

Synthesis and characterization of weakly coordinating anion salts of a new, stable carbocationic reagent, the dibenzosubereryl (dibenzotropylium) ion†

Adina Cordoneanu, Mark J. Drewitt, Neda Bavarian and Michael C. Baird*

Received (in Gainesville, FL, USA) 26th March 2008, Accepted 8th May 2008

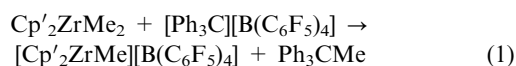
First published as an Advance Article on the web 18th July 2008

DOI: 10.1039/b804868a

The new, bright red compounds [DBS][B(C₆F₅)₄], [DBS][BCl(C₆F₅)₃], [DBS][B(C₆F₅)₃-OH...H₂O-B(C₆F₅)₃] and [DBS][B(CH₂CMe₃)(C₆F₅)₃] (DBS = C₁₅H₁₁, dibenzosubereryl, dibenzotropylium, dibenzo[*a,e*]tropylium or dibenzo[*a,d*]cycloheptenocarbonium) have been synthesized and characterized spectroscopically and, except for [DBS][B(CH₂CMe₃)(C₆F₅)₃], crystallographically. The crystal structures show that the DBS⁺ carbocation is planar and suggest pronounced delocalization of the positive charge over part of the seven-membered ring, in particular the CH carbon and the carbon atoms α and β to it. The electrophilic DBS⁺ carbocation activates alkene polymerization catalyst precursors of the type Cp'₂ZrMe₂, its efficacy being comparable to that of the well known but sterically more hindered trityl carbocation, Ph₃C⁺. As with the Ph₃C⁺ ion, DBS⁺ does not initiate carbocationic polymerization of isobutene in dichloromethane directly, but rather by reacting with trace amounts of water to generate protons.

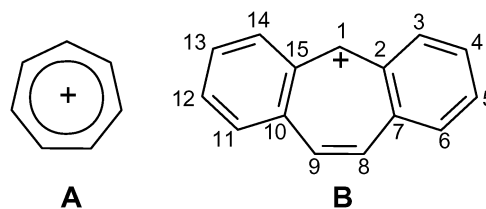
Introduction

The highly electrophilic trityl carbocation, [Ph₃C]⁺, is a powerful carbanion abstracting reagent which, in combination with the weakly coordinating counteranion [B(C₆F₅)₄][−] behaves as a very effective activator of dimethylmetallocenes for olefin polymerization.¹ Thus treatment of dimethylzirconocenes Cp'₂ZrMe₂ (Cp' = substituted cyclopentadienyl) with [Ph₃C][B(C₆F₅)₄] results in abstraction of a methyl group to give Ph₃CMe and the excellent alkene polymerization catalysts [Cp'₂ZrMe]⁺ as the [B(C₆F₅)₄][−] salts (eqn (1)).



Intrigued with the possibility of developing alternative carbocationic species as carbanion abstracting reagents (and prompted by the occasional formation of oils during attempts to synthesize crystalline [Ph₃C][B(C₆F₅)₄], we earlier^{2a} investigated the use of the tropylium ion (A) as the salt [C₇H₇][B(C₆F₅)₄].^{2b-e} The tropylium ion is a nonbenzenoid, aromatic 6 π -electron system with a thermodynamic stability somewhat higher than that of the trityl ion.³ Unfortunately, although we were able to demonstrate (NMR) that the [C₇H₇]⁺ ion does abstract a methyl group from *e.g.* Cp*TiMe₃ and

Cp₂ZrMe₂ to generate viable olefin polymerization catalysts, we found that the solubility of [C₇H₇][B(C₆F₅)₄] in most solvents is sufficiently low that only suspensions of the salt can be used. We have therefore extended our interests to the dibenzosubereryl carbocation (B)⁴ (alternatively dibenzotropylium, dibenzo[*a,e*]tropylium or dibenzo[*a,d*]cycloheptenocarbonium ion) as the previously unknown salt [C₁₅H₁₁][B(C₆F₅)₄], or [DBS][B(C₆F₅)₄]. (Henceforth the atom labels shown for B will be utilized to denote the various hydrogen and carbon atom positions during discussions of NMR spectra and X-ray crystal structures.)



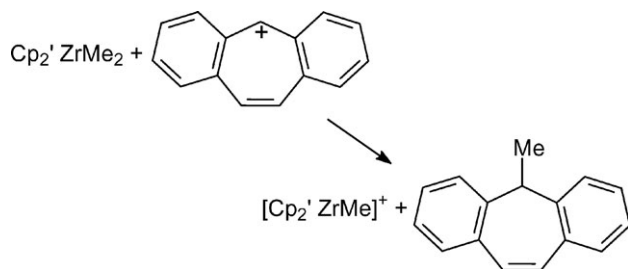
Dibenzosubereryl chloride, 1-ClC₁₅H₁₁, has found use as an alkylating agent, *i.e.* as a source of the DBS carbocation,^{4a-d} but when desired free this cationic species has usually been generated in strongly acidic solutions at low temperatures (*e.g.* FSO₃H-SO₂ClF at −78 °C).^{4f,g} Thus, although its gas phase photochemistry has in fact been studied,^{4h} the carbocation itself has not been readily available for study in other media. Thus a reliable synthesis of [DBS][B(C₆F₅)₄] as a stable salt, possibly for use as an alkylating agent superior to 1-ClC₁₅H₁₁, would be of general interest.

The DBS carbocation is a derivative of the tropylium ion and is thermodynamically destabilized relative to C₇H₇⁺ by the benzo-annulation.³ Although also thermodynamically more stable than the trityl ion,³ the DBS carbocationic center

Department of Chemistry, Queen's University, Kingston, Canada ON K7L 3N6

† Electronic supplementary information (ESI) available: Crystallographic details, including figures of [DBS][B(C₆F₅)₄] (1), [DBS][BCl(C₆F₅)₃] (2) and [DBS][B(C₆F₅)₃-OH...H₂O-B(C₆F₅)₃] (3), showing complete numbering schemes and thermal ellipsoid figures, tables of positional and thermal parameters and bond lengths and angles. CCDC reference numbers 687298–687300. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b804868a

is less sterically hindered than is that of the trityl ion and we anticipated that the DBS⁺ cation would be capable of methyl carbanion abstraction as in Scheme 1.



Scheme 1

We find that the new compound [DBS][B(C₆F₅)₄] is readily synthesized as a bright red, thermally stable crystalline compound, and describe here the preparation and both spectral and crystallographic characterization of [DBS][B(C₆F₅)₄]. We have also, for purposes of comparisons of structures and reactivities, prepared the analogous DBS salts of the anions [BCl(C₆F₅)₃][−], [B(C₆F₅)₃−OH⋯H₂O−B(C₆F₅)₃][−] and [B(CH₂CMe₃)(C₆F₅)₃][−]. We have verified that the DBS carbocation does indeed activate metallocene catalyst precursors of the type Cp₂'ZrMe₂, as in Scheme 1, and we make a brief comparison of [DBS][B(C₆F₅)₄], [Ph₃C][B(C₆F₅)₄] and [DBS][B(CH₂CMe₃)(C₆F₅)₃] as initiators of metallocene induced olefin polymerization processes.

