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Synthesis of Cyclopentadienyl-, Indenyl-, and Fluorenylbis(pentafluorophenyl)boranes as Ligands in Titanium and Zirconium Half-Sandwich Complexes. The Crystal Structures of $C_{13}H_9B(C_6F_5)_2\cdot t\text{-}BuNH_2$, $C_{13}H_8SiMe_3B(C_6F_5)_2$, and $\{\eta^5\text{-}C_5H_4B(C_6F_5)_2\}TiCl_3$

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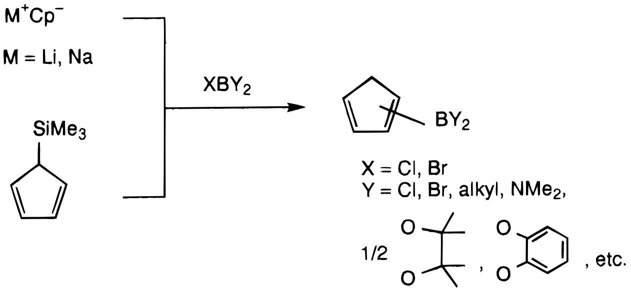
Bis(pentafluorophenyl)boron fluoride $(C_6F_5)_2BF\cdot OEt_2$ (**1**), readily accessible from $BF_3\cdot OEt_2$ and 2 equiv of C_6F_5MgBr, reacts with fluorenyllithium to give $(Flu)B(C_6F_5)_2$ (**4**), while the reaction with indenyllithium leads to the regioisomers 1- and 2-$IndB(C_6F_5)_2$ **5** and **6**, which are separated by fractional crystallization. **4** and **5** form crystalline adducts with *tert*-butylamine. The trimethylsilyl derivatives $Flu(SiMe_3)B(C_6F_5)_2$ (**9**) and $Ind(SiMe_3)B(C_6F_5)_2$ (**10**) are similarly prepared. Heating $(C_6F_5)_2BF\cdot OEt_2$ leads to ether cleavage and formation of $(C_6F_5)_2BOEt$. Treatment of **5** and **6** with $Zr(NMe_2)_4$ at room temperature gives indenylzirconium amido half-sandwich complexes; however, the reaction is accompanied by the unexpected exchange of one boron-C_6F_5 substituent by NMe_2, to form 1- and 2-$\{C_9H_6B(C_6F_5)(NMe_2)\}Zr(NMe_2)_3$. Reaction with $SiClMe_3$ affords the trichlorides 1- and 2-$\{C_9H_6B(C_6F_5)(NMe_2)\}ZrCl_3$. The NMe_2 substituent reduces the Lewis acidity of boron, so that donor ligands such as THF or DME coordinate exclusively to zirconium. Whereas **9** and **10** fail to react with group 4 metal chlorides, the cyclopentadienylborane $C_5H_4(SiMe_3)B(C_6F_5)_2$ undergoes smooth dehalosilylation with $TiCl_4$ to give $\{C_5H_4B(C_6F_5)_2\}TiCl_3$. Both 2-$\{C_9H_6B(C_6F_5)(NMe_2)\}ZrCl_3$ and $\{C_5H_4B(C_6F_5)_2\}TiCl_3$ in the presence of low concentrations of $AlEt_3$ are active ethene polymerization catalysts, while under comparable conditions mixtures of $AlEt_3$ and either $IndZrCl_3$ or $CpTiCl_3$ are inactive. The molecular structures of $(Flu)B(C_6F_5)_2\cdot NH_2CMe_3$, $Flu(SiMe_3)B(C_6F_5)_2$, and $\{C_5H_4B(C_6F_5)_2\}TiCl_3$ have been determined by X-ray diffraction.

Introduction

Cyclopentadienylboranes of the type $C_5H_{5-n}(BX_2)_n$ (n = 1 or 2) are generally accessible by the reaction of sodium cyclopentadienide with boron trihalides (X = Cl, Br, I)[1] or from trialkylsilylcyclopentadienes by elimination of R_3SiX.[2] Dialkylborane derivatives $(C_5H_5)BR_2$ are obtained similarly (Scheme 1).[3] Most of these are thermally sensitive and undergo facile Diels−Alder dimerization. The use of these compounds as ligands in early transition metal complexes was pioneered by Jutzi and Seufert, who prepared a series of titanium complexes $(C_5H_3RBX_2)TiCl_3$ (R = H, Me; X = Cl, Br, OEt, Me) by the dehalosilylation of $(C_5H_3RBX_2)SiMe_3$ (eq 1).[4] The direct borylation of a coordinated cyclopentadienyl ligand by the electrophilic attack with BX_3 (X = Cl, Br, I), RBI_2, or B_2Cl_4, which is a successful approach in the case of 18-electron metallocenes,[5] is not applicable in early transition metal systems.[6]

Scheme 1



We have recently reported the synthesis of borato (BR_3)-substituted cyclopentadienyl complexes of type **I**

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1997.

[1] (a) Brit. Pat. Application 768,083 (to Ethyl Corp.), 1957; *Chem. Abstr.* **1957**, *51*, 15584d. (b) Lockman, B.; Onak, T. *J. Org. Chem.* **1973**, *38*, 2552. (c) Jutzi, P.; Krato, B.; Hursthouse, M. B.; Howes, A. J. *Chem. Ber.* **1987**, *120*, 565.

[2] (a) Jutzi, P.; Seufert, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 295. (b) Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1979**, *169*, 357.

