentane (2 × 25 mL) and dried in vacuo to give **3** as a yellow powder (0.45 g, 21% yield vs ligand).

(Cp-CMe_2-Flu)Y(CH_2SiMe_3)(THF) (4). To a suspension of **1** (0.11 g, 0.210 mmol) in toluene (20 mL) was added $LiCH_2SiMe_3$ (0.020 g, 0.212 mmol). The reaction mixture was stirred for 8 h at room temperature, the resulting yellow-orange solution was filtered, and volatiles were removed in vacuo. The oily residue was recrystallized from pentane to give **4** as a yellow powder (0.073 g, 65%). ^1H NMR (toluene-d_8, 300 MHz, −40 °C): δ 8.06 (d, 1H, J_{H-H} = 7.5, Flu), 7.82 (d, 1H, J_{H-H} = 7.5, Flu), 7.73 (d, 1H, J_{H-H} = 7.5, Flu), 7.70 (d, 1H, J_{H-H} = 7.5, Flu), 7.31 (t, 1H, J_{H-H} = 7.5, Flu), 7.24 (t, 1H, J_{H-H} = 7.5, Flu), 6.83 (t, 1H, J_{H-H} = 7.5, Flu), 6.70 (s, 1H, J_{H-H} = 2.1, Cp), 6.61 (t, 1H, J_{H-H} = 7.5, Flu), 5.97 (s, 1H, J_{H-H} = 2.1, Cp), 5.62 (s, 1H, J_{H-H} = 2.1, Cp), 5.55 (br s, 1H, J_{H-H} = 2.1, Cp), 2.55 (br m, 4H, α-CH_2, THF), 2.32 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 0.82 (br m, 4H, β-CH_2, THF), 0.19 (s, 9H, SiCH_3), −2.18 (dd, 1H, J_{Y-H} = 3.4, J_{H-H} = 11.9, CH*H*), −2.55 (dd, 1H, J_{Y-H} = 3.4, J_{H-H} = 11.9, C*H*H). ^1H NMR (toluene-d_8, 200 MHz, 25 °C): δ 8.03 (br d, 1H, Flu), 7.80 (br d, 3H, Flu), 7.20 (br m, 2H, Flu), 6.87 (br t, 1H, Flu), 6.62 (br t, 1H, Flu), 6.59 (br s, 1H, Cp), 5.97 (br s, 1H, Cp), 5.70 (br s, 1H, Cp), 5.53 (br s, 1H, Cp), 2.78 (br s, 4H, α-CH_2, THF), 2.30 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.00 (br s, 4H, β-CH_2, THF), 0.08 (s, 9H, SiCH_3),), −2.26 (br d, 1H, CH*H*), −2.50 (br d, 1H, C*H*H). ^1H NMR (toluene-d_8, 200 MHz, 60 °C): δ aromatic signals are broad, 2.96 (br s, 4H, α-CH_2, THF), 2.30 (s, 6H, CH_3), 1.08 (br s, 4H, β-CH_2, THF), 0.08 (s, 9H, SiCH_3),), −2.30 (br s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75 MHz, 25 °C): δ 145.5, 142.4, 137.8, 137.06, 129.1, 126.5, 124.4, 123.2, 122.0, 121.0, 120.4, 119.4, 118.1, 111.2, 109.4, 104.6, 102.3, 93.9 (Flu and Cp), 71.3 (α-CH_2, THF), 41.0 (CCH_3), 30.2 (CCH_3), 29.9 (CCH_3), 25.5 (β-CH_2, THF), 24.6 (d, $^1J_{Y-C}$ = 45.1, YCH_2), 4.41 ($SiCH_3$). Anal. Calcd for $C_{29}H_{37}OSiY$: C, 67.16; H, 7.19. Found: C, 67.89; H, 7.25.