Experimental

All manipulations were carried out using standard Schlenk techniques and flame-dried glassware under dry, deoxygenated nitrogen or argon, or in an MBraun Labmaster glove box unless otherwise indicated. Dichloromethane was dried by refluxing over calcium hydride, toluene by passage through a column of activated alumina. The residual water content of the solvents was less than 9 ppm as measured by Karl Fischer titrations. NMR solvents were purchased from Cambridge Isotope Laboratories Inc. or CDN Isotopes. CDCl₃ was dried using 4A molecular sieves, CD₂Cl₂ and C₆D₅CD₃ by passing through activated alumina. Ethylene, propylene and isobutene (polymerization grades; 99+%) were purchased from Air Products and were dried by passing through columns of activated 3A or 4A molecular sieves which had been activated under vacuum at ~150 °C for ~15 h prior to use. Dibenzosuberonyl (Aldrich) was purified by recrystallization from hexanes, while Cp₂ZrCl₂ (Strem), Indenyl₂ZrCl₂ (Strem), SBIZrCl₂ (Strem) and [Ph₃C][B(C₆F₅)₄] (Asahi Glass) were used as received. The compounds B(C₆F₅)₃,^{5a} Li[B(C₆F₅)₄],^{5b} dibenzosuberonyl chloride,^{5c} Cp₂ZrMe₂,^{5d} Indenyl₂ZrMe₂^{5d} and SBIZrMe₂^{5e} were synthesized as described in the literature.

All ¹H, NOESY, ¹³C and ¹⁹F NMR spectra were run on Bruker Avance 400 or 500 NMR spectrometers, mass spectra analyses on a Fisons Quattro Pro Quadrupole Mass Spectrometer or an Applied Biosystems/MDS Sciex QSTAR XL QqTOF mass spectrometer in EI± modes using dichloromethane as solvent. Elemental analyses were performed by

Canadian Microanalytical Services, Delta, B.C. X-Ray crystallographic studies of [DBS][B(C₆F₅)₄], [DBS][BCl(C₆F₅)₃] and [DBS][B(C₆F₅)₃−OH⋯H₂O−B(C₆F₅)₃] were carried out by Dr. R. Wang on the departmental Bruker AXS SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), controlled with a Cryostream Controller 700. In a typical experiment, the crystals were mounted on a glass fibre with epoxy glue. The structures were solved using a Pentium PC operating a Bruker AXS Windows NT and SHELXTL software (version 5.10). No significant decay was observed during data collections. Neutral atom scattering factors were taken from Cromer and Waber.⁶ The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure amplitudes and their esd's using the program SAINT, which corrects for Lp and decay. Absorption corrections were applied using SADABS program. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated (unless otherwise stated) and their contributions were included in the structure factors and calculations. Crystallographic data are summarized in Table 1, important bond lengths and angles in Table 2.

Molecular weights of atactic polypropylene and polyisobutene were determined at 75 °C on a Waters Associates model GPC-2690 liquid chromatograph equipped with a Waters 2410 RI detector. The separation columns used were a series of Styragel HR 5, HR 4E and HMW 7 columns. Gel permeation chromatography analyses of the polypropylene and polyisobutene samples were done using filtered toluene HPLC grade (99.99%) as eluent at a flow rate of 1.0 mL min^{−1}. Calibration of the instrument was done using commercially available polystyrene standards with molecular weights ranging from 770 to 6 500 000 g mol^{−1}. Molecular weight determinations of isotactic polypropylene samples were carried out at 145 °C in 1,2,4-trichlorobenzene using a Waters 150-C GPC.

Synthesis of [DBS][B(C₆F₅)₄]

Addition of 0.2 g dibenzosuberonyl chloride (0.88 mmol) to a solution of 0.5 g Li[B(C₆F₅)₄] (0.73 mmol) in 100 mL dry dichloromethane resulted in the instant formation of a deep red color; the solution was stirred for 90 min under argon as LiCl precipitated. The LiCl was removed by filtration and the product was precipitated by the addition of 200 mL of dry hexanes. The solvent volume was then reduced to 20 mL under reduced pressure and the mixture was warmed to 70 °C while being stirred for 10 min. The resulting red powder was isolated by decantation, washed with 20 mL of hexanes and dried under reduced pressure; yield 0.45 g (71%). Alternatively a solution of 0.35 g [Ph₃C][B(C₆F₅)₄] (0.38 mmol) and 0.176 g dibenzosuberonyl chloride (0.38 mmol) in 100 mL dry dichloromethane was stirred for 60 min under argon. The red product was isolated as above; yield 0.22 g (67%). In order to obtain very pure [DBS][B(C₆F₅)₄], the warming and decantation steps were carried out at least twice by adding fresh amounts of 30 mL hexanes each time. ¹H NMR (CD₂Cl₂): (δ 10.37 (s, 1H), 9.13 (s, 2H), 8.97 (d, 2H), 8.76 (m, 4H), 8.52 (m, 2H). ¹⁹F NMR (CD₂Cl₂): δ −134.2 (s, 8F, *o*-F), −164.6 (t, 4F, *p*-F),

Table 1 Crystallographic data for [DBS][B(C₆F₅)₄] (1), [DBS][BCl(C₆F₅)₃] (2) and [DBS][B(C₆F₅)₃-OH...H₂O-B(C₆F₅)₃] (3)^a

	1	2	3
Empirical formula	C ₃₉ H ₁₁ BF ₂₀	C ₃₃ H ₁₁ BClF ₁₅	C ₅₁ H ₁₄ B ₂ F ₃₀ O ₂
<i>M_r</i>	870.29	738.68	1250.24
<i>T</i> /K	180(2)	180(2)	180(2)
<i>λ</i> /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>a</i> /Å	9.779(2)	10.3060(19)	12.512(5)
<i>b</i> /Å	22.098(5)	7.4208(15)	13.248(6)
<i>c</i> /Å	15.386(4)	36.756(7)	14.052(6)
<i>α</i> /°			81.676(7)
<i>β</i> /°	96.055(4)	93.601(3)	82.635(8)
<i>γ</i> /°			76.977(8)
<i>V</i> /Å ³	3306.3(13)	2805.5(9)	2234.4(16)
<i>Z</i>	4	4	2
<i>D_c</i> /Mg m ⁻³	1.748	1.749	1.858
<i>μ</i> /mm ⁻¹	0.180	0.263	0.199
<i>F</i> (000)	1720	1464	1232
Crystal size/mm	0.40 × 0.30 × 0.30	0.50 × 0.30 × 0.20	0.10 × 0.10 × 0.08
<i>θ</i> range for data collection/°	1.62–26.00	1.98–26.00	1.47–26.00°
Index ranges, <i>hkl</i>	–11 to 12, –26 to 27, –17 to 18	–11 to 12, –9 to 9, –43 to 45	–15 to 15, –16 to 16, –17 to 15
Reflections collected	20843	14398	14087
Independent reflections	6489	5486	8721
<i>R</i> _{int}	0.0211	0.0196	0.0927
Completeness to <i>θ</i> = 26.00° (%)	100.0	99.5	99.2
Max., min. transmission	1.0000, 0.7728	0.9493, 0.8798	1.000, 0.876
Data/restraints/parameters	6489/0/585	5486/0/495	8721/1/796
Goodness-of-fit on <i>F</i> ²	0.979	1.073	0.723
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0322, <i>wR</i> 2 = 0.0741	<i>R</i> 1 = 0.0414, <i>wR</i> 2 = 0.0989	<i>R</i> 1 = 0.0672, <i>wR</i> 2 = 0.0821
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0521, <i>wR</i> 2 = 0.0802	<i>R</i> 1 = 0.0556, <i>wR</i> 2 = 0.1061	<i>R</i> 1 = 0.2552, <i>wR</i> 2 = 0.1069
Largest diff. peak, hole/e Å ⁻³	0.272, –0.193	0.647, –0.220	0.281, –0.260

^a Details in common: absorption correction: empirical (Bruker SADABS), refinement method: full-matrix least-squares on *F*².