[3] (a) Grunke, H.; Paetzold, P. I. *Chem. Ber.* **1971**, *104*, 1136. (b) Klang, J. A.; Collum, D. B. *Organometallics* **1988**, *7*, 1532. (c) Herberich, G. E.; Fischer, A. *Organometallics* **1996**, *15*, 58. (d) Larkin, S. A.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Foo, D. M. J.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2393.

[4] Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1979**, *169*, 373.

[5] (a) McVey, S. ; Morrison, I. G.; Pauson, P. L. *J. Chem. Soc. C* **1967**, 1847. (b) Kotz, J. C.; Post, E. W. *J. Am. Chem. Soc.* **1968**, 4503. (c) Kotz, J. C.; Post, E. W. *Inorg. Chem.* **1970**, *9*, 1661. (d) Ruf, W.; Fuller, M.; Siebert, W. *J. Organomet. Chem.* **1974**, *64*, C45. (e) Renk, T.; Ruf, W.; Siebert, W. *J. Organomet. Chem.* **1976**, *120*, 1. (f) Wrackmeyer, B., Dörfler, V.; Herberhold, M. *Z. Naturforsch.* **1993**, *48B*, 121. (g) Appel, A.; Nöth, H.; Schmidt, M. *Chem. Ber.* **1995**, *128*, 621.

[6] For borylation of cyclopentadienyl ligands in early transition metal complexes, see, for example: (a) Braunschweig, H.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1613. (b) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. (c) Hartwig, J. F.; He, X. *Organometallics* **1996**, *15*, 5350. (d) Deck, P. A.; Fisher, T. S.; Downey, J. S. *Organometallics* **1997**, *16*, 1193. (e) Bohra, R.; Hitchcock, P. B.; Lappert, M. F.; An-Yeung, S. F.; Leung, W. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2999. (f) The synthesis of boryl-substituted cobaltocenes has been reported: Herberich, G. E.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1996**, *15*, 3106.

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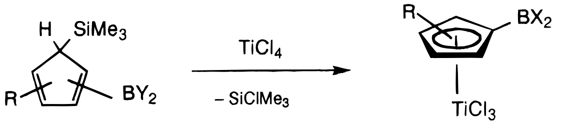


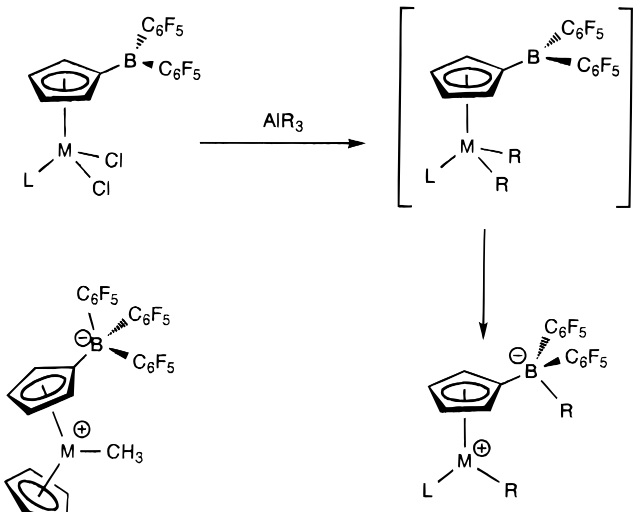
(1)

as "single-component" zwitterionic catalysts for olefin polymerizations which, for the very weakly coordinating substituents R = C_6F_5, show good ethene polymerization activity.[7] These complexes provide an alternative to the widely used method of catalyst generation by activating metallocene dialkyls with $B(C_6F_5)_3$ and similar cation generating reagents.[8] We wanted to extend our studies to the synthesis of boryl (BR_2)-substituted systems containing highly Lewis acidic boron centers since, on suitable alkylation with aluminium trialkyls in stoichiometric quantities, such complexes have the potential to act as self-activating polymerization catalysts of type **II** (Scheme 2). While this work was in progress, a similar strategy to catalyst design was pursued by Reetz et al., who reported the synthesis of a series of boryl-substituted zirconocenes $(C_5H_4BR_2)_2ZrCl_2$ (R = Me, Et, OEt, C_6F_5) and showed that in the presence of $AlEt_3$ (Al:Zr = 25:1) compounds with R = C_6F_5 possess high polymerization activity.[9] Similarly, Spence and Piers synthesized propylbis(pentafluorophenyl)borane-substituted compounds such as $[(C_5H_4CH_2CH_2CH_2B(C_6F_5)_2]_2ZrR_2$ which show alkyl transfer from zirconium to boron, though in this case no catalytic results were reported.[10] We were particularly interested in extending our studies to strongly Lewis acidic indenyl- and fluorenylboranes and report here the preparation of a series of new indenyl- and fluorenylbis(pentafluorophenyl)boranes and the formation of bis(pentafluorophenyl)borylcyclopentadienyltitanium trichloride and (dimethylamino)(pentafluorophenyl)borylindenylzirconium amido and chloro complexes.

Results and Discussion

The synthesis of diarylboron halides $(C_6F_5)_2BX$ (X = Cl, Br), the precursors for the preparation of the corresponding cyclopentadienylboranes, from the corresponding boron trihalides and the stannyl compounds $C_6F_5SnMe_3$ or $(C_6F_5)_2SnMe_2$ has been reported.[11] Although, unlike most boranes,[12] $B(C_6F_5)_3$ and BBr_3 do not undergo comproportonation reactions,[13a] the compounds $C_6F_5BBr_2$ and $(C_6F_5)_2BBr$ can be prepared by a convenient alternative route from BBr_3 and 1 or 2 equiv of C_6F_5HgBr in 80 and 35% yield, respectively, obviating the need for lengthy separation of the borane from the Me_3SnX byproduct.[13b] However, initial attempts to obtain pure products from the reaction of $(C_6F_5)_2BBr$ with indenyllithium were disappointing. In view of this and the low yield of $(C_6F_5)_2BBr$ (see Experimental Section) a better diarylborane starting material was sought.

