Conformational Behavior of Tris(pentafluorophenyl)borane-Benzotriazole Adducts

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SUPPORTING INFORMATION

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Results for the Homopolimerization of 1-Hexene with Adducts 1–3

The homopolymerization of liquid 1-hexene was chosen as a simple screening tool to evaluate the performance of compounds **1–3** in alpha-olefin polymerization. The results are shown in Table S1. The choice of the metallocene catalyst selected for these experiments, that is dimethylsilyl{(1-(2,4,7-trimethylindenyl)-7-(2,5-dimethyl-cyclopenta[1,2-*b*:4,3-*b*′]-dithiophene)} zirconium dimethyl, was based on its known ability to efficiently polymerize alpha-olefins to isotactic polyolefins.[3,10]

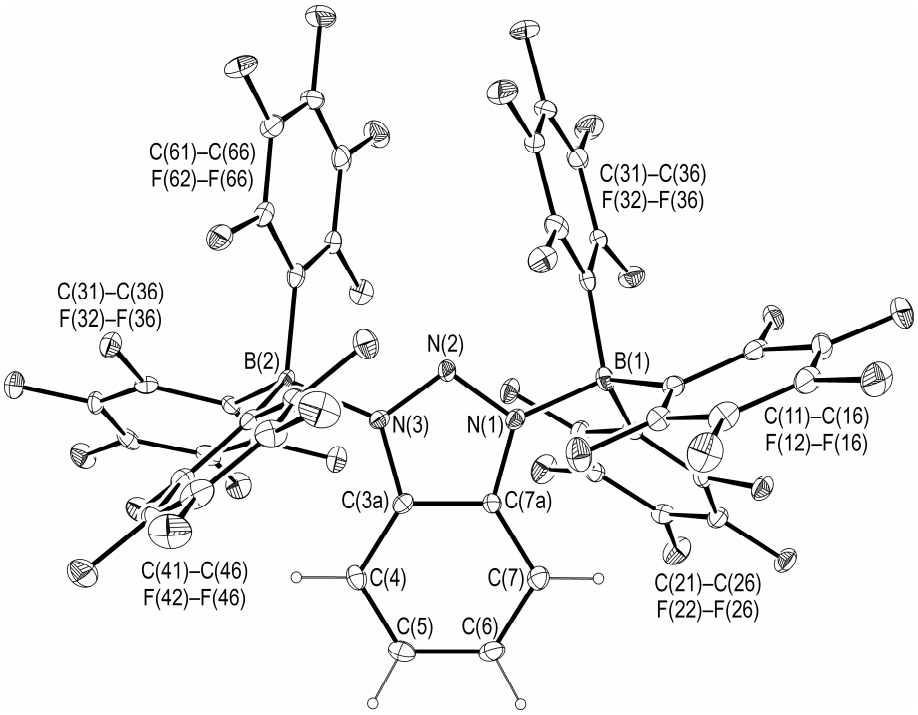
Although the results shown in Table S1 are preliminary and may be influenced by the purity of the various batches of 1-hexene used, nevertheless the indication is that in this process the efficency of adduct **3** is comparable to that of $[Ph_3C][B(C_6F_5)_4]$ and $[HNMe_2Ph][B(C_6F_5)_4]$, with adduct **3** giving higher molecular weights. Furthermore, **3** seems to be more effective even than methylalumoxane (MAO).

Table S1. 1-Hexene Polymerization Yields Using Borates or MAO as Cocatalysts.[a]

