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Synthesis, Structure, and Reactivity of $(\mathrm{C_5H_4SiMe_3})_2\mathrm{Y}\{(\mu\text{-}\mathrm{FC_6F_4})(\mu\text{-}\mathrm{Me})\mathrm{B}(\mathrm{C_6F_5})_2\}$: Tight Ion Pairing in a Cationic Lanthanide Complex

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Summary: The reaction of $[\mathrm{Cp'_2YMe}]_2$ *(*$\mathrm{Cp'} = \mathrm{C_5H_5}$, $\mathrm{C_5H_4SiMe_3}$*) with* $\mathrm{B(C_6F_5)_3}$ *affords the complexes* $\mathrm{Cp'_2Y\{MeB(C_6F_5)_3\}}$*. The anion is coordinated in a chelating fashion via one ortho-fluorine atom and agostic interactions to two of the methyl hydrogens; the complexes are highly fluxional in solution. They act as initiators for the carbocationic polymerization of isobutene.*

Metallocene complexes of group 3 and lanthanide metals of the type $\mathrm{Cp_2MR}$ have attracted considerable attention in recent years because of their pronounced Lewis acidic character and their catalytic activity.[1] There are, however, only few reports of cationic lanthanide complexes, all of which are stabilized by donor ligands, $[\mathrm{Cp_2ML_2}]^+\mathrm{X}^-$ (L = THF, $\mathrm{N_2H_4}$, DME, or tetrahydrothiophene; M = Sm,[2] Ce,[3] La,[4] Yb;[5] X = $\mathrm{BPh_4}$[2−4,5b] or $\mathrm{Co(CO)_4}$[5a]). In view of our recent synthesis of the aluminocenium cation $[\mathrm{AlCp_2}]^+$ which proved to be a highly effective initiator for carbocationic polymerizations,[6] we became interested in the possibility of synthesizing "base-free" group 3 complexes $[\mathrm{MCp_2}]^+$ which might offer promise as cationic initiators or as activators for group 4 metal alkyl catalyst precursors.[7] We describe here the synthesis of zwitterionic yttrium complexes $\mathrm{Cp'_2Y(\mu\text{-}Me)B(C_6F_5)_3}$ (**2a**, $\mathrm{Cp'} = \mathrm{C_5H_5}$; **2b**, $\mathrm{Cp'} = \mathrm{C_5H_4SiMe_3}$) and their use as polymerization initiators.

The complexes $[\mathrm{Cp'_2Y(\mu\text{-}Me)}]_2$ (**1a**, $\mathrm{Cp'} = \mathrm{C_5H_5}$; **1b**, $\mathrm{Cp'} = \mathrm{C_5H_4SiMe_3}$) react with $\mathrm{B(C_6F_5)_3}$ in dichloromethane at −70 to 0 °C to give $\mathrm{Cp'_2Y(\mu\text{-}Me)B(C_6F_5)_3}$ (**2**); according to the ^{1}H and ^{19}F NMR spectra, the conversion is quantitative.[8] If only 1 equiv of $\mathrm{B(C_6F_5)_3}$ per mole of **1** is employed, the formation of **2** together with unreacted **1** is observed. Surprisingly, at no stage was it possible to observe the expected binuclear cationic methyl-bridged species $[\mathrm{Cp'_2Y(\mu\text{-}Me)YCp'_2}]^+[\mathrm{MeB(C_6F_5)_3}]^-$ (**3**), even at low temperature. It seems that even if **3** is an intermediate in the formation of **2**, any equilibrium between **2** and **3** lies strongly on the side of **2** (Scheme 1).

By contrast, following the reaction of **1a** with 2 equiv of $[\mathrm{CPh_3}][\mathrm{B(C_6F_5)_4}]$ in $\mathrm{CD_2Cl_2}$ by NMR at −65 °C provides evidence for $[(\mathrm{C_5H_5})_2\mathrm{Y}(\mu\text{-}\mathrm{Me})\mathrm{Y}(\mathrm{C_5H_5})_2][\mathrm{B(C_6F_5)_4}]$ (^{1}H NMR: δ −0.74 (t, 3 H, $J_{\mathrm{Y-H}} = 3.3$ Hz, μ-Me), 6.40 (20 H, $\mathrm{C_5H_5}$)) as an unstable intermediate. Warming to 0 °C results in the replacement of the Cp and $\mathrm{CH_3}$ signals by a new Cp resonance at δ 6.16, assigned to the decomposition product $[(\mathrm{C_5H_5})_2\mathrm{YCl}]_2$. The same reaction carried out in toluene at room temperature gave an oily precipitate, which, on addition of THF, afforded crystalline $[(\mathrm{C_5H_5})_2\mathrm{Y(THF)_2}][\mathrm{B(C_6F_5)_4}]$ (**4a**).[9]