Scheme 2



II

I, M = Ti, Zr, Hf

Both BCl_3 and BBr_3 are too aggressive to react selectively with 2 equiv of C_6F_5MgBr to afford $(C_6F_5)_2BX$ (X = Cl, Br), giving instead $B(C_6F_5)_3$ as the major boron product. In contrast, $BF_3{\cdot}OEt_2$ reacts smoothly with two equiv of C_5F_5MgBr in Et_2O to give $(C_6F_5)_2BF{\cdot}OEt_2$ (**1**) as a sticky solid in 70% yield. Attempts to remove the coordinated diethyl ether from the product by distillation from the solid (100−200 °C, 0.2 mmHg) gave not $(C_6F_5)_2BF$ but $(C_6F_5)_2BOEt$ (**2**) as a colorless oil, evidently formed by ether cleavage by the Lewis acidic borane (Scheme 3). Attempts to transform **2** into the corresponding boron halides by reaction with $SiCl_4$, $TiCl_4$, $AlCl_3$, or BBr_3 failed.

The question of whether **2** was suitable as a starting material for cyclopentadienylboranes was explored by reacting it with IndLi (Ind = indenyl). The product, $[(C_6F_5)_2B(OEt)IndH]Li{\cdot}2THF$ (**3**), was obtained as a pale yellow oil which slowly crystallized over a period of several weeks. Clearly, quaternization is favored over substitution of the ethoxide group. The ^{11}B NMR spectrum of **3** shows a singlet at 4.0 ppm, characteristic for a borate. The presence of an aliphatic CH resonance in the ^1H and ^{13}C NMR spectra of **3** (Table 1) indicates that the boron is bonded to the aliphatic carbon of the indenyl ring.

Compound **1** can be isolated if elevated temperatures are avoided. Extraction of the sticky crude product with a toluene/petroleum mixture and removal of the solvent from the filtrate led to a light brown oil which crystallized on thorough drying. This crude $(C_6F_5)_2BF{\cdot}OEt_2$ can be further purified by recrystallization from petroleum in which it is moderately soluble. Any warming of the $(C_6F_5)_2BF{\cdot}OEt_2$ solution above room temperature leads to decomposition and contamination of the product with **2**. For further reactions, these purification steps proved unnecessary, however, and crude $(C_6F_5)_2BF{\cdot}OEt_2$ was therefore used for the subsequent transformations.

Treatment of an ether solution of **1** with 1 equiv of fluorenyllithium (FluLi) at low temperature and sub-

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[7] Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081.

[8] Reviews: (a) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

[9] Reetz, M. T.; Brümmer, H.; Kessler, M.; Kuhnigk, J. *Chimia* **1995**, *49*, 501.

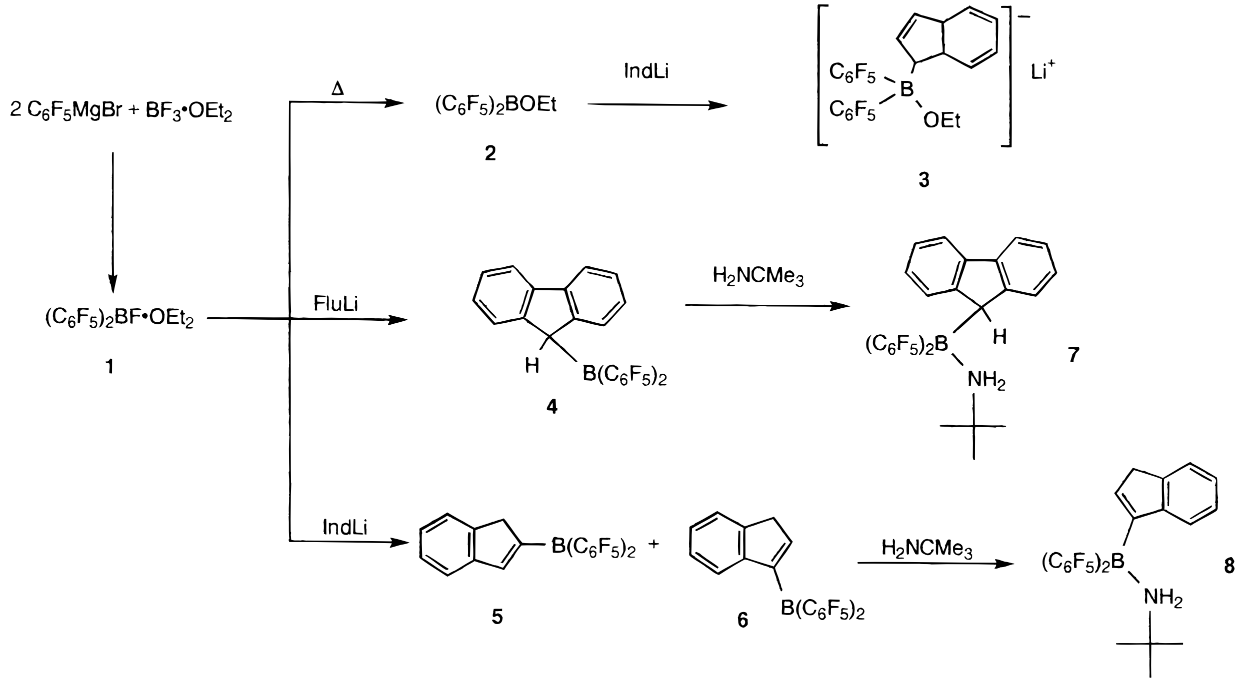
[10] Spence, R. E. v. H.; Piers, W. E. *Organometallics* **1995**, *14*, 4617.