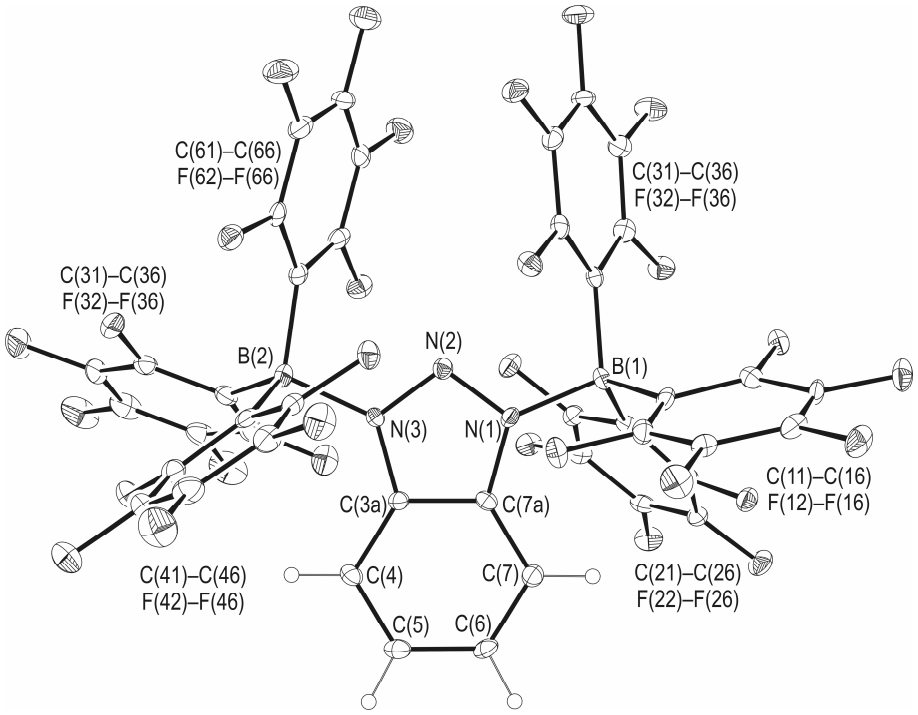
Cocatalyst	Mg	Yield (g)	Productivity (kg/g_{cat})	Productivity (kg/g_{cocat})	M_w (kg/mol)	M_w/M_n
MAO[b] (10% PhMe solution, Al/Zr = 200)	37.0	10.37	20.7	0.3	236.4	3.10
$[Ph_3C][B(C_6F_5)_4]$	8.5	15.2	30.4	1.8	411.7	3.37
$[HNMe_2Ph][B(C_6F_5)_4]$	7.4	14.4	28.8	1.9	400.3	3.83
{Benzotriazole-$[B(C_6F_5)_3]_2$}$[NHEt_3]$[b]	11.0	13	26.0	1.2	602.2	3.09
Benzotriazole-$B(C_6F_5)_3$	5.8	0	0.0	0.0		
[Benzotriazole-$B(C_6F_5)_3$]$[HNEt_3]$[b]	6.7	0	0.0	0.0		
[Benzotriazole-$B(C_6F_5)_3$]$[HNEt_3]$[c]	6.7	0	0.0	0.0		

[a]Conditions: 20 g 1-hexene, 50 °C, 30 min. Catalyst: dimethylsilyl{(1-(2,4,7-trimethylindenyl)-7-(2,5-dimethyl-cyclopenta[1,2-*b*:4,3-*b*′]-dithiophene)} zirconium dimethyl, 0.5 mg. 100 Equiv of Al^iBu_3 added as scavenger. 1-Hexene was percolated over activated alumina prior to use. GPC data were calculated using polybutene molecular weight constants. [b]Sequence of addition: 1) 1-hexene + Al^iBu_3, 2) metallocene in toluene into 1-hexene, 3) cocatalyst in toluene into 1-hexene. [c]Sequence of addition: 1) 1-hexene + Al^iBu_3, 2) cocatalyst in toluene into 1-hexene, 3) metallocene in toluene into 1-hexene.