Attempted Preparation of (Cp-CMe_2-Flu)Y(CH_2SiMe_3)(THF) (4) via the Alkane Elimination Reaction between CpH-CMe_2-FluH and $Y(CH_2SiMe_3)_3(THF)_2$. Generation of (η^5-Cp-CMe_2-FluH)$_2$Y(CH_2SiMe_3)(THF)$_2$. Anhydrous YCl_3 (0.417 g, 2.14 mmol) was slurried in THF (20 mL) and stirred at 80 °C for 1 h. The solvent was removed in vacuo, and the solid residue was suspended in pentane (20 mL). The suspension was cooled to −78 °C, a solution of $LiCH_2SiMe_3$ (6.4 mL of 1 M solution in pentane, 6.4 mmol) was added, and the suspension was stirred at 0 °C for 2 h. The suspension was filtered, and the white solid was extracted with pentane (2 × 10 mL). LiCl was filtered off, and a solution of CpH-CMe_2-FluH (0.460 g, 1.68 mmol) in pentane (30 mL) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 10 h. The solution was concentrated in vacuo to give colorless microcrystals of (η^5-Cp-CMe_2-FluH)$_2$Y(CH_2SiMe_3)(THF)$_2$ (0.40 g, 24%). ^1H NMR (toluene-d_8, 200 MHz, 25 °C): δ 7.62 (d, 4H, J_{H-H} = 7.0, Flu), 7.3−7.1 (m, 8H, Flu), 6.80 (br m, 4H, Flu), 6.2−6.0 (br m, 8H, Cp), 4.04 (s, 2H, 9-Flu), 3.39 (br s, 8H, α-CH_2, THF), 1.20 (s, 12H, CH_3), 1.17 (br s, 8H, β-CH_2, THF), 0.40 (s, 9H, SiCH_3), −0.71 (d, 2H, $^2J_{Y-H}$ = 3.5, Y−CH_2). $^{13}C\{^1H\}$ NMR (toluene-d_8, 50 MHz, 25 °C): δ 146.7, 143.3, 137.5, 127.8, 126.8, 120.4, 120.1, 110.9, 109.3 (Flu and Cp), 70.6 (α-THF), 62.4 (C-9, Flu), 40.1 (CCH_3), 35.8 (CCH_3), 26.1 (β-THF), 22.2 (d, $^1J_{Y-C}$ = 100.0, Y−CH_2), 0.67 ($SiCH_3$).

[(μ:η^5,η^5-Cp-CMe_2-Flu)Y(μ-H)(THF)]$_2$ (5). Synthesis from 3 and $PhSiH_3$. To a solution of **3** (0.020 g, 38.6 μmol) in benzene (0.5 mL) was added $PhSiH_3$ (4.7 μL, 38.6 μmol) via syringe. The reaction mixture was kept at room temperature for 48 h. The yellow crystals of **5** formed were washed with benzene and dried in vacuo (0.0125 g, 75%).

Synthesis from 3 and H_2. A glass reactor equipped with magnetic stirring was loaded with a solution of **3** (0.250 g, 1.62 mmol) in toluene (20 mL). Argon was removed, and the reaction mixture was exposed to 1 atm of H_2 for 20 h under vigorous stirring. The yellow microcrystalline precipitate of **5** was filtered, washed with toluene (2 × 2 mL), and dried (0.602 g, 86%).

Synthesis from 1 and $NaHBEt_3$. In the glovebox, to a suspension of **1** (0.647 g, 0.89 mmol) in toluene (40 mL) was added sodium triethylborohydride (0.89 mL of 1.0 M solution in toluene, 0.89 mmol). The reaction mixture was stirred for 8 h at room temperature, the resulting red solution was

filtered, and volatiles were removed in vacuo. The residue was washed with toluene (2 × 15 mL) and dried in vacuo to give **5** as a yellow powder (0.297 g, 77%). Anal. Calcd for $C_{50}H_{54}O_2Y_2$: C, 69.44; H, 6.29. Found: C, 68.33; H, 5.98.

[(η^5,η^5-Cp-CMe$_2$-Flu)Y(μ-Br)]$_2$ (6). To a suspension of **1** (0.210 g, 0.29 mmol) in toluene (30 mL) was added a solution of $PhCH_2MgBr$ (0.33 mL of a 0.87 M solution in Et_2O, 0.29 mmol). The reaction mixture was stirred for 8 h at room temperature, the resulting yellow-orange solution was filtered, and volatiles were removed in vacuo. The pale yellow crystalline residue was washed with toluene (2 × 3 mL) to yield **6** (0.065 g, 47%). Anal. Calcd for $C_{42}H_{36}Br_2Y_2$: C, 57.43; H, 4.13; Br, 18.19. Found: C, 57.96; H, 4.55; Br, 17.89.