–168.4 (s, 8F, *m*-F). ¹³C NMR for DBS carbocation (CD₂Cl₂): δ 172.0, 146.4, 144.1, 143.0, 141.6, 137.6, 135.5, 134.5. Anal. Calc. for C₃₉H₁₁BF₂₀: C, 53.76; H, 1.26. Found: C, 53.61; H, 1.12%. The identity of the compound was confirmed (ES-MS) by observation of a peak at *m/z* 191.11 in the positive ion mode, corresponding to the [DBS]⁺ carbocation, and *m/z* 679.02 in the negative ion mode, corresponding to the [B(C₆F₅)₄][–] anion. In addition, recrystallization of [DBS][B(C₆F₅)₄] from dichloromethane–hexanes at room temperature afforded red crystals suitable for X-ray diffraction.

Synthesis of [DBS][BCl(C₆F₅)₃]

A solution of 14 mg dibenzosubereryl chloride (0.06 mmol) and 75 mg B(C₆F₅)₃ (0.12 mmol) in 50 mL of dried dichloromethane was stirred for 3 h under argon. A red powder was then precipitated by the addition of 50 mL hexanes, and the product was isolated by decantation and dried under reduced pressure. The compound could not be purified satisfactorily for elemental analyses, but a few red crystals suitable for X-ray crystallography were obtained through layering a solution in dichloromethane with hexanes. ¹H NMR (CD₂Cl₂): δ 10.37 (s, 1H), 9.13 (s, 2H), 8.97 (d, 2H), 8.76 (dd, 4H), 8.52 (m, 2H). ¹⁹F NMR (CD₂Cl₂): δ –129.9 (s, 6F, *o*-F), –166.9 (br, s, 3F, *p*-F), –160.5 (s, 6F, *m*-F).

Synthesis of [DBS][B(C₆F₅)₃-OH...H₂O-B(C₆F₅)₃]

A solution of 0.1 g dibenzosubereryl chloride (0.48 mmol) in 50 mL dried dichloromethane was treated with 0.61 g B(C₆F₅)₃

(0.96 mmol) and quickly turned red. The solution was stirred at room temperature for 3 h, and precipitation of a red powder was induced by adding 50 mL of hexanes. The product was isolated by decantation and then dried under reduced pressure. The compound could not be purified satisfactorily for elemental analyses, but a small number of crystals suitable for X-ray crystallography were obtained through layering a solution in dichloromethane with hexanes. ¹H NMR (CD₂Cl₂): δ 10.37 (s, 1H), 9.13 (s, 2H), 8.97 (d, 2H), 8.76 (dd, 4H), 8.52 (m, 2H), 8.16 (br s, 3H, H₂O). ¹⁹F NMR (CD₂Cl₂): δ –137.1 (d, 6F, *o*-F), –160.9 (t, 3F, *p*-F), –166.5 (br, t, 6F, *m*-F).

Synthesis of [DBS][B(CH₂CMe₃)(C₆F₅)₃]

A mixture of 0.2 g Li[B(CH₂CMe₃)(C₆F₅)₃]⁷ (0.34 mmol) and 80 mg of dibenzosubereryl chloride (0.34 mmol) in 50 mL of hexanes was stirred for 10 h. The resulting red solid was filtered, dissolved in dichloromethane, and filtered again to remove LiCl and the solvent was then removed under reduced pressure to give the red product. Alternatively a solution of 0.5 g Li[B(CH₂CMe₃)(C₆F₅)₃] (0.85 mmol) and 0.19 g dibenzosubereryl chloride (0.85 mmol) in 40 mL dichloromethane was stirred for 15 min to give a red solution and white precipitate. The latter was filtered off and the solvent was removed to give the product as a red solid. Yields 65–70%. Attempted recrystallizations resulted in apparent decomposition to DBSCH₂CMe₃ (see below), but successful synthesis was confirmed by ES-MS (peaks at *m/z* 190.7 and 582.9 in the positive and negative ion modes, respectively, corresponding to the

Table 2 Important bond lengths (Å) and angles (°) for DBS carbocations of [DBS][B(C₆F₅)₄] (1), [DBS][B(C₆F₅)₃] (2) and [DBS][B(C₆F₅)₃-OH...H₂O-B(C₆F₅)₃] (3)

	1	2	3
C(1)–C(2)	1.412(3)	1.401(3)	1.393(8)
C(1)–C(15)	1.419(3)	1.402(3)	1.379(8)
C(8)–C(9)	1.355(3)	1.356(4)	1.331(8)
C(9)–C(10)	1.424(3)	1.427(4)	1.407(8)
C(7)–C(8)	1.418(3)	1.420(4)	1.414(8)
C(2)–C(7)	1.435(2)	1.444(3)	1.403(8)
C(10)–C(15)	1.431(2)	1.433(3)	1.419(8)
C(2)–C(3)	1.419(3)	1.418(3)	1.404(8)
C(3)–C(4)	1.353(3)	1.360(4)	1.366(8)
C(4)–C(5)	1.395(3)	1.401(4)	1.379(10)
C(5)–C(6)	1.367(3)	1.359(4)	1.364(9)
C(6)–C(7)	1.433(3)	1.412(3)	1.425(9)
C(10)–C(11)	1.416(3)	1.404(4)	1.391(8)
C(11)–C(12)	1.382(3)	1.364(4)	1.352(8)
C(12)–C(13)	1.394(3)	1.391(5)	1.391(8)
C(13)–C(14)	1.344(3)	1.362(4)	1.324(8)
C(14)–C(15)	1.421(3)	1.424(3)	1.423(8)
C(2)–C(1)–C(15)	134.13(19)	134.2(2)	134.9(7)
C(8)–C(9)–C(10)	131.46(19)	131.3(2)	133.5(7)
C(1)–C(2)–C(7)	124.7(7)	125.9(2)	124.7(7)
C(2)–C(7)–C(8)	127.7(7)	125.3(2)	127.7(7)
C(9)–C(10)–C(15)	124.4(7)	125.4(2)	124.4(7)
C(7)–C(8)–C(9)	130.6(2)	131.5(2)	128.7(7)
C(1)–C(15)–C(10)	125.23(18)	126.2(2)	125.8(7)
C(10)–C(15)–C(14)	118.68(17)	118.8(2)	118.0(7)
C(9)–C(10)–C(11)	115.99(18)	117.2(3)	117.2(7)
C(10)–C(11)–C(12)	121.3(2)	122.2(3)	122.0(7)
C(11)–C(12)–C(13)	119.7(2)	120.5(3)	119.2(7)
C(12)–C(13)–C(14)	121.1(2)	119.9(3)	121.7(7)
C(13)–C(14)–C(15)	121.3(2)	121.1(3)	120.7(8)
C(2)–C(3)–C(4)	121.8(2)	122.1(2)	120.5(7)
C(3)–C(4)–C(5)	120.3(2)	119.4(3)	118.8(8)
C(4)–C(5)–C(6)	120.5(2)	120.9(2)	122.9(8)
C(5)–C(6)–C(7)	121.4(2)	122.0(2)	119.5(8)
C(2)–C(7)–C(6)	117.24(18)	117.4(2)	117.4(7)
C(1)–C(2)–C(3)	116.01(18)	115.8(2)	114.5(7)
C(3)–C(2)–C(7)	118.68(18)	118.2(2)	120.8(7)
C(6)–C(7)–C(8)	116.05(19)	117.2(2)	114.9(7)
C(11)–C(10)–C(15)	117.79(17)	117.3(2)	118.3(7)
C(1)–C(15)–C(14)	116.09(18)	115.0(2)	116.2(7)

molecular ions of the carbocation and the anion, respectively) and NMR spectroscopy (¹H NMR (CD₂Cl₂): (δ 10.35 (s, 1H), 9.10 (s, 2H), 8.97 (d, 2H), 8.75 (m, 4H), 8.51 (m, 2H), 1.48 (br s, 2H), 0.63 (s, 9H)).