Compounds **2a** and **2b** were isolated as colorless solids in high yields by reacting **1** with 2 equiv of $\mathrm{B(C_6F_5)_3}$

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[8] **1b**: Prepared from 2.25 g (2.8 mmol) of $[(\mathrm{C_5H_4SiMe_3})_2\mathrm{YCl}]_2$ and MeLi (4.0 mL, 5.6 mmol) in 200 mL of diethyl ether at 0 °C. White microcrystals were obtained from light petroleum (3.0 g, 70%).^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C): δ −0.70 (t, $J_{\mathrm{Y-H}} = 3.1$ Hz, 6H, μ-$\mathrm{CH_3}$), 0.32 (s, 36 H, $\mathrm{SiMe_3}$), 6.35 (t, $J = 2.4$ Hz, 8 H, Cp′), 6.77 (t, $J = 2.4$ Hz, 8 H, Cp′). ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C): δ 0.62 ($\mathrm{SiMe_3}$), 24.7 (t, $J_{\mathrm{Y-C}} = 25.0$ Hz, μ-Me), 114.7 (Cp′), 118.8 (s, ipso-C of Cp′), 120.7 (Cp′). Anal. Calcd (found) for $\mathrm{C_{17}H_{29}Si_2Y}$: C, 53.98 (53.90); H, 7.67 (7.35). **2a**: Toluene (30 mL) was added to a mixture of 0.42 g (0.9 mmol) of $[(\mathrm{C_5H_5})_2\mathrm{YMe}]_2$ and 0.92 g (1.8 mmol) of $\mathrm{B(C_6F_5)_3}$ at room temperature. The mixture was stirred for 2 h, pumped to dryness, and washed with 3 × 10 mL of light petroleum to give a white powder (1.1 g, 80%). ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C): δ 0.90 (br, 3 H, μ-Me), 5.90 (s, 10 H, Cp). ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C): δ 15.0 (br, μ-Me), 113.7 (Cp). ^{11}B NMR ($\mathrm{C_6D_6}$, 25 °C): δ −14.4. ^{19}F NMR: ($\mathrm{C_6D_6}$, 25 °C) δ −134.1 (d, $J = 22.9$ Hz, 6 F, *o*-F), −159.8 (t, $J = 21.0$ Hz, 3 F, *p*-F), −164.7 (t, $J = 19.5$ Hz, 6 F, *m*-F); ($\mathrm{CD_2Cl_2}$, −20 °C) δ −134.8 (d, $J = 25.9$ Hz, 6 F, *o*-F), −162.0 (t, $J = 20.7$ Hz, 3 F, *p*-F), −166.1 (t, $J = 20.7$ Hz, 6 F, *m*-F). Anal. Calcd (found) for $\mathrm{C_{29}H_{13}BF_{15}Y}$: C, 46.65 (46.35); H, 1.74 (1.95). **2b**: Prepared from 0.60 g (0.80 mmol) of **1b** and 0.85 g (1.66 mmol) of $\mathrm{B(C_6F_5)_3}$ in toluene (20 mL) at room temperature; isolated at −20 °C from toluene/light petroleum as colorless crystals (1.0 g, 70%). ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C): δ −0.06 (s, 18 H, $\mathrm{SiMe_3}$), 1.10 (br, 3 H, μ-Me), 6.00 (t, 4 H, $J = 2.4$ Hz, Cp′), 6.58 (t, 4 H, $J = 2.4$ Hz, Cp′). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, −20 °C): δ −0.31 ($\mathrm{SiMe_3}$), 14.0 (br, μ-Me), 118.8, 123.9, 127.8 (Cp′). ^{11}B NMR ($\mathrm{C_6D_6}$, 25 °C): δ −15.5. ^{19}F NMR ($\mathrm{CD_2Cl_2}$, −80 °C): δ −134.8 (d, $J = 20.7$ Hz, 6 F, *o*-F), −160.5 (t, $J = 20.7$ Hz, 3 F, *p*-F), −164.8 (t, $J = 20.7$ Hz, 6 F, *m*-F). Anal. Calcd (found) for $\mathrm{C_{35}H_{29}BF_{15}Si_2Y}$: C, 47.20 (46.75); H, 3.26 (3.30); F, 32.03 (31.65).