[(3-^{t}Bu-C$_5$H$_3$)-CMe$_2$-Flu]YCl(THF) (7). To a solution of (3-^{t}Bu-CpH)-CMe_2-FluH (0.596 g, 1.814 mmol) in Et_2O (50 mL) at −10 °C was added under vigorous stirring 2 equiv of *n*-BuLi (2.27 mL of a 1.6 M solution in hexane, 3.32 mmol). The reaction mixture was warmed to room temperature, and the solution turned pink after 4 h. To this solution of the dilithium salt in ether cooled to −20 °C was added a suspension of $YCl_3(THF)_{3.5}$ (0.812 g, 1.814 mmol) in Et_2O (30 mL). The reaction mixture turned bright yellow upon vigorous stirring and warming to room temperature. This solution was decanted and separated from the precipitate, and volatiles were removed under vacuum to give **7** as a bright yellow powder (0.825 g, 87%). ^{1}H NMR (300 MHz, toluene-d_8, −50 °C): δ 8.27 (d, 1H, J_{H-H} = 8.0, Flu), 7.94 (d, 1H, J_{H-H} = 8.0, Flu), 7.80 (d, 1H, J_{H-H} = 8.0, Flu), 7.67 (d, 1H, J_{H-H} = 8.0, Flu), 7.37 (m, 2H, Flu), 6.82 (t, 1H, J_{H-H} = 8.0, Flu), 6.62 (t, 1H, J_{H-H} = 8.0, Flu), 6.12 (br t, 1H, Cp), 5.60 (br t, 1H, Cp), 5.47 (br t, 1H, Cp), 2.76 (dd, 4H, $^2J_{H-H}$ = 17.9, $^3J_{H-H}$ = 6.8, α-CH_2, THF), 2.29 (s, 6H, CMe_2), 1.44 (s, 9H, ^{t}Bu), 0.70 (br m, 4H, β-CH_2, THF). ^{1}H NMR (200 MHz, toluene-d_8, 25 °C): δ 8.16 (m, 1H, Flu), 8.00−7.70 (m, 3H, Flu), 7.35−7.20 (m, 2H, Flu), 6.89 (t, 1H, J_{H-H} = 7.4, Flu), 6.67 (t, 1H, J_{H-H} = 7.4, Flu), 6.09 (br t, 1H, Cp), 5.57 (m, 2H, Cp), 3.08 (br m, 4H, α-CH_2, THF), 2.29 (s, 6H, CMe_2), 1.34 (s, 9H, ^{t}Bu), 1.08 (br m, 4H, β-CH_2, THF). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 25 °C): δ 142.1 (quat. Cp), 125.4 (2 quat. C from Flu and Cp), 125.3 (overlapped with toluene), 123.8, 122.3, 120.42, 119.6, 119.5, 119.3 (two signals overlapped), 117.0 (1,8-C, Flu), 106.8 (Cp), 102.2 (Cp), 101.7 (Cp), 93.3 (9-C, Flu), 71.3 (α-C, THF), 40.8 (*C*(CH$_3$)$_2$), 32.4 (*C*(CH$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 29.7 (C(*C*H$_3$), CMe_2), 29.5 (C(*C*H$_3$), CMe_2), 25.0 (β-C, THF). Anal. Calcd for $C_{29}H_{34}ClOY$: C, 66.61; H, 6.55. Found: C, 66.01; H, 6.87.