[11] (a) Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1964**, 4783. (b) Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1965**, 3933.

[12] Odom, J. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 1, p 279.

[13] (a) In a footnote to ref 7, we stated erroneously that $(C_6F_5)_2BBr$ had been prepared from BBr_3 and $B(C_6F_5)_3$. The compound is in fact made from BBr_3 and $(C_6F_5)HgBr$, as described here in detail, following ref 13b. (b) Chambers, R. D. ; Coates, G. E. ; Livingstone, J. G. ; Musgrave, W. K. R. *J. Chem. Soc.* **1962**, 4367.

Scheme 3



sequent extraction with light petroleum afforded $(C_6F_5)_2B(FluH)$ (**4**) in moderate yield as a cotton wool-like solid. Recrystallization from diethyl ether affords **4**•OEt_2. The diethyl ether is only weakly bound and dissociates readily in solution; for example, solutions of $CDCl_3$ show only free Et_2O, and the ^{11}B NMR chemical shift of δ 68.7 is consistent only with a donor-free three-coordinate $B(C_6F_5)_2$ moiety. An ether-free sample is readily obtained by warming to 60 °C at 0.2 mmHg for 4 h.[14] The Lewis acidity of boron in compounds such as **4** is evidently rather less than that of $B(C_6F_5)_3$.

The reaction of **1** with IndLi under similar conditions yields a sticky light brown foam which consists of two regioisomers, **5** and **6**, in the approximate ratio 2:5. The two compounds can be separated by fractional crystallization from light petroleum. The formation of the 2-boryl-substituted indene **5** was unexpected. The compound is the minor isomer and is isolated as pale yellow crystals, while the more soluble 1-indenylborane **6** forms pale orange needle cushions. Unlike in **3**, the boryl groups in **5** and **6** are attached to vinylic carbons of the indenyl ring, as is typical for boryl-substituted cyclopentadienes.[1−3] Both the previously characterized triindenylborane and dimethylindenylboronate are described as 1-allyl isomers. However prototropic rearrangement (1,3-shift) to 1-vinyl substitution occurs in the presence of bases.[15] With respective ^{11}B NMR resonances at δ 68.7, 57.2, and 60.9, the compounds **4**, **5**, and **6** show a very similar chemical shift to $B(C_6F_5)_3$ (δ 57).

The addition of *tert*-butylamine to **4** afforded the adduct $C_{13}H_9B(C_6F_5)_2$•*t*-$BuNH_2$ (**7**) as colorless crystals suitable for single-crystal X-ray diffraction (see below). The reaction of *tert*-butylamine with a crude sample of a mixture of **5** and **6** gave colorless crystals of the 1-indenylborane adduct $C_9H_7B(C_6F_5)_2$•*t*-$BuNH_2$ (**8**) as the only isolable product in good yield.

Initial attempts to prepare titanium or zirconium complexes of **4**−**8** were not successful. Herberich and Fischer have recently described the deprotonation of cyclopentadienylboranes with lithium amides to give borylcyclopentadienyl anions $Li[C_5H_4BR_2]$, sometimes in equilibrium with the borates $Li[C_5H_5BR_3]$.[3c] Similar deprotonation attempts of the fluorenyl and indenyl compounds **4** and **6** with lithium tetramethylpiperidide, however, gave complex dark brown reaction mixtures which could not be characterized. Evidently deprotonation does not proceed cleanly in these cases, ruling out the metathesis of boryl anions $Li[YB(C_6F_5)_2]$ (Y = Ind, Flu) with metal halides as a route for the introduction of these ligands, although this strategy had previously been very successful in our preparation of borato−Cp complexes.[7] The reaction of **4**, **5**, or **6** with titanium or zirconium tetrachloride in the presence of NEt_3 gave black tars, while the *t*-$BuNH_2$ adducts **7** and **8** did not react with MCl_4 in toluene and were recovered unchanged. Prolonged heating of **7** with $Zr(NMe_2)_4$ in refluxing toluene merely led to the recovery of minor quantities of $ZrF(NMe_2)_3$ as the only isolable product.

The reaction of tetrabenzylzirconium with **5** in toluene at <0 °C led initially to the precipitation of feathery orange crystals which were, however, too insoluble even in CD_2Cl_2 to be analyzed by NMR spectroscopy. On warming to room temperature, this material dissolved to form a red solution from which a red oil ultimately settled. Although there was evidence for benzyl transfer from zirconium to boron along with the loss of the aliphatic CH_2 signal for the indenyl group, unequivocal spectroscopic characterization of the products was complicated by the presence of several types of benzyl group and indenyl resonances in the same spectral region.

In light of earlier reports on the preparation of cyclopentadienyltitanium and -zirconium compounds by dehalosilylation of $SiMe_3$-substituted cyclopentadi-

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(14) For amino-substituted fluorenylboranes, see: Glaser, B.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 416.

(15) Mikhailov, B. M.; Baryshnikova, T. K. ; Bogdanov, V. S. *Zh. Obsch. Khim.* **1973**, *43*, 1949.