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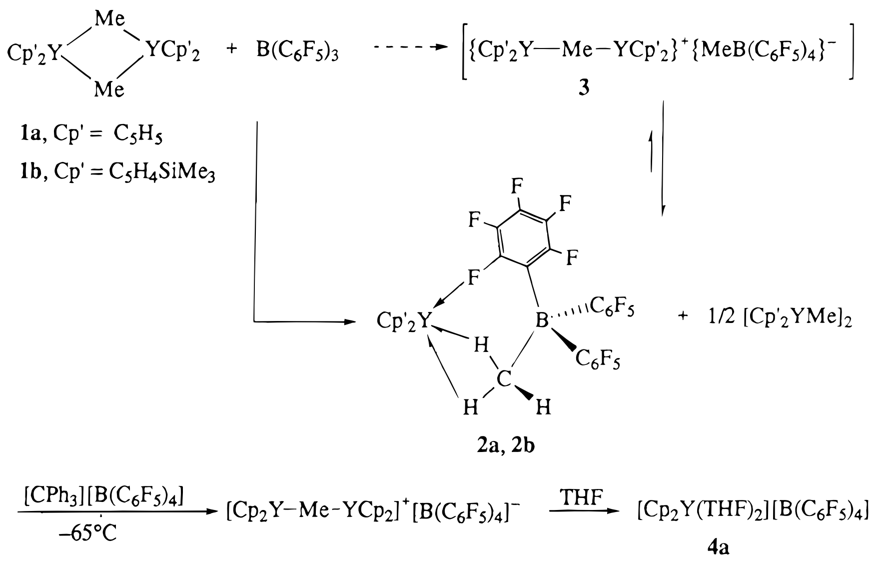
Scheme 1



in toluene at room temperature. While **2a** is a microcrystalline solid that is only poorly soluble in toluene once isolated, **2b** is readily recrystallized from toluene. Whereas cationic group 4 complexes such as [Cp$_2$ZrMe]$^+$ tend to decompose readily in dichloromethane at >0 °C by halide abstraction from the solvent,[10] solutions of **2** are remarkably stable in chlorinated solvents over a period of hours at room temperature. According to the NMR data, the structures of **2a** and **2b** in solution are essentially identical.[8] The ^{1}H and ^{13}C chemical shifts of the methyl group of the [CH$_3$BC$_6$F$_5$)$_3$]$^-$ anion as well as the ^{19}F chemical shift differences for the *p*-F and *m*-F atoms of >4 ppm[11] suggest that the compounds exist as tight ion pairs both in toluene and dichloromethane solutions. The addition of THF to these solutions gives the THF adducts [(C$_5$H$_5$)$_2$Y(THF)$_2$][MeB(C$_6$F$_5$)$_3$] (**5a**) and [(C$_5$H$_4$SiMe$_3$)$_2$Y(THF)$_2$][MeB(C$_6$F$_5$)$_3$] (**5b**), which, by contrast, are ionic and show the spectroscopic characteristics of the uncoordinated anion.