Synthesis of DBSCH₂CM₃

A solution of 1.45 g of dibenzosuberonyl chloride in 60 mL of dichloromethane was added dropwise to 0.5 g of LiCH₂CM₃ cooled in an ice bath. The mixture was stirred for 1 h, becoming light pink and cloudy, and then filtered through Celite to give a yellow solution which was taken to dryness under reduced pressure. The resulting crude DBSCH₂CM₃ was purified by eluting through an alumina column with hexanes to give a clear yellow oil (1.22 g, 71% yield). ¹H NMR of DBSCH₂CM₃ (CD₂Cl₂): δ 0.66 (s, 9H, CH₂CM₃), 1.70 (d, 2H, CH₂CM₃), 4.18 (t, 1H, H(1) of DBS), 6.98–7.34 (m, 10H, C(2)–C(14)). To confirm the identity, a high resolution mass spectrum (TOF MS EI⁺) was obtained: observed 261.1648; calc. for C₂₀H₂₁ (DBSCH₂CM₃-H)⁺ 261.1643. Difference 1.7 ppm.

NMR studies of the reaction of Cp₂ZrMe₂ with [DBS][B(C₆F₅)₄]

The reaction of Cp₂ZrMe₂ with [DBS][B(C₆F₅)₄] was monitored by NMR spectroscopy in CD₂Cl₂ at room temperature and at –30 °C. In a typical experiment, a solution of 35 mg [DBS][B(C₆F₅)₄] (0.04 mmol) in 0.5 mL dried CD₂Cl₂ was combined with a solution of 10 mg Cp₂ZrMe₂ (0.04 mmol) in 0.5 mL of the same deuterated solvent in an NMR tube. The NMR tube was shaken and ¹H and ¹⁹F NMR spectra were acquired. Similar experiments were carried out at room temperature in toluene-d₈.

Ethylene polymerizations

Ethylene polymerization experiments were carried out using Cp₂ZrMe₂ activated by [DBS][B(C₆F₅)₄], [Ph₃C][B(C₆F₅)₄] or [C₇H₇][B(C₆F₅)₄]; the polymerizations were performed under 1 atm of ethylene in a 200 mL glass reactor which was flame-dried under reduced pressure prior to use. In a typical procedure, a solution of 0.04 mmol Cp₂ZrMe₂ dissolved in 5 mL of dry toluene was added to a solution of 0.04 mmol co-catalyst in 10 mL of dry toluene in the glass reactor. The mixture solution was stirred for 2 min at room temperature, after which dried ethylene was bubbled through the solution for 30 min. The solution immediately became hot and polyethylene began to precipitate, causing the mixture to become very viscous. The polymerization was quenched after 30 min with 10 mL acidified methanol and the polyethylene was collected by filtration, washed with methanol and dried under reduced pressure overnight. The results are reported in Table 3.

Propylene polymerizations

Propylene polymerization experiments were carried out as above but at 0 °C using 0.024 mmol of Cp₂ZrMe₂ activated by 1.5 molar equivalents of [DBS][B(C₆F₅)₄] or [Ph₃C][B(C₆F₅)₄] in the presence of 0.048 mmol of Al(*i*-Bu)₃ as scavenger. A series of complementary propylene polymerization experiments was also carried out using [DBS][B(CH₂CM₃)(C₆F₅)₃] as the co-catalyst to activate Cp₂ZrMe₂,^{5d} (Indenyl)₂ZrMe₂^{5d} and SBIZrMe₂.^{5e} Polymerization conditions and polymer manipulations were similar to those described above, and the results are reported in Table 3. The polymerizations were carried out under continuous bubbling of propylene for 2–5 min, after which the reaction was terminated by stopping the propylene flow and quenching with 10 mL of acidified methanol. The solvent was removed under reduced pressure to give viscous oils of atactic polypropylene (Cp₂ZrMe₂ and (Indenyl)₂ZrMe₂) or white, solid isotactic polypropylene (SBIZrMe₂). The atactic materials were purified by dissolving in hexanes and elution through a silica column. The solvent was removed under reduced pressure, and the polypropylenes obtained were characterized by NMR spectroscopy and GPC. Isotactic polypropylene was washed with methanol and acetone, dried under reduced pressure and characterized by NMR spectroscopy.

Isobutene polymerizations initiated by [DBS][B(C₆F₅)₄]

Isobutene polymerizations initiated by [DBS][B(C₆F₅)₄] were carried out in methyl chloride/dichloromethane mixtures at

Table 3 Alkene polymerization results

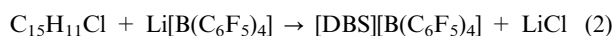
Initiator system	Alkene	Yield/g	$10^{-3}M_w$	M_w/M_n
$\text{Cp}_2\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^a$	Ethylene	1.4	—	—
$\text{Cp}_2\text{ZrMe}_2/[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]^a$	Ethylene	0.8	—	—
$\text{Cp}_2\text{ZrMe}_2/[\text{C}_7\text{H}_7][\text{B}(\text{C}_6\text{F}_5)_4]^a$	Ethylene	1.3	—	—
$\text{Cp}_2\text{ZrMe}_2/[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]^b$	Propylene	4.4	38	2.0
$\text{Cp}_2\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^b$	Propylene	4.9	55	2.0
$\text{Cp}_2\text{ZrMe}_2/[\text{DBS}][\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]^c$	Propylene	2.4	78	1.99
$\text{Ind}_2\text{ZrMe}_2/[\text{DBS}][\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]^c$	Propylene	1.6	98	1.76
$\text{SBIZrMe}_2/[\text{DBS}][\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]^{c,d}$	Propylene	3.1	84	1.75 ^d
Initiator system	Alkene	Conversion (%)	$10^{-3}M_w$	M_w/M_n
$[\text{DBS}][\text{BC}_6\text{F}_5)_4] (1.25 \text{ mM})^e$	Isobutene	99	1.7	3.0
$[\text{DBS}][\text{BC}_6\text{F}_5)_4] (1.25 \text{ mM})^{e,f}$	Isobutene	6.7	1.3	1.4
$[\text{DBS}][\text{BC}_6\text{F}_5)_4] (1.8 \text{ mM})^e$	Isobutene	96	2.2	2.5
$[\text{DBS}][\text{BC}_6\text{F}_5)_4] (1.8 \text{ mM})^{e,f}$	Isobutene	24	1.2	1.3
$[\text{DBS}][\text{BC}_6\text{F}_5)_4] (2.8 \text{ mM})^e$	Isobutene	95	2.0	2.8
$[\text{DBS}][\text{BC}_6\text{F}_5)_4] (3.7 \text{ mM})^{e,f}$	Isobutene	10	0.5	1.4

^a Catalyst : activator ratio = 1 : 1; 0.040 mmol catalyst and 0.040 mmol activator in 15 mL toluene; initiated at 25 °C; 1 atm ethylene; time = 30 min; terminated with methanol. ^b In the presence of $\text{Al}(i\text{-Bu})_3$. Catalyst : activator : $\text{Al}(i\text{-Bu})_3$ ratio = 1 : 1.5 : 2; 0.024 mmol catalyst and 0.036 mmol cocatalyst in 50 mL toluene at 0 °C; 1 atm propylene; time = 2 min. ^c In the presence of $\text{Al}(i\text{-Bu})_3$. Catalyst : activator : $\text{Al}(i\text{-Bu})_3$ ratio = 1 : 2 : 2; 0.024 mmol catalyst and 0.048 mmol cocatalyst in 50 mL toluene at 0 °C; 1 atm propylene; time = 2 min. ^d mmmm = 95%. ^e Temperature = −80 °C; time = 1 h; vol of isobutene = 10 mL; vol of CH_3Cl = 13 mL; vol of dichloromethane = 2 mL. ^f In the presence of DTBP. Initiator : DTBP = 1 : 2.