Figure S1. ORTEP views of the μ-(1*H*-benzotriazolato-1κN^1:2κN^3)diborate anion **3** with a partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are given arbitrary radii. The two independent molecules are shown.



molecule I



molecule II

Table S2. Selected Geometric Parameters (Å and °) for **3**.[a]

	I	II	average[b]
N(1)–N(2)	1.3254(18)	1.3141(18)	1.319
N(3)–N(2)	1.3176(18)	1.3189(18)	
N(1)–C(7a)	1.376(2)	1.3743(19)	1.375
N(3)–C(3a)	1.3740(19)	1.375(2)	
C(3a)–C(7a)	1.404(2)	1.392(2)	1.398
C(3a)–C(4)	1.392(2)	1.401(2)	1.397
C(7a)–C(7)	1.397(2)	1.399(2)	
C(4)–C(5)	1.371(2)	1.382(2)	1.375
C(6)–C(7)	1.372(2)	1.374(2)	
C(5)–C(6)	1.421(2)	1.398(2)	1.410
N(1)–B(1)	1.593(2)	1.596(2)	1.596
N(3)–B(2)	1.5996(19)	1.596(2)	
B(1)–C(11)	1.646(2)	1.640(2)	1.641
B(2)–C(41)	1.637(2)	1.641(2)	
B(1)–C(21)	1.633(2)	1.641(2)	1.640
B(2)–C(51)	1.635(2)	1.650(3)	
B(1)–C(31)	1.631(2)	1.640(2)	1.636
B(2)–C(61)	1.642(2)	1.629(2)	
N(2)–N(1)–C(7a)	109.75(12)	110.05(12)	109.92
N(2)–N(3)–C(3a)	109.93(12)	109.95(12)	
N(1)–N(2)–N(3)	108.85(12)	108.55(12)	108.70
N(3)–C(3a)–C(4)	132.04(14)	131.97(14)	132.36
N(1)–C(7a)–C(7)	132.74(14)	132.67(14)	
N(3)–C(3a)–C(7a)	105.87(13)	105.67(13)	105.73
N(1)–C(7a)–C(3a)	105.59(13)	105.78(13)	
C(4)–C(3a)–C(7a)	122.01(14)	122.36(14)	121.90
C(7)–C(7a)–C(3a)	121.67(14)	121.54(14)	
C(3a)–C(4)–C(5)	116.25(14)	115.64(14)	115.86
C(7a)–C(7)–C(6)	115.94(14)	115.63(14)	
C(4)–C(5)–C(6)	121.75(15)	121.61(15)	122.22
C(7)–C(6)–C(5)	122.32(15)	123.21(15)	
N(2)–N(1)–B(1)	120.13(12)	121.27(12)	120.54
N(2)–N(3)–B(2)	120.87(12)	119.87(12)	
C(7a)–N(1)–B(1)	129.14(12)	128.17(12)	128.90
C(3a)–N(3)–B(2)	128.82(12)	129.46(13)	

N(1)–B(1)–C(11)	111.51(12)	110.24(12)	111.29
N(3)–B(2)–C(41)	111.11(12)	112.29(14)	
N(1)–B(1)–C(21)	103.05(12)	101.00(11)	102.02
N(3)–B(2)–C(51)	101.97(11)	102.08(12)	
N(1)–B(1)–C(31)	105.60(12)	108.97(12)	107.04
N(3)–B(2)–C(61)	107.61(12)	105.96(12)	
C(11)–B(1)–C(21)	114.33(13)	115.86(13)	114.72
C(41)–B(2)–C(51)	114.13(12)	114.58(13)	
C(11)–B(1)–C(31)	107.03(12)	106.91(12)	106.48
C(41)–B(2)–C(61)	105.44(11)	106.53(13)	
C(21)–B(1)–C(31)	115.01(13)	113.65(12)	115.07
C(51)–B(2)–C(61)	116.47(12)	115.15(14)	
N(2)–N(1)–B(1)–C(11)	115.19(16)	119.86(15)	119.2
N(2)–N(3)–B(2)–C(41)	121.34(15)	120.59(16)	
N(1)–B(1)–C(11)–C(12)	–3.9(2)	–11.5(2)	–9.2
N(3)–B(2)–C(41)–C(42)	–12.0(2)	–9.3(3)	
N(1)–B(1)–C(21)–C(22)	54.72(19)	54.79(18)	57.5
N(3)–B(2)–C(51)–C(52)	61.20(17)	59.2(2)	
N(1)–B(1)–C(31)–C(32)	62.66(19)	57.7(2)	59.5
N(3)–B(2)–C(61)–C(62)	59.2(2)	58.3(2)	

[a]I and II refer to the two independent molecules in the asymmetric unit of $[NHEt_3]$**3**·½C_7H_8. [b]Computed taking into account the idealized C_2 symmetry of anion **3**.