[(3-^{t}Bu-C$_5$H$_3$)-CMe$_2$-Flu]Y(CH(SiMe$_3$)$_2$) (8). One-Pot Synthesis from YCl$_3$. To a solution of (3-^{t}Bu-CpH)-CMe_2-FluH (0.596 g, 1.81 mmol) in Et_2O (50 mL) at −10 °C was added under vigorous stirring 2 equiv of *n*-BuLi (2.27 mL of a 1.6 M solution in hexanes, 3.63 mmol). The reaction mixture was allowed to warm to room temperature, and the solution turned yellow. To this solution of the dilithium salt in ether cooled to −20 °C was added a suspension of $YCl_3(THF)_{3.5}$ (0.812 g, 1.81 mmol) in Et_2O (20 mL). Upon vigorous stirring and warming to room temperature, the reaction mixture turned bright yellow. The solution was decanted from precipitate and evaporated in vacuo to give a yellow powder (1.00 g). The latter was placed into a Schlenk flask, and a solution of $LiCH(SiMe_3)_2$ (0.32 g, 1.93 mmol) in toluene (30 mL) was added. The reaction mixture was stirred overnight at room temperature, the resulting yellow solution was filtered, and volatiles were removed in vacuo. The residue was washed with pentane (2 × 15 mL) and dried in vacuo to give **8** as a bright yellow powder (0.45 g, 69% yield vs ligand). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 7.99 (d, 1H, J_{H-H} = 8.3, Flu), 7.91 (d, 1H, J_{H-H} = 8.3, Flu), 7.76 (m, 2H, Flu), 7.3−7.12 (m, 2H, Flu), 7.03 (t, 1H, J_{H-H} = 8.3, Flu), 6.92 (t, 1H, J_{H-H} = 8.3, Flu), 6.48 (br t, 1H, J_{H-H} = 2.7, Cp), 5.94 (t, 1H, J_{H-H} = 2.7, Cp), 5.72 (t, 1H, J_{H-H} = 2.7, Cp), 2.21 (s, 3H, CMe_2), 2.12 (s, 3H, CMe_2), 1.06 (s, 9H, CCH_3), 0.07 (s, 9H, SiCH_3), −0.49 (s, 8H, SiCH_3), −2.66 (s, 1H, $^2J_{Y-H}$ = 1.8, C*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 75 MHz, 25 °C): δ 141.0 (quat. Cp), 129.0 (3 signals from quat. C Flu), 128.1 (2 signals from CH Flu; overlapped with benzene signals), 123.4 (Cp), 123.1 (2 signals from CH Flu), 120.6, 120.5, 119.7, 118.7, 118.0 (Flu), 107.7 (Cp), 105.6 (Cp), 101.1 (Cp), 91.9 (C-9, Flu), 40.6 (*C*Me$_2$), 31.6 (C(*C*H$_3$)$_3$), 29.5 (C(*C*H$_3$)$_2$), 29.4 (*C*HSiCH$_3$), 5.1 (Si*C*H$_3$), 2.0 (Si*C*H$_3$) (the signal for *C*Me$_3$ was not been observed). Anal. Calcd for $C_{32}H_{45}Si_2Y$: C, 66.87; H, 7.89. Found: C, 67.02; H, 8.00.

Determination of K_{diss} and Energetic Parameters. Determination of K_{diss} from the temperature dependence of the chemical shift of the THF methylene protons was carried out as reported in detail by Okuda et al.[8] The errors on K_{diss} were estimated assuming ±2% uncertainty in the chemical shifts and temperature. The errors on the enthalpy and entropy values were derived from the standard deviations of the best linear regression in the Eyring analysis.

Crystal Structure Determination of Complexes 3, 5, and 6. Suitable single crystals of all investigated compounds were mounted onto glass fibers using the "oil-drop" method. All diffraction data were collected at 100 K using a NONIUS Kappa CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A combination of ω- and ϕ-scans was carried out to obtain at least a unique data set. Crystal structures were solved by means of the Patterson method, and the remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[31] Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. The cell of **5** was found to contain one benzene molecule of crystallization and that of **6** two toluene molecules. Crystal data and details of data collection and structure refinement are given in Table 1. Atomic coordinates, thermal parameters, and complete listings of bond lengths and angles are available as Supporting Information.

Typical Procedure for Ethylene Polymerization. A solvent (50 mL), typically toluene, was introduced in a 300 mL glass reactor (TOP-Industrie) equipped with a mechanic stirrer rotating at speeds up to 1500 rpm. The reactor was kept at 80 °C. Solvent was saturated with ethylene (Air Liquide, N35) (4−8 atm, kept constant via a back-pressure regulator). A solution of the catalyst (ca. 50 mg) in toluene (10 mL) was transferred via syringe into the reactor under stirring. The ethylene flow rate was monitored using a mass flowmeter (Aalborg, GFM17) connected to a totalizing controller (KEP), which acts as a flow rate integrator. The reaction was quenched by the addition of 3 mL of a 10% HCl methanol solution to the mixture. The resulting precipitate was filtered, washed with methanol, and dried under vacuum.

Polymerization of MMA. In a typical experiment, to a preweighed amount of yttrium complex (ca. 20 mg) in toluene (20 mL) was added methyl methacrylate (3.0 mL, 27.7 mmol) by syringe and vigorous magnetic stirring was immediately started at the appropriate temperature. After a given time period, the Schlenk flask was opened to air and acetone (30 mL) was added to quench the reaction and dissolve the polymer formed. The polymer was precipitated by adding methanol (ca. 200 mL), filtered, washed with methanol (2 × 30 mL), and dried in vacuo. Molecular weights and molecular mass distributions were determined by GPC in THF using

(31) (a) Sheldrick, G. M. *SHELXS-97*, Program for the Determination of Crystal Structures; University of Goettingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Goettingen: Germany, 1997.

universal calibration relative to polystyrene standards. The PMMA microstructure was determined by ^{1}H NMR in $CDCl_3$.

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Supporting Information Available: Details of structure determinations of complexes **3**, **5**, and **6**, including final coordinates, thermal parameters, bond distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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