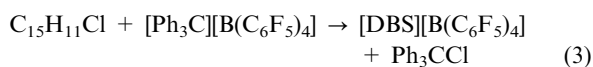
−80 °C as described previously.⁸ Similar polymerization experiments were also carried out in the presence of the proton trap 2,6-di-*tert*-butylpyridine (ratio of DTBP : DBS = 2 : 1). In all cases, 10 mL of isobutene were polymerized using concentrations of initiator as indicated below. The results are presented in Table 3.

Results and discussion

The new, stable carbocationic salt $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ was synthesized by two methods. In the first, dibenzosuberonyl chloride was reacted with $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ in dichloromethane at room temperature as in eqn (2).



In the second method $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ was prepared by reaction of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ with dibenzosuberonyl chloride as in eqn (3).



The latter result is consistent with the above-mentioned greater stability of the DBS cation.³

In both cases, the deep red color of the DBS carbocation developed quickly and the ionic product of metathesis was readily precipitated in good yield by the addition of hexanes. Identification of $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ was confirmed by elemental analyses and ¹H and ¹⁹F NMR spectroscopy and the structure was determined crystallographically (see below). The DBS salt is quite stable when stored in a dry environment, and the procedure outlined here can readily be used to synthesize this source of the DBS carbocation for use in other than strongly acidic media at low temperatures.^{4f,g}

The analogous red compound $[\text{DBS}][\text{BCl}(\text{C}_6\text{F}_5)_3]$ was prepared in small amounts during an investigation of the abstraction

of chloride ion from dibenzosuberonyl chloride by $\text{B}(\text{C}_6\text{F}_5)_3$; $[\text{DBS}][\text{BCl}(\text{C}_6\text{F}_5)_3]$ has not been reported previously although Bochmann *et al.* have reported the crystal structure of the analogous $[\text{Ph}_3\text{C}][\text{BCl}(\text{C}_6\text{F}_5)_3]$.^{1f} Similarly $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_3\text{OH} \cdots \text{H}_2\text{O} \cdots \text{B}(\text{C}_6\text{F}_5)_3]$ was prepared inadvertently during a reaction of DBSOH with $\text{B}(\text{C}_6\text{F}_5)_3$ in an attempt to obtain $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_3(\mu\text{-OH})\text{B}(\text{C}_6\text{F}_5)_3]$. Trace amounts of water present in the solution resulted instead in the formation of a small amount of the $[\text{B}(\text{C}_6\text{F}_5)_3\text{OH} \cdots \text{H}_2\text{O} \cdots \text{B}(\text{C}_6\text{F}_5)_3]^-$ anion in which a water molecule has been incorporated. While $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_3\text{OH} \cdots \text{H}_2\text{O} \cdots \text{B}(\text{C}_6\text{F}_5)_3]$ has not previously been reported, the $[\text{B}(\text{C}_6\text{F}_5)_3\text{OH} \cdots \text{H}_2\text{O} \cdots \text{B}(\text{C}_6\text{F}_5)_3]^-$ anion was previously synthesized as the $[\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}]^+$ and $[\text{NH}_4\text{Et}_3]^+$ salts.⁹ The compounds $[\text{DBS}][\text{BCl}(\text{C}_6\text{F}_5)_3]$ and $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_3\text{OH} \cdots \text{H}_2\text{O} \cdots \text{B}(\text{C}_6\text{F}_5)_3]$ could not be obtained analytically pure, but the formation of a few small crystals of each made crystallographic structure determinations possible (see below).

We have previously described the use of $[\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]^-$ as a weakly coordinating anion during olefin polymerizations,⁷ and we decided to investigate also the DBS⁺ salt of the $[\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]^-$ anion. The compound $[\text{DBS}][\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]$ was accordingly synthesized *via* a metathesis reaction involving $\text{Li}[\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]$ and dibenzosuberonyl chloride, and the red salt was characterized as such by NMR spectroscopy and mass spectrometry. Unfortunately, all attempts to purify it resulted in conversion to what appeared to be $\text{C}_{15}\text{H}_{11}\text{CH}_2\text{CMe}_3$ on the basis of its ¹H NMR spectrum. This would be the product of neopentyl anion transfer from boron to the DBS carbocation, and it was therefore also synthesized by treating dibenzosuberonyl chloride with neopentyl-lithium. The ¹H NMR spectrum of the resulting compound was identical to that of the compound obtained from the decomposition of $[\text{DBS}][\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]$ and also very similar to that of $\text{C}_{15}\text{H}_{11}\text{Me}$, a known compound discussed

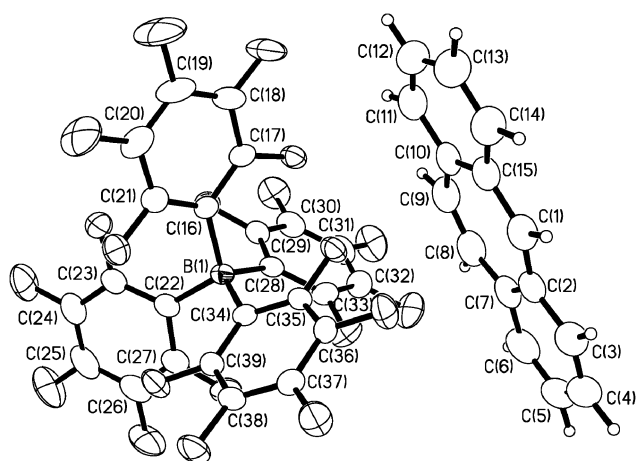


Fig. 1 Structure of [DBS][B(C₆F₅)₄] (1).

below. Thus the nature of the thermal degradation of [DBS][B(CH₂CMe₃)(C₆F₅)₃] seems confirmed.

X-Ray quality crystals of the compounds [DBS][B(C₆F₅)₄], [DBS][BCl(C₆F₅)₃] and [DBS][B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃] were grown from dichloromethane solutions by layering with hexanes and their crystal structures were determined. The structures of [DBS][B(C₆F₅)₄], [DBS][BCl(C₆F₅)₃] and [DBS][B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃] are shown in Fig. 1, 2 and 3, respectively, crystallographic data for all in Table 1 and important bond lengths and angles for the cation of each in Table 2. To our knowledge, these crystal structures are the first reported for the DBS carbocation.

As expected, the structures of the cations in the three salts are all essentially planar and the carbon-carbon bond lengths are also very similar although the relatively large esds for [DBS][B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃] render comparisons involving this salt tenuous. The average of the six C(1)–C(2)/C(1)–C(15) bond lengths is ~1.40 Å, that of the six C(2)–C(7)/C(10)–C(15) bond lengths is ~1.43 Å and that of the six C(7)–C(8)/C(9)–C(10) bond lengths is ~1.42 Å while the average of the three C(8)–C(9) bond lengths is ~1.35 Å. Thus

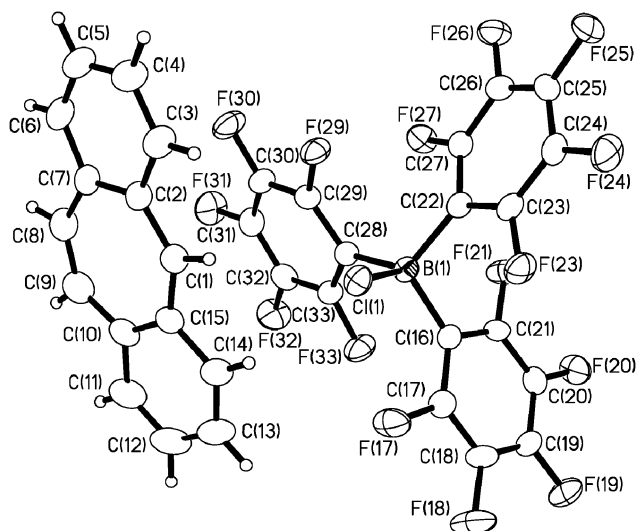


Fig. 2 Structure of [DBS][BCl(C₆F₅)₃] (2).