Table 1. ^{1}H, ^{11}B and ^{13}C{^{1}H} NMR Data for New Boron Compounds and Complexes

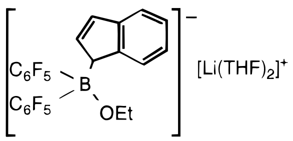
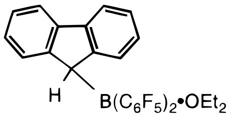
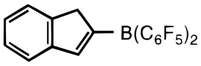
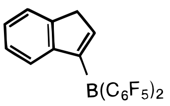
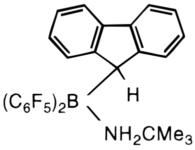
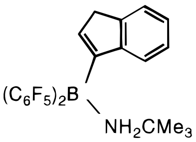
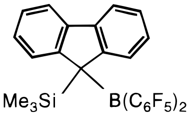
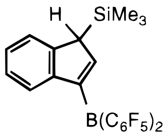
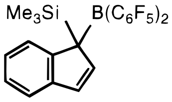
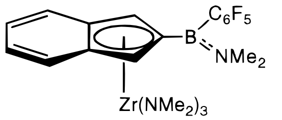
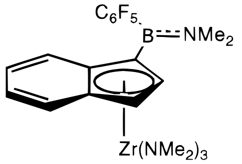
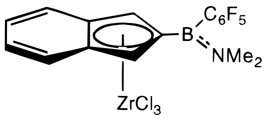
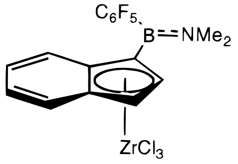
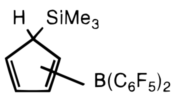
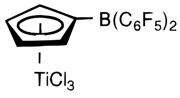
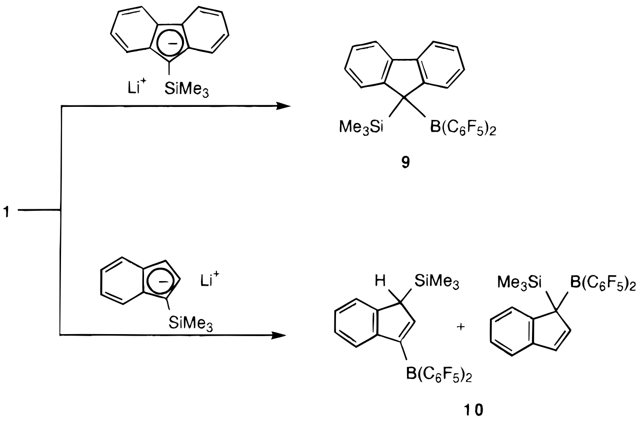
complex	^{11}B NMR	^{1}H NMR	assignt	^{13}C NMR	assignt
$B(C_6F_5)_2F{\cdot}OEt_2$ (**1**)	12.4	3.41 (q, 4 H, $J = 7$ Hz)	$\mathrm{CH_3C}H_2\mathrm{O}$	148.60 (d, $J_{CF} = 243$ Hz)	*m*-C_6F_5
		0.67 (t, 6 H, $J = 7$ Hz)	$\mathrm{C}H_3\mathrm{CH_2O}$	141.19 (d, $J_{CF} = 287$ Hz)	*p*-C_6F_5
				137.71 (d, $J_{CF} = 268$ Hz)	*o*-C_6F_5
				70.40	OCH_{2CH3}
				13.43	OCH_2C_{H3}
$B(C_6F_5)_2OEt$ (**2**) ($CDCl_3$, 20 °C)	43.1	4.29 (q, 2H, $J = 7$ Hz)	$\mathrm{OC}H_2\mathrm{CH_3}$	147.5 (d, $J_{CF} = 245$ Hz)	*m*-C_6F_5
		1.42 (t, 3H, $J = 7$ Hz)	$\mathrm{OCH_2C}H_3$	142.9 (d, $J_{CF} = 257$ Hz)	*p*-C_6F_5
				137.4 (d, $J_{CF} = 253$ Hz)	*o*-C_6F_5
				109.5 (br s)	*ipso*-C_6F_5
				67.4	OCH_{2CH3}
				17.4	$\mathrm{OCH_2}C_{H3}$
 **3** (CD_2Cl_2, 20°C)	4.0	7.1 (m, 5H)	4 C6, 1 C5 Ind	150.0	*m*-C_6F_5
		6.55 (d, 1H , $J = 5$ Hz)	1 C5 Ind	147.5 (d , $J_{CF} = 234$ Hz)	Ind
		4.15 (br s, 1H)	CH-B	145.3	Ind
		3.74 (m, 8H)	THF	143.9	Ind
		3.54 (m, 2H,)	$\mathrm{OC}H_2\mathrm{CH_3}$	138,3 (d, $J_{CF} = 242$ Hz)	*p*-C_6F_5
		1.91 (m, 8H)	THF	136.7 (d, $J_{CF} = 249$ Hz)	*o*-C_6F_5
		1.08 (t, 3H , $J = 8$ Hz)	$\mathrm{OCH_2C}H_3$	126.0, 123.4, 122.9, 121.9, 119.5	Ind
				68.1	THF
				59.5	$\mathrm{O}CH_2\mathrm{CH_3}$
				51.3	B-CH
				25.0	THF
				16.7	$\mathrm{OCH_2}CH_3$
 **4** ($CDCl_3$, 20°C)	68.7 ($CDCl_3$)	7.89 (d, 2 H, $J = 7$)	Flu	146,5 (d, $J_{CF} = 262$ Hz)	*m*-C_6F_5
		7.43 (m, 6H, Ar)	Flu	142.9 (d, $J_{CF} = 258$ Hz)	*p*-C_6F_5