Compound **1** – HF/6-31G optimized geometry

Energy calculated at HF/6-31G: –2590.32549456

C	-2.74668800	1.96146800	3.95697600
C	-3.50264700	2.78847100	3.16463000
C	-3.30766300	2.86060700	1.76653400
C	-2.35689900	2.10512700	1.12825600
C	-1.59215100	1.25375800	1.93040700
C	-1.78316600	1.19537400	3.30003400
N	-0.85308000	0.28070100	3.72853800
N	-0.15171100	-0.18711500	2.72842200
N	-0.55998000	0.36634000	1.65013600
H	-0.65684300	-0.04565600	4.64389900
B	0.02691000	-0.05635900	0.18220200
H	-2.88640200	1.90999000	5.01750500
H	-4.25814100	3.40180300	3.61322800
H	-3.91754100	3.53024600	1.19444700
H	-2.20275400	2.17737500	0.07269200
C	-1.94627300	-1.78186400	-0.04033700
C	-1.33479900	-0.64464900	-0.55209000
C	-1.99752400	-0.08944200	-1.63192600
C	-3.13829300	-0.62985600	-2.18967900
C	-3.67994100	-1.77237900	-1.65921400
C	-3.07890400	-2.35127600	-0.56491000
F	-1.40690000	-2.38725500	1.06046000
F	-1.58056100	1.09470200	-2.17527200
F	-3.73837400	-0.02142500	-3.24244300
F	-4.80393100	-2.30969000	-2.18652100
F	-3.61553800	-3.46499900	-0.00848400
C	1.19403300	1.06903400	-1.85722900
C	0.73834400	1.23501700	-0.55598600
C	1.05655800	2.45727600	0.00732600
C	1.74316300	3.44703600	-0.66715800
C	2.15623800	3.23439000	-1.95693900
C	1.88004200	2.02713100	-2.55907100
F	0.95290600	-0.11760200	-2.48841100
F	0.70215600	2.75355000	1.29376400
F	2.01258800	4.62770200	-0.05577100
F	2.83074800	4.19568700	-2.62955500
F	2.28964800	1.79683700	-3.83009300
C	2.33000900	-0.83008900	1.19838200
C	1.23734500	-1.15574400	0.40503200
C	1.33956600	-2.38869500	-0.22005300
C	2.41002200	-3.24094500	-0.04708900
C	3.44994100	-2.87794400	0.77108300
C	3.40982000	-1.65568900	1.39872900
F	2.37121400	0.38684200	1.82069500
F	0.36956300	-2.82933100	-1.06889200
F	2.44132100	-4.43697100	-0.68433800
F	4.50417700	-3.70656100	0.95290100
F	4.43317300	-1.27127800	2.20232900