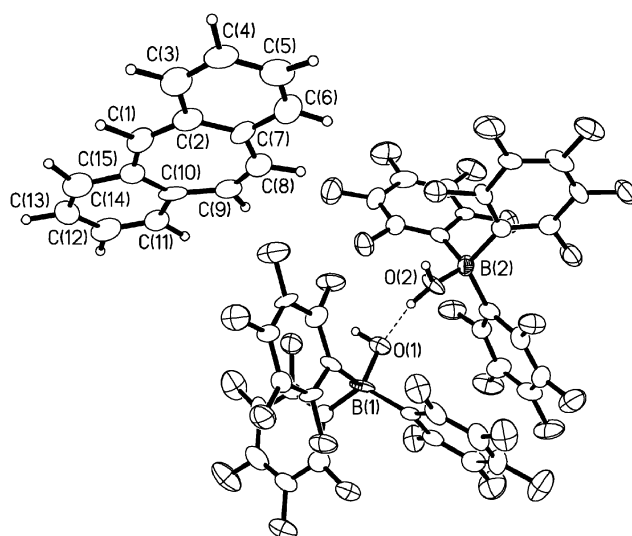
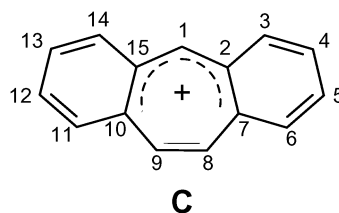


Fig. 3 Structure of [DBS][B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃] (3).

only the C(8)–C(9) bond lengths are sufficiently short to approximate that of the tropylium ion (average ~1.35 Å).¹⁰ Indeed, the C(1)–C(2)/C(1)–C(15) and C(2)–C(7)/C(10)–C(15) bonds are relatively long, implying an extensively delocalized, conjugated structure as in **C** rather than the localized structure implied by **B**.



The structures of the anions are similar to those of [Ph₃C][BCl(C₆F₅)₃]^{1f} or the [C₁₀H₆(NMe₂)₂H]⁺ and [NHEt₃]⁺ salts of [B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃].⁹

NMR spectra

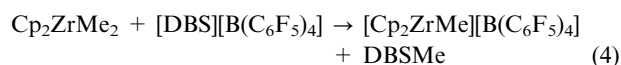
The numbering scheme used to assign ¹H NMR chemical shifts is shown in **B** and **C**. The ¹H NMR spectra (CD₂Cl₂) of the DBS salts of [B(C₆F₅)₄][–], [BCl(C₆F₅)₃][–], [B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃][–] and [B(CH₂CMe₃)(C₆F₅)₃][–] all exhibited resonances at δ 10.37 (s, 1H, H(1)), 9.13 (s, 2H, H(8,9)), and 8.97 (d, 2H), 8.76 (m, 4H) and 8.52 (m, 2H), attributed to H(3–6, 11–14). These chemical shifts are similar to those reported elsewhere for DBS⁺ generated in FSO₃H–SO₂ClF at –78 °C (δ 10.98 (H(1)), 9.65 (H(8,9)), 8.9–9.54).^{4f,g} For purposes of comparison, we note that the ¹H chemical shift of [C₇H₇][B(C₆F₅)₄] is δ 9.27 (CD₃CN).^{2a}

The ¹H NMR spectrum of [DBS][B(C₆F₅)₃-OH·H₂O-B(C₆F₅)₃] also exhibited a broad resonance at δ 8.16, attributed to the H₃O⁺ moiety,⁹ while the ¹H NMR spectrum of [DBS][B(CH₂CMe₃)(C₆F₅)₃] exhibited singlets at δ 0.63 and 1.48, attributed to the Me₃C and CH₂ groups, respectively.⁷ The ¹³C NMR spectrum (CD₂Cl₂) of [DBS][B(C₆F₅)₄] exhibited resonances with chemical shifts (δ 172.0, 146.4, 144.1, 143.0, 141.6, 137.6, 135.5, 134.5) very similar to those reported previously for other DBS salts in FSO₃H–SO₂ClF at –78 °C

(δ 170.7, 147.1, 144.9, 143.6, 142.5, 138.3, 136.2, 135.0),^{4f,g} while the ^{19}F NMR spectra of all three salts were consistent with the literature for the various anions.^{1f,9}

Activation of dimethylzirconocene by $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$

The reaction of Cp_2ZrMe_2 with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ at room temperature has been shown to proceed as in eqn (1).^{1f} In order to assess and compare the ability of the DBS carbocation to likewise abstract a methyl group, the room-temperature reaction of $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ with Cp_2ZrMe_2 was monitored by ^1H NMR spectroscopy in CD_2Cl_2 and toluene- d_8 . The ^1H NMR spectrum of a representative reaction mixture in CD_2Cl_2 , run a few minutes after mixing of the reactants, is shown in Fig. 4 and, as can be seen, the Cp and Me resonances of Cp_2ZrMe_2 at δ 6.13 and -0.38 , respectively, have disappeared and have been replaced by the Cp and Me resonances of $[\text{Cp}_2\text{ZrMe}]^+$ at δ 6.42 and 0.77, respectively.^{1f} Thus clean methyl abstraction as in eqn (4) has indeed occurred.



Concomitantly with these changes, the resonances of $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ at δ 10.37 (s, 1H), 9.13 (s, 2H), 8.97 (d, 2H), 8.76 (m, 4H), 8.52 (m, 2H) have disappeared and have been replaced by a new set of resonances at δ 7.2–7.5 (m), 6.95 (s) and 7.17 (s), 3.50 (q, J 7.32 Hz) and 4.18 (q, J 7.32 Hz), 1.31 (d, J 7.32 Hz) and 1.90 (d, J 7.32 Hz), which are very similar to the resonances of DBSMe reported previously.^{5c} Thus, as hoped, the DBS carbocation does indeed readily abstract a methyl carbanion from Cp_2ZrMe_2 .

That there are two sets of resonances in the spectrum of the hydrocarbon product is a result of there being present in solution almost equal amounts of two isomers in which the methyl group exists in the pseudo-axial or the pseudo-equatorial position as in **D** and **E**, respectively.

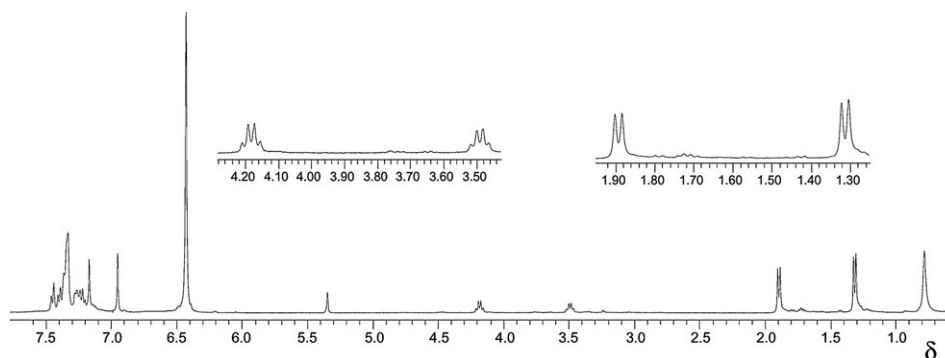
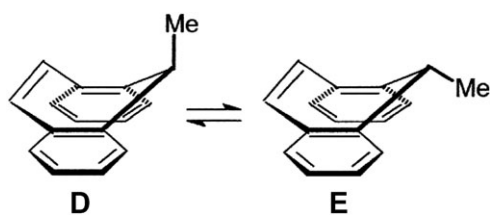


Fig. 4 ^1H NMR spectrum of a reaction of $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ with Cp_2ZrMe_2 in CD_2Cl_2 at -30°C .