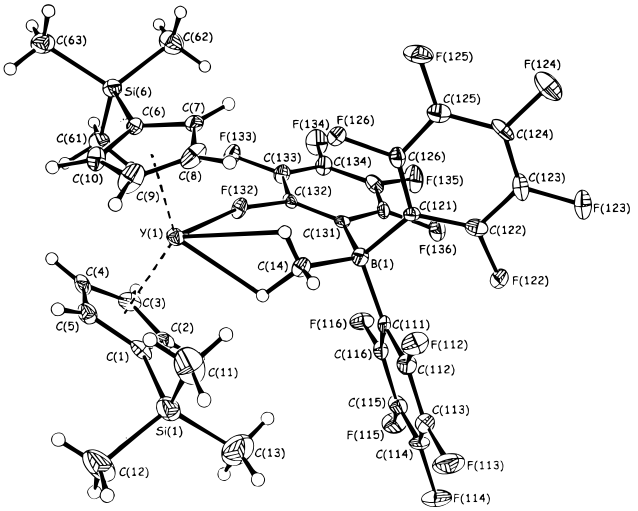


Figure 1. Crystal structure of (C$_5$H$_4$SiMe$_3$)$_2$YMeB(C$_6$F$_5$)$_3$ (**2b**), showing the atomic-numbering scheme. Ellipsoids are drawn at 40% probability. Selected bond distances (Å) and angles (deg): Y−F(132), 2.366(3); Y−C(14), 2.853(7); Y−H(81), 2.43(4); Y−H(82), 2.18(5); Y−C(1), 2.603(5); Y−C(2), 2.592(5); Y−C(3), 2.586(5); Y−C(4), 2.572(5); Y−C(5), 2.572(5); B−C(14), 1.647(8); B−C(111), 1.649(8); B−C(121), 1.636(7); B−C(131), 1.660(7); B−Y−C(14), 134.6(4); Y−F(132)−C(132), 158.2(3); C(14)−H(81)−Y, 111(4); C(14)−H(82)−Y, 116(4); H(81)−C(14)−H(82), 96(4); C(14)−B−C(111), 104.3(5); C(14)−B−C(121), 109.5(5); C(14)−B−C(131), 112.8(5); C(131)−C(132)−F(132), 120.8(4).

Crystals of **2b** suitable for X-ray diffraction were obtained from toluene at room temperature. The structure is shown in Figure 1. The yttrocenium cation is coordinated to the [MeB(C$_6$F$_5$)$_3$]$^-$ anion via one *ortho*-F atom of one of the C$_6$F$_5$ substituents as well as agostic interactions to two of the three hydrogen atoms of the boron−methyl group, with Y−H contacts of 2.18(5) and 2.43(4) Å while the distance to the third hydrogen atom is 3.28 Å. The shorter of these contacts falls within the range of Y−H distances to bridging hydrides, as in [(C$_5$H$_4$Me)$_2$Y(μ-H)(THF)]$_2$ and [(C$_5$H$_5$)$_2$Y(μ_3-H)(μ-H)AlH$_2$-(THF)]$_2$.[12] The solid-state structure of the yttrium complex may be compared to those of the zwitterionic zirconocene derivatives (1,2-C$_5$H$_3$Me$_2$)$_2$ZrMe(μ-Me)B-(C$_6$F$_5$)$_3$ (**6**)[13] and Cp$_2$Zr{η^3-C$_4$H$_6$B(C$_6$F$_5$)$_3$} (**7**)[14] but reveals significant differences in the coordination of the anion. Although yttrium and zirconium have nearly identical covalent radii and the C$_5$H$_4$SiMe$_3$ ligands do not exert significant steric hindrance, the Y−C(14) distance to the bridging methyl group of 2.853(7) Å is too long to be regarded as a bonding interaction, in

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[9] The reaction between **1b** and [CPh$_3$][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$ only proceeds at ≥−10 °C and leads to decomposition. Toluene solutions at room temperature give a yellow product consistent with the formation of [(C$_5$H$_4$SiMe$_3$)$_2$Y][B(C$_6$F$_5$)$_4$]. Once isolated, the compound proved insufficiently soluble in toluene to allow recrystallization. ^{1}H NMR (C$_7$D$_8$, 25 °C): δ 0.04 (SiMe$_3$), 5.93 (br, Cp′), 6.35 (br, Cp′). ^{13}C NMR (C$_7$D$_8$, 25 °C): δ −0.97 (SiMe$_3$), 120.3, 124.2, 125.6 (Cp′). ^{11}B NMR (C$_7$D$_8$, 25 °C): δ −15.9. ^{19}F NMR (C$_7$D$_8$, 25 °C): δ −133.4 (br, 6 F, *o*-F), −160.4 (br, 3 F, *p*-F), −165.3 (br, 6 F, *m*-F).

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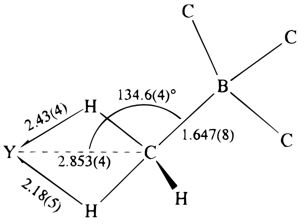
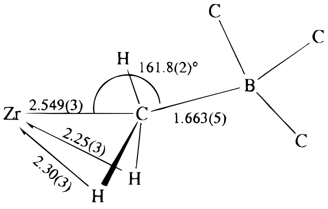
contrast to a Zr−C distance of 2.549(3) Å in **6**. By comparison, yttrium−alkyl bond lengths in neutral cyclopentadienyl complexes are considerably shorter, ranging from 2.468(7) Å in mononuclear $(C_5Me_5)_2YCH(SiMe_3)_2$ to 2.67(2) Å for bridging methyl ligands in $[(C_5Me_5)_2Y(\mu\text{-}Me)_2AlMe_2]_2$, with an average value of 2.545 Å for $[(C_5H_5)_2YMe]_2$ being typical.[15]

Both **2b** and **6** contain agostic interactions to the methyl hydrogens. It has been argued that in compounds of type **6** the anion is primarily bonded via the methyl hydrogens, with possibly negligible bonding to carbon,[13b] although it is noteworthy that in all cases the Zr−C distances fall well within a range consistent with a metal−carbon bonding interaction.[13b,c] By contrast, in **2b**, agostic metal−hydrogen interactions are the only bonding contributions between the metal center and the methyl group. Structures **A** and **B** illustrate the difference in the methyl bonding in **2b** and **6**, respectively.