		5.58 (s, 1H)	C5, Flu	142.6	*ipso*-C of Flu
				139.3	*ipso*-C of Flu
				137.0 (d, $J_{CF} = 272$ Hz)	*o*-C_6F_5
				128.3, 127.5, 126.5, 121.1	Flu
				112.9	*ipso*-C_6F_5
				52.7	B-CH
	57.2 (br)	7.79 (s, 1H)	C5 Ind	162.26, 150.96	Ind
		7.41−7.15 (m, 4H)	C6 Ind	146.31 (d, $J_{CF} = 240$ Hz)	*m*-C_6F_5
5 (C_6D_6, 20 °C)		3.41 (s, 2H)	C5 Ind	143.78	Ind
				142.57 (d, $J_{CF} = 255$ Hz)	*p*-C_6F_5
				137.67 (d, $J_{CF} = 254$ Hz)	*o*-C_6F_5
				130.52, 127.49, 125.58, 124.84	Ind
				41.78	Ind-CH_2
 **6** (C_6D_6, 20°C)	60.9 (br)	7.49−7.21 (m, 4H)	C6 Ind	164.00	Ind
		7.00 (m, 1H)	C5 Ind	147.30 (d, $J_{CF} = 245$ Hz)	*m*-C_6F_5
		3.14 (s, 2H)	Ind-CH_2	144.87, 143.94	Ind
				143.52 (d, $J_{CF} = 258$ Hz)	*p*-C_6F_5
				137.75 (d, $J_{CF} = 258$ Hz)	*o*-C_6F_5
				127.05, 126.33, 124.52, 121.79	Ind
				114.42	*ipso*-C_6F_5
				41.72	Ind-CH_2
 **7**	−4.2	7.84 (d, 2H, $J = 8$ Hz)	Flu	148.8 (d, $^1J_{CF} = 235$ Hz)	*m*-C_6F_5
		7.67 (d, 2H, $J = 7$ Hz)	Flu	148.7	*ipso*-Flu
		7.53 (m, 4H)	Flu	141.7	*ipso*-Flu
		5.16 (s, 2H)	NH_2	140.1 (d, $J_{CF} = 235$ Hz)	*p*-C_6F_5
		4.84 (s, 1H)	$\mathrm{BC}H$	137.4 (d, $J_{CF} = 250$ Hz)	*o*-C_6F_5
		1.65 (s, 9H)	$\mathrm{C(C}H_{3)3}$	126.0, 125.8, 123,8, 119.5	Flu
				116.7 (br)	*ipso*-C_6F_5
				58.0	$C\mathrm{(CH_3)_3}$
				47.0	$\mathrm{B}C\mathrm{H}$
				30.0	$\mathrm{C(}CH_3\mathrm{)_3}$
 **8** ($CDCl_3$)	−7.6	7.48−7.45(m, 1H)	Ind	148.31	Ind
		7.16−7.06 (m, 3H)	Ind	148.27 (d, $J_{CF} = 242$ Hz)	*m*-C_6F_5
		6.36 (s, 2H)	Ind	144.98	Ind
		4.93 (s, (br), 2H)	NH_2	140.07 (d, $J_{CF} = 251$ Hz)	*p*-C_6F_5
		3.37 (s, 2H)	$\mathrm{Ind\text{-}C}H_2$	137.37 (d, $J_{CF} = 241$ Hz)	*o*-C_6F_5
		1.27 (s, 9H)	$\mathrm{C(C}H_{3)3}$	134.22, 126.08, 124.04, 123.84, 120.97	Ind
				118.67	*ipso*-C_6F_5
				57.34	$C\mathrm{(CH_3)_3}$
				39.70	$\mathrm{Ind\text{-}}CH_2$
				29.58	$\mathrm{C(}CH_3\mathrm{)_3}$
 **9** ($CDCl_3$)	75.8	8.01(d, 2H, $J = 7.6$)	Flu	143.71 (d, $J_{CF} = 241$ Hz)	*m*-C_6F_5
		7.46 (t, 2H, $J = 7.3$)	Flu	141.85 (d, $J_{CF} = 256$ Hz)	*p*-C_6F_5
		7.29 (t, 2H, $J = 7.7$)	Flu	139.35	*ipso*-C5 Flu
		7.16 (d, 2H, $J = 7.8$)	Flu	137.92 (d, $J_{CF} = 263$ Hz)	*o*-C_6F_5
		−0.01 (s, 9H)	$SiMe_3$	126.38, 126.00, 123.70, 120.44	Flu
				−1.10	$SiMe_3$