Utilizing the atom labeling scheme of **B** and **C**,^{5c} the multiplet at δ 7.2–7.5 in the ^1H NMR spectrum of Fig. 4 may be assigned to H(3–6, 11–14) of the two isomers, the singlets at δ 6.95 and 7.17 to H(8,9) of the two isomers, the quartets at δ 3.50 (J 7.32 Hz) and 4.18 (J 7.32 Hz) to the methyne hydrogens H(1) of the two isomers and the doublets at δ 1.31 (J 7.32 Hz) and 1.90 (J 7.32 Hz) to the methyl groups of the two isomers. A NOESY experiment run in CD_2Cl_2 at -30°C demonstrated correlations between the resonances at δ 1.90 and 3.50 and between those at δ 1.31 and 4.18. There was also a correlation between the methyl resonance at δ 1.90 and a resonance in the aromatic region at $\delta \sim 7.5$ and another between the methyne resonance at δ 4.18 and a resonance in the aromatic region at $\delta \sim 7.3$, suggesting that the resonances at δ 1.90 and 4.18 are both to be attributed to pseudo-equatorial groups. Therefore, while neither of the olefinic resonances at δ 6.95 and 7.17 correlated with any of the methyl or methyne resonances and thus cannot be assigned to **D** or **E**, the resonances at δ 1.31 and 4.18 can confidently be assigned to **D**, those at δ 1.90 and 3.50 to **E**. These assignments have not previously been attempted.^{5c} A similar reaction of $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ with Cp_2ZrMe_2 in toluene- d_8 resulted in the precipitation of an orange oil, presumably of $[\text{Cp}_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ in view of the appearance in the solution phase of the resonances of the two isomers, **D** and **E**, of DBSMe.

We note that the ^1H NMR spectrum of $\text{DBSCH}_2\text{CMe}_3$, obtained *via* both the thermal decomposition of $[\text{DBS}][\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]$ and the reaction of $\text{Li}[\text{B}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{F}_5)_3]$ with dibenzosuberonyl chloride, exhibited a quartet methyne resonance at δ 4.18 but not one at $\delta \sim 3.50$. On this basis, it seems that $\text{DBSCH}_2\text{CMe}_3$ exists in solution with the bulky neopentyl group in the pseudo-axial position.

Ethylene, propylene polymerizations

Ethylene and propylene polymerization experiments were carried out to compare the efficiency of $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$ as cocatalyst with that of the well known $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$; $[\text{C}_7\text{H}_7][\text{B}(\text{C}_6\text{F}_5)_4]$ was also investigated briefly. In the case of ethylene, the precursor Cp_2ZrMe_2 was activated with $[\text{DBS}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{C}_7\text{H}_7][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in 1 : 1 molar ratios. Polymerizations were carried out in flame-dried glass reactors in 15 mL of dry toluene and were terminated by methanol injection after 30 min. In a typical polymerization run, ethylene was continuously bubbled

through the catalyst mixture throughout the whole course of polymerization experiment in order to keep the ethylene pressure constant at 1 atmosphere. Polymerization experiments were carried out with the reactors immersed in a water at 25 °C, although all became warmer during the polymerizations. In all cases polyethylene precipitated as the polymerizations proceeded, causing the solutions to become highly viscous. Similar behavior has been reported previously for similar types of metallocene polymerization catalysts,¹⁷ and it is likely that monomer diffusion was subject to mass-transport limitations and that the polymer yields obtained for ethylene polymerization should be regarded as the lower limits. As can be observed in Table 3, in which we report data which are averages of results of two or three experiments, the polymer yields obtained using [DBS][B(C₆F₅)₄], [C₇H₇][B(C₆F₅)₄] and [Ph₃C][B(C₆F₅)₄] are probably not significantly different. Thus the activity of [DBS][B(C₆F₅)₄] is, as anticipated, comparable to that of the much better studied [Ph₃C][B(C₆F₅)₄].

The results of the propylene polymerizations with Cp₂ZrMe₂ activated by [DBS][B(C₆F₅)₄] and, for comparison, with [Ph₃C][B(C₆F₅)₄], in the presence of Al(*i*-Bu)₃ as scavenger at 0 °C are shown in Table 3. Again we report data which are averages of results of two or three experiments. As in the ethylene polymerizations, the reactions were carried out in 50 mL dry toluene in a flame-dried glass reactor and Cp₂ZrMe₂ was activated with [DBS][B(C₆F₅)₄] or [Ph₃C][B(C₆F₅)₄] in a 1 : 1 molar ratio. In a typical experiment, the toluene solution was saturated with propylene followed by addition of toluene solutions of both Cp₂ZrMe₂ and [DBS][B(C₆F₅)₄] or [Ph₃C][B(C₆F₅)₄], respectively. Polymerizations were rapid at 1 atm propylene pressure and the reaction temperatures rose somewhat. All reactions were terminated by injection with methanol after 2 min. As with ethylene the yields and molecular weights of the products varied somewhat but there appears to be no significant difference between DBS and trityl carbocations as initiators.

Similar experiments were carried out in order to assess and compare the utility of [DBS][B(CH₂CMe₃)(C₆F₅)₃] as a co-initiator of Cp₂ZrMe₂, Ind₂ZrMe₂ and SBIZrMe₂. As can be seen in Table 3, while the polymer yields obtained using the Cp₂ZrMe₂/[DBS][B(CH₂CMe₃)(C₆F₅)₃] and Ind₂ZrMe₂/[DBS][B(CH₂CMe₃)(C₆F₅)₃] catalyst systems appear to be lower than those of Cp₂ZrMe₂/[DBS][B(C₆F₅)₄] and Ind₂ZrMe₂/[DBS][B(C₆F₅)₄], the resulting polymers have significantly higher molecular weights. The activities of these [B(CH₂CMe₃)(C₆F₅)₃][−]-based catalyst systems are also comparable with activities reported previously for analogous catalysts, as is the tacticity of the isotactic polypropylene produced by the SBIZrMe₂/[DBS][B(CH₂CMe₃)(C₆F₅)₃] catalyst system.⁷

Isobutene polymerizations initiated by [DBS][B(C₆F₅)₄]

Polymerizations of isobutene were carried out in methyl chloride–dichloromethane mixtures at −80 °C as described previously,⁸ with typical results (all averages of 2–4 experiments) shown in Table 3. As can be seen, conversions were generally high, but molecular weights of the polymers obtained were considerably lower than observed previously using

other initiators under the same conditions.⁸ The molecular weight distributions were also rather broad,⁸ suggesting the presence of more than one initiator species in solution.

Although cations such as DBS⁺ can in principal induce carbocationic polymerization of isobutene directly,^{11a} it has been shown that isobutene polymerizations initiated by the electrophilic species B(C₆F₅)₃,^{11b} Ph₃C⁺,^{11b} and Me₃Si⁺^{11c} occur because of the release of protons formed *via* reaction of these cations with trace amounts of water in the solvent systems used. This would involve the reaction of eqn (5) for DBS⁺, and, since dichloromethane is in fact very difficult to dry rigorously, initiation by residual protons needed to be considered.