On the other hand, the Y−F(134) bond length of 2.366(3) Å is quite short compared to the Zr−F(42) distance of 2.423(3) Å in the electronically more saturated η^3-allyl complex **7**. However, whereas in **7** exchange of the C_6F_5 substituents is sufficiently slow at −86 °C to allow the pattern of coordinated and uncoordinated fluorine atoms to be resolved, cooling solutions of **2b** to −95 °C resulted merely in broadening of the signals for the *ortho*-, *meta*-, and *para*-fluorine atoms.



A



B

Although anion displacement by a weakly coordinating solvent such as CD_2Cl_2 might possibly be expected, the data, such as the ^{19}F chemical shift differences between the *m*-F and *p*-F atoms, are consistent with anion coordination over the temperature range from −95 to −20 °C and suggest facile rotation of the anion and rapid exchange of all six *o*-F atoms within the metal coordination sphere, even at low temperature.

To allow for fluorine coordination, the Y−C(14)−B moiety significantly deviates from linearity (angle 134.6(4)°), compared to the corresponding Zr−C−B angle of 161.8(2)° in **6**. Both crystallographic and NMR data support the notion that **2b** is more ionic in character than related zwitterionic complexes of group 4 metals and is best regarded as a tight ion pair.

Table 1. Isobutene Polymerizations Initiated by $[Y(C_5H_4SiMe_3)_2]^+$

initiator	amount (μmol)	*T* (°C)	time (min)	yield (g)	M_w ($\times10^{-3}$)	M_w/M_n
1b	50	−78	5.0	0		
2b[a]	50	−78	5.0	0.15	1180	2.2
2b[a]	50	−50	8.0	0.34	513	2.0
1b + $[CPh_3][B(C_6F_5)_4]$[b]	42	−78	5.0	0.30	1380	2.4
1b + $[CPh_3][B(C_6F_5)_4]$[b]	42	−50	5.0	0.43	1180	2.6

[a] Conditions: 50 μmol of **2b** dissolved in 2 mL of CH_2Cl_2 at −78 °C was injected into 10 mL of isobutene condensed into a flame-dried all-glass reactor and equilibrated at the given temperature. The reaction was quenched by injecting 2 mL of methanol. [b] A 0.19 g (0.25 mmol) amount of **1b** in toluene (20 mL) was added to 0.46 g (0.50 mmol) of $[CPh_3][B(C_6F_5)_4]$ in 100 mL of toluene at room temperature. The solution was stirred for 2.5 h, during which time the color of $[CPh_3][B(C_6F_5)_4]$ disappeared. Initiation was carried out as stated above by injecting a solution containing 42 μmol of the yttrium complex.

In view of the activity of $[AlCp_2]^+$ as an initiator for carbocationic polymerizations,[6] the activity of **2b** in isobutene polymerizations was tested.[16] Dichloromethane solutions were used for **2b**, whereas **1b**/$[CPh_3][B(C_6F_5)_4]$ mixtures are unstable in chlorinated solvents and were prepared in toluene. The results are collected in Table 1. Both the polymer yields and molecular weights are comparable to those found for $[AlCp_2][MeB(C_6F_5)_3]$ and considerably higher than those reported for $(C_5Me_5)TiMe_3/B(C_6F_5)_3$.[17] There was no isobutene polymerization with **1a** or **1b** in the absence of $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$.

The results provide the first examples of cationic group 3 metallocene cations $[MCp'_2]^+$ stabilized by fluoroarylborate association rather than N- or O-donor ligands. These complexes have significant ionic character, which results in weak agostic bonding and highly fluxional anion coordination. As expected, the yttrocenium cation behaves as a strong Lewis acid, and its reactivity is exemplified by its effectiveness as an initiator for the carbocationic polymerization of isobutene. Catalytic applications of these complexes are currently being explored.

Acknowledgment. This work was supported by the Engineering and Physical Sciences Research Council. We are grateful to Professor M. B. Hursthouse (Crystallographic National Service, University of Cardiff) for the collection of the data set of **2b**.

Supporting Information Available: Text giving general preparative details and spectroscopic data for **4** and **5** and tables of crystal data, atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates, interatomic distances, and bond angles (12 pages). Ordering information is given on any current masthead page.

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