Table 1 (Continued)

complex	^{11}B NMR	^{1}H NMR	assignt	^{13}C NMR	assignt
	58 (br)	7.79 (m, 1H)	Ind C5	167.77	*ipso*-Ind
		7.58 (m, 1H)	Ind	146.65 (d, $J_{CF} = 248$ Hz)	*m*-C_6F_5
		7.38−7.24 (m, 3H)	Ind C6	145.51, 143.67	Ind
		4.20 (s, 1H)	Ind CH	137.32 (d, $J_{CF} = 237$ Hz)	*o*-C_6F_5
		0.11 (s, 9H)	$SiMe_3$	125.41, 125.08, 122.72, 121.62	Ind
				53.49	Ind-*C*H$SiMe_3$
10A, major isomer ($CDCl_3$, 20°C)				−2.25	$SiMe_3$
	58 (br)	7.12 (d, 1H, $J = 5.0$ Hz)[a]	Ind C5[b]	*c*	
		6.77 (d, 1H, $J = 5.0$ Hz)	Ind C5		
		0.01 (s, 9H)	$SiMe_3$		
10B, minor isomer					
	38.3	7.46 −7.43 (m, 2H)	C6 Ind	143.89, 123.72, 121.93, 106.96	Ind
		6.88 - 6.84 (m, 2H)	C6 Ind	44.30	
		6.53 (s, 2H)			$ZrNMe_2$
		2.73 (s, 18H)	$Zr(NMe_2)_3$	42.18	N-*C*H_3
		2.89 (s, 3H)	N-C*H*$_3$	40.45	N-*C*H_3
		2.38 (s, 3H)	N-C*H*$_3$		
11 (C_6D_6, 20°C)					
	39.1	7.52−7.36 (m, 2H)	C6 Ind	146.09 (d, $J_{CF} = 249$ Hz)	*m*-C_6F_5
		6.92−6.89 (m, 2H)	C6 Ind	137.63 (d, $J_{CF} = 252$ Hz)	*o*-C_6F_5
		6.70 (d, 1H, $J = 3.5$ Hz)	C5 Ind	131.08, 129.09, 125.77, 124.09, 123.62, 123.54, 123.06, 102.75	Ind
		6.39 (d, 1H, $J = 3.5$ Hz)	C5 Ind		
		2.92	B-NMe_2		
		2.71	$Zr(NMe_2)_3$	44.00	$Zr(NMe_2)_3$
		2.48	B-NMe_2	42.01	B-NMe_2
				40.63	B-NMe_2
12 (C_6D_6, 20°C)					
	36.0	7.56−7.44 (br m, 2H)	C5 Ind	146.45 (d, $J_{CF} = 240$ Hz)	*m*-C_6F_5
		7.18 (br m, 2H)	C6 Ind	137.78 (d, $J_{CF} = 259$ Hz)	*o*-C_6F_5
		7.01 (br m, 2H)	C6 Ind	130.65, 128.87, 117.31	Ind
		3.03 (br s, 3H)	B-NMe_2	42.80	B-NMe_2
		2.42 (br s, 3H)	B-NMe_2	41.41	B-NMe_2
13 (C_6D_6, 20°C)					
	39.6 (C_6D_6)	7.57−7.54 (br m, 1H)	C6 Ind	145.83 (d, $J_{CF} = 238$ Hz)	*m*-C_6F_5
		7.22−7.01 (m, 4H)	3 C6, 1C5 Ind	137.41 (d, $J_{CF} = 257$ Hz)	*o*-C_6F_5
	36.7 (THF)	6.78−6.76 (br m, 1H)	C5 Ind	131.64, 131.15, 129.38, 128.19, 126.81, 126.35, 111.91	Ind
		2.93 (s, 3H)	B-NMe_2		
		2.78 (s, 3H)	B-NMe_2		
				42.36	B-NMe_2
				42.27	B-NMe_2
14 ($CDCl_3$, 20°C)					
$\{2-C_9H_6B(C_6F_5)(NMe_2)\}ZrCl_3\cdot$ DME **15** ($CDCl_3$, 20 °C)	35.2	7.62−7.60 (m, 2H)	C6 Ind	145.93 (d, $J_{CF} = 241$ Hz)	*m*-C_6F_5
		7.27−7.23 (m, 2H)	C6 Ind	140.83 (d, $J_{CF} = 253$ Hz)	*p*-C_6F_5
		6.86 (s, 2H)	C5 Ind	137.33 (d, $J_{CF} = 266$ Hz)	*o*-C_6F_5
		3.93 (br s, 4H)	OCH_2	130.37, 127.68, 125.66, 116.70	Ind
		3.72 (br s, 6H)	CH_3O		
		3.30 (s, 3H)	B-NMe_2	72.70	OCH_2
		2.85 (s, 3H)	B-NMe_2	64.41	CH_3O
				43.00	B-NMe_2
				41.40	B-NMe_2
$\{1-IndB(C_6F_5)(NMe_2)\}ZrCl_3\cdot$ 2THF **16** (THF-d_8, 20 °C)	36.2	7.64 (d, 1H, $J = 8.4$ Hz)	C6 Ind	146.8 (d)	*m*-C_6F_5
		7.44 (d, 1H, $J = 8.6$ Hz)	C6 Ind	138.19 (d)	*o*-C_6F_5
		7.23 (t, 1H, $J = 7.6$ Hz)	C6 Ind	135.26, 130.34, 129.58, 127.33, 126.60, 126.51, 126.47, 110.96	Ind
		7.14 (t, 1H, $J = 7.5$ Hz)	C6 Ind		
		6.83 (d, 1H, $J = 3.3$ Hz)	C5 Ind		
		6.70 (d, 1H, $J = 3.3$ Hz)	C5 Ind	43.89	B-NMe_2
		3.26 (s, 3H)	B-NMe_2	42.68	B-NMe_2
		2.92 (s, 3H)	B-NMe_2		
	54.1	7.23 (br, 1H)	vinyl-C5	164.37, 155.74	C5
		6.52 (br, 2H)	vinyl-C5	146.79 (d, $J_{CF} = 244$ Hz)	*m*-C_6F_5
		4.6 (br, 1H)	allyl-C5	143.38	C5
		−0.31 (s, 9H)	$SiMe_3$	142.59 (d, $J_{CF} = 256$ Hz)	*p*-C_6F_5
				137.73 (d, $J_{CF} = 253$ Hz)	*o*-C_6F_5
				132.29	C5
17 (C_6D_6, 20°C)				115.62	*ipso*-C_6F_5
				49.59	allyl-C5
				−1.46	$SiMe_3$
	59.8	6.66 (s, br, 2 H)	C5	146.97 (d, $J_{CF} = 236$ Hz)	*m*-C_6F_5
		6.32 (s, br, 2 H)	C5	143.73 (d, $J_{CF} = 258$ Hz)	*p*-C_6F_5
				137.85 (d, $J_{CF} = 259$ Hz)	*o*-C_6F_5
				131.80 (2,5-C5)	2,5-C5
				128.15 (3,4-C5)	3,4-C5
18 (toluene-d_8, 25°C)				112.0	*ipso*-C_6F_5