To assess the possibility that isobutene polymerization was initiated by the protons arising from the partial hydrolysis of [DBS][B(C₆F₅)₄] by adventitious water present in the system, polymerization experiments were carried out in the presence of 2,6-di-*tert*-butylpyridine (DTBP). The non-nucleophilic DTBP generally behaves as a strong, sterically hindered base which does not react with most electrophiles but is readily protonated and thus behaves as a very effective proton scavenger.^{11d}

To ensure DTBP does not in fact react with the [DBS]⁺ cation, we carried out initially a ¹H NMR study in which we combined 0.015 mmol of [DBS][B(C₆F₅)₄] with 0.03 mmol of DTBP in CD₂Cl₂ in an NMR tube. As expected, the only resonances observable were those of the [DBS]⁺ cation and of DTBP and therefore [DBS][B(C₆F₅)₄] does not react with DTBP. DTBP was then added to several [DBS][B(C₆F₅)₄] solutions prior to initiation of isobutene polymerization and, as can be seen from the results shown in Table 3, the addition of DTBP significantly reduces the yield of the product formed. Thus the number of active sites is indeed decreased by the presence of DTBP and hydrolysis as in eqn (5) is indeed a factor in these polymerization reactions.

Summary

The bright red compounds [DBS][B(C₆F₅)₄], [DBS][BCl(C₆F₅)₃], [DBS][B(C₆F₅)₃–OH⋯H₂O–B(C₆F₅)₃] and [DBS][B(CH₂CMe₃)(C₆F₅)₃] (DBS = dibenzosuberonyl or dibenzotropylium or dibenzo[*a,e*]tropylium or dibenzo[*a,d*]cycloheptenocarbenium), all of them new, have been synthesized and characterized spectroscopically and, for the first three, crystallographically. The three crystal structures show that the DBS⁺ carbocation is planar, as expected, and are consistent with delocalization of the positive charge over part of the seven-membered ring, in particular the CH carbon and the carbon atoms α and β to it. The DBS⁺ carbocation is an efficient carbanion abstractor and activates metallocene catalyst precursors of the type Cp'₂ZrMe₂, its efficacy being comparable to that of the well known but sterically more hindered trityl carbocation, Ph₃C⁺. As with Ph₃C⁺, DBS⁺ does not initiate carbocationic polymerization of isobutene in dichloromethane directly, but rather by reacting with trace amounts of water to generate protons.

Acknowledgements

We thank Queen's University, the Natural Sciences and Engineering Research Council of Canada (Discovery Grant to M. C. B.), the Government of Ontario and Lanxess, Inc. for financial support, Drs Andrew Carr and Kevin Kulbaba (Lanxess) for helpful discussions and advice, and Dr Q. Wang of NOVA Chemicals for molecular weight measurements of the isotactic polypropylene samples.

References

- (a) J. C. W. Chien, W.-M. Tsai and M. D. Rausch, *J. Am. Chem. Soc.*, 1991, **113**, 8570; (b) M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255; (c) L. Jia, X. Yang, C. L. Stem and T. J. Marks, *Organometallics*, 1997, **16**, 842; (d) M. Bochmann, *Top. Catal.*, 1999, **7**, 9; (e) E. Y. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391; (f) J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223.
- (a) S. W. Ewart and M. C. Baird, unpublished results; For mention of $[\text{C}_7\text{H}_7][\text{B}(\text{C}_6\text{F}_5)_4]$ as an activator in patents, see: (b) Q. Yang, K. C. Jayaratne, M. D. Jensen, M. P. McDaniel, J. L. Martin, M. G. Thorn, J. T. Lanier and T. R. Crain, *US Pat. Appl.*, 2007/0197374 A1, Aug. 23, 2007; (c) A. Z. Voskoboinikov, V. V. Izmer, A. F. Asachenko, M. V. Nikulin, A. N. Ryabov, A. Y. Lebedev, C. L. Coker and J. A. M. Canich, *PCT Int. Appl.*, 2006/065809 A2, June 22, 2006; (d) Q. Wang, P. Lam, G. Baxter and J. A. Auger, *Eur. Pat. Appl.*, 1400541 A2, Mar. 24, 2004; (e) M. Sone, A. Hasegawa, S. Yamada and A. Yano, *Jpn. Kokai Tokkyo Koho*, JP 05310829 A, Nov. 22, 1993.
- (a) K. Yamane, H. Yamamoto and M. Nitta, *J. Org. Chem.*, 2002, **67**, 8114, and references therein.
- (a) M. Ilies, M. D. Banciu, A. Scozzafava, M. A. Ilies, M. T. Caproiu and C. T. Supuran, *Bioorg. Med. Chem.*, 2003, **11**, 2227; (b) C. Stavarache, A.-M. Pocsan, M. Vinatoru and T. J. Mason, *Ultrason. Sonochem.*, 2003, **10**, 49; (c) A. Rosowsky, H. Fu and S. F. Queener, *J. Heterocycl. Chem.*, 2000, **37**, 921; (d) M. Noda and M. Kiffe, *J. Pept. Res.*, 1997, **50**, 329; (e) G. Berti, *J. Org. Chem.*, 1957, **22**, 230; (f) G. A. Olah and G. Liang, *J. Org. Chem.*, 1975, **40**, 2108; (g) B. Eliasson, D. Johnels, I. Sethson, U. Edlund and K. Muellen, *J. Chem. Soc., Perkin Trans. 2*, 1990, 897; (h) L. J. Johnson, J. Lobaugh and V. Wintgens, *J. Phys. Chem.*, 1989, **93**, 7370.
- (a) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245; (b) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1966, **5**, 218; (c) A. Hjelmencrantz, A. Friberg and U. Berg, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1293; (d) E. Samuel and M. D. Rausch, *J. Am. Chem. Soc.*, 1973, **95**, 6263; (e) M. Bochmann, S. J. Lancaster, M. B. Hursthouse and K. M. A. Malik, *Organometallics*, 1994, **13**, 2235.
- D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham UK, 1974, vol. 4, Table 2.2A.
- (a) N. Bavarian and M. C. Baird, *Dalton Trans.*, 2004, 4089; (b) N. Bavarian and M. C. Baird, *Organometallics*, 2005, **24**, 2889.
- (a) C. K. W. Tse, K. R. Kumar, M. J. Drewitt and M. C. Baird, *Macromol. Chem. Phys.*, 2004, **205**, 1439; (b) P. J. McInenly, M. J. Drewitt and M. C. Baird, *Macromol. Chem. Phys.*, 2004, **205**, 1707; (c) A. Cordoneanu and M. C. Baird, *Macromolecules*, 2004, **37**, 6744; (d) C. K. W. Tse, A. Penciu, P. J. McInenly, K. R. Kumar, M. J. Drewitt and M. C. Baird, *Eur. Polym. J.*, 2004, **40**, 2653; (e) S. Mitu and M. C. Baird, *Eur. Polym. J.*, 2006, **42**, 2039.
- (a) M. J. Drewitt, M. Niedermann and M. C. Baird, *Inorg. Chim. Acta*, 2002, **340**, 207; (b) A. Saverio, F. Focante, I. Camurati, L. Resconi, T. Beeringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, *Inorg. Chem.*, 2005, **44**, 5030.
- M. Lämä, T. Suorsa, J. Pursiainen, J. Huuskonen and K. Rissanen, *Chem. Commun.*, 1996, 1443.
- (a) M. Sawamoto, *Prog. Polym. Sci.*, 1991, **16**, 111; (b) T. D. Schaffer and J. D. Ashbaugh, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 329; (c) Z. Pi, S. Jacob and J. P. Kennedy, in *Ionic Polymerizations and Related Processes*, ed. J. E. Puskas, Kluwer, The Netherlands, 1999, p. 1; (d) Y. C. Bae and R. Faust, *Macromolecules*, 1997, **30**, 7341.