Compound **3** – C_2 isomer, HF/6-31G optimized geometry

Energy calculated at HF/6-311+G(d): –4789.71701728

N	0.32644500	1.01217200	0.78151800
N	0.00000000	0.00000000	0.04023300
N	-0.32644500	-1.01217200	0.78151800
C	-0.21027900	-0.65826600	2.11261200
C	-0.41845200	-1.36140000	3.30314200
H	-0.71716300	-2.38801100	3.30892500
C	-0.20444900	-0.67578600	4.47113500
H	-0.34963700	-1.17444000	5.40900800
C	0.20444900	0.67578600	4.47113500
H	0.34963700	1.17444000	5.40900800
C	0.41845200	1.36140000	3.30314200
H	0.71716300	2.38801100	3.30892500
C	0.21027900	0.65826600	2.11261200
B	0.88103100	2.39083900	0.17637300
C	-0.10849100	3.66606000	0.55864800
C	-1.37444900	3.60932800	1.11598000
C	-2.16374400	4.72539000	1.31560000
C	-1.70867500	5.96299700	0.94228500
C	-0.46309200	6.07224600	0.36798700
C	0.29394700	4.94260800	0.18827800
C	2.40502300	2.47783100	0.83439800
C	3.35353900	1.52761200	0.47342000
C	4.63074200	1.48789500	0.97469200
C	5.02140000	2.42207400	1.90632200
C	4.11991500	3.36739800	2.31930300
C	2.84639200	3.37641000	1.78795300
C	0.84359600	2.31860500	-1.47683000
C	-0.35917600	2.06188400	-2.12384600
C	-0.50384500	2.02794200	-3.49071800
C	0.58222800	2.28413300	-4.29307600
C	1.78740600	2.57562600	-3.70730900
C	1.89835600	2.59447400	-2.33287400
F	-1.92533800	2.42553200	1.50839900
F	-3.39252500	4.60392000	1.88112500
F	-2.47452500	7.06646100	1.13317200
F	0.00000000	7.29069700	-0.01416800
F	1.52050700	5.10684700	-0.39221300
F	3.02325200	0.57325000	-0.43984400
F	5.51164300	0.54105800	0.56516900
F	6.27665600	2.39802100	2.41936900
F	4.47768100	4.28003100	3.26123500
F	2.00090700	4.31690200	2.31619600
F	-1.49076000	1.86209700	-1.38933500
F	-1.71059600	1.76136800	-4.05429300
F	0.45757500	2.26928900	-5.64276200
F	2.86308200	2.85856900	-4.48629000
F	3.12919800	2.93300100	-1.85396600
B	-0.88103100	-2.39083900	0.17637300
C	0.10849100	-3.66606000	0.55864800
C	1.37444900	-3.60932800	1.11598000
C	2.16374400	-4.72539000	1.31560000
C	1.70867500	-5.96299700	0.94228500
C	0.46309200	-6.07224600	0.36798700
C	-0.29394700	-4.94260800	0.18827800
C	-2.40502300	-2.47783100	0.83439800
C	-3.35353900	-1.52761200	0.47342000
C	-4.63074200	-1.48789500	0.97469200
C	-5.02140000	-2.42207400	1.90632200
C	-4.11991500	-3.36739800	2.31930300
C	-2.84639200	-3.37641000	1.78795300
C	-0.84359600	-2.31860500	-1.47683000

C	0.35917600	-2.06188400	-2.12384600
C	0.50384500	-2.02794200	-3.49071800
C	-0.58222800	-2.28413300	-4.29307600
C	-1.78740600	-2.57562600	-3.70730900
C	-1.89835600	-2.59447400	-2.33287400
F	1.92533800	-2.42553200	1.50839900
F	3.39252500	-4.60392000	1.88112500
F	2.47452500	-7.06646100	1.13317200
F	0.00000000	-7.29069700	-0.01416800
F	-1.52050700	-5.10684700	-0.39221300
F	-3.02325200	-0.57325000	-0.43984400
F	-5.51164300	-0.54105800	0.56516900
F	-6.27665600	-2.39802100	2.41936900
F	-4.47768100	-4.28003100	3.26123500
F	-2.00090700	-4.31690200	2.31619600
F	1.49076000	-1.86209700	-1.38933500
F	1.71059600	-1.76136800	-4.05429300
F	-0.45757500	-2.26928900	-5.64276200
F	-2.86308200	-2.85856900	-4.48629000
F	-3.12919800	-2.93300100	-1.85396600

Compound **3** – C_s isomer, HF/6-31G optimized geometry

Energy calculated at HF/6-311+G(d): –4789.71431984

N	-1.07978300	0.18582800	-0.81969900
N	-0.00932700	-0.15244500	-0.16874400
N	1.04775000	0.25843700	-0.79555100
C	0.66565800	0.92814000	-1.94193400
C	1.38922400	1.58523100	-2.94200800
H	2.45609500	1.65292700	-2.91490300
C	0.66574600	2.13568500	-3.96767600
H	1.17738000	2.64797000	-4.75824800
C	-0.74176000	2.02918100	-4.01984300
H	-1.26377500	2.45156800	-4.85560700
C	-1.45030400	1.39238300	-3.03434000
H	-2.51316000	1.29259100	-3.09002500
C	-0.71499900	0.85736600	-1.97140300
B	-2.55442400	-0.01153400	-0.20713800
C	-3.40248800	-1.18472000	-1.00733200
C	-2.96119600	-1.96220600	-2.06305000
C	-3.71447700	-2.97674000	-2.62094300
C	-4.96114500	-3.25672900	-2.12516900
C	-5.44601200	-2.51348300	-1.07366000
C	-4.67060300	-1.51229600	-0.54693700
C	-2.40078700	-0.54523000	1.35543300
C	-2.91346400	0.06863200	2.48762500
C	-2.77975700	-0.44401900	3.76068900
C	-2.11825500	-1.62878300	3.95535900
C	-1.61108100	-2.29263200	2.86477400
C	-1.76922600	-1.75641200	1.60895200
C	-3.21886100	1.50994100	-0.33198800
C	-4.35723000	1.86755200	-1.03192900
C	-4.84399000	3.15840400	-1.09378800
C	-4.18120400	4.16873900	-0.44894000
C	-3.02979900	3.87488800	0.24475600
C	-2.57996000	2.57959700	0.28492700
F	-1.73776500	-1.75851900	-2.62737600
F	-3.22854800	-3.69944200	-3.66297500
F	-5.71137100	-4.24989900	-2.66521400
F	-6.68176500	-2.77558100	-0.57376400
F	-5.20751900	-0.79208100	0.48431300
F	-3.61983900	1.23316000	2.40663000
F	-3.30999300	0.21356200	4.82411400
F	-1.97997100	-2.14536600	5.20088500
F	-0.96256200	-3.47457300	3.03594500
F	-1.28136900	-2.49748100	0.57225000
F	-5.05188400	0.95163900	-1.77304900
F	-5.96506000	3.43475600	-1.81062500
F	-4.64164200	5.44276800	-0.50796100
F	-2.35171200	4.86818000	0.87331400
F	-1.43249800	2.35387700	0.98757500
B	2.51688500	0.11115700	-0.16150300
C	3.60589700	-0.55330700	-1.22634300
C	3.33205800	-1.23186600	-2.40246500
C	4.30605000	-1.84520500	-3.16700800
C	5.61567800	-1.81444300	-2.76532400
C	5.93926600	-1.16952900	-1.59404400
C	4.94672800	-0.56934100	-0.86161300
C	2.84936300	1.67861100	0.27846500
C	2.14983500	2.26418900	1.32766600
C	2.32192300	3.56443100	1.73423300
C	3.21777200	4.36904300	1.06865600
C	3.91499600	3.85343900	0.00761500
C	3.71873600	2.53997700	-0.36574200

C	2.47624600	-0.98499600	1.07657200
C	1.99452100	-2.26658100	0.83497400
C	1.99854500	-3.27868000	1.76510600
C	2.51367800	-3.04081700	3.01698400
C	3.02313800	-1.79970500	3.30327300
C	3.00631700	-0.80830700	2.34445700
F	2.06293600	-1.33289400	-2.88426900
F	3.97246200	-2.48229100	-4.31924600
F	6.58037300	-2.41335600	-3.50787500
F	7.23114600	-1.13721300	-1.17546900
F	5.32566000	0.04155400	0.30056500
F	1.23655100	1.52505800	2.01786500
F	1.62174300	4.06466100	2.78230200
F	3.39997600	5.65772100	1.44997000
F	4.78574200	4.64007600	-0.67849300
F	4.42501000	2.13339300	-1.46863900
F	1.52578600	-2.58197100	-0.40578700
F	1.53107800	-4.51156300	1.45024800
F	2.54183300	-4.02541000	3.94804100
F	3.55829200	-1.55892100	4.52877700
F	3.57735600	0.37367400	2.71436100