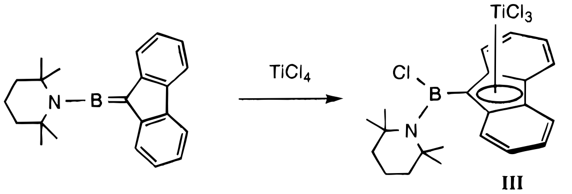
[a] ^{11}B signal obscured by broad peak for major isomer. [b] C_6 resonances obscured by major isomer. [c] Concentration in the mixture was insufficient for ^{13}C NMR.

Scheme 4



enes,[4,9,16] the silylated analogues of **4** and **6** were prepared by the reaction of Li[$C_{13}H_8SiMe_3$] and Li[$C_9H_6SiMe_3$] with $(C_6F_5)_2BF\cdot OEt_2$ to give, respectively, $C_{13}H_8(SiMe_3)B(C_6F_5)_2$ (**9**) and $C_9H_6(SiMe_3)B(C_6F_5)_2$ (**10**) (Scheme 4). Compound **9** proved to considerably less soluble than the other cyclopentadienylboranes isolated but could be separated from the salt byproducts by extraction with a large volume of a 1:1 toluene/light petroleum mixture. The compound crystallizes readily, and crystals suitable for a structure determination were obtained by cooling a saturated toluene solution to 5 °C (see below). The indenyl derivative **10** was obtained as an orange oil which crystallized very slowly on cooling to 5 °C; it exists in solution as a mixture of two regioisomers.

Neither **9** nor **10** could be induced to undergo dehalosilylation with $TiCl_4$, $TiCl_3$, or $ZrCl_4$ under a range of reaction conditions, such as extended stirring in CH_2Cl_2, heating toluene solutions at 80 °C, or refluxing the mixtures in heptane. This is somewhat surprising in view of the fact that dechlorosilylations proceed smoothly even with the sterically hindered $C_5Me_5SiMe_3$,[16b,e] and in the light of Nöth's report of the facile synthesis of the boryl-substituted fluorenyltitanium complex **III** (eq 2).[17] On the other hand, the lack of reactivity of silylindenes is not without precedent; Okuda et al. recently reported the failure of 1-(chlorodimethylsilyl)-3-(trimethylsilyl)indene to react in the expected fashion with $TiCl_4$.[18,19]



III

(2)

Protolysis reactions of metal dialkylamides with cyclopentadienes, a reaction originally demonstrated by Chandra and Lappert,[20] are increasingly used as an efficient route to group 4 cyclopentadienyl complexes.[21]

Both **5** and **6** react with $Zr(NMe_2)_4$ under mild conditions in toluene to give **11** and **12**, respectively, as orange oils (Scheme 5). The ^1H NMR spectra indicate the retention of the boron substitution pattern, the loss of the indenyl-CH_2 resonance, and the formation of a zirconium indenyl complex. In solution, the 2-boryl complex **11** possesses an apparent plane of symmetry perpendicular to the plane of the indenyl ligand, indicative of facile rotation of the boryl substituent about the B−C vector on the NMR time scale. Compound **12** displays the two-doublet pattern characteristic of a 1-substituted indenyl group. Both **11** and **12** have sharp $Zr(NMe_2)_3$ resonances. It was, however, at first surprising to find that both compounds showed the presence of two additional inequivalent *N*-methyl groups. The ^{11}B resonances of δ 38.3 and 39.1, respectively, were unexpectedly high for a $B(C_6F_5)_2$ group, which typically has an ^{11}B chemical shift of ca. 60 ppm (cf. **6**, δ 60.9). Values of δ 30−40 typically indicate the presence of a substituent capable of π-bonding to boron; for example, both $C_5H_5B(NMe_2)_2$ and Li[$C_5H_4B(NMe_2)_2$] have an ^{11}B resonance at δ 30.[3c] Even under the mild conditions employed here, one pentafluorophenyl substituent on boron has evidently been exchanged for NMe_2 to generate zirconium complexes of $IndB(C_6F_5)(NMe_2)$ ligands (Scheme 5).

Complexes **11** and **12** are quantitatively converted to the chlorides **13** and **14** by treatment with excess $SiClMe_3$ in toluene at room temperature. While **13** is an amorphous golden foam, **14** forms a microcrystalline solid from either CH_2Cl_2 or C_6D_6 once all volatile impurities are removed in vacuo. Once crystalline, the material is only sparingly soluble in toluene but dissolves in coordinating solvents such as THF and is presumably polymeric with halide bridges. Mass spectrometry and elemental analyses of **13** and **14** confirm the presence of a (dimethylamino)boryl substituted indenyl ligand, while ^{19}F NMR spectroscopy shows a single B−C_6F_5 substituent with inequivalent ortho- and meta-F atoms, indicative of hindered rotation about the B−C_6F_5 vector. The ^{11}B resonances (**13**, δ 36.0; **14**, δ 36.7) are essentially identical to those of the amido complexes **11** and **12**.

The complexes form adducts with Lewis bases. Thus, **13** gives the DME adduct **15** as a fine yellow powder, while **14** forms {1-$IndB(C_6F_5)(NMe_2)$}$ZrCl_3\cdot 2THF$ (**16**) as yellow needle cushions from a THF/petroleum solution.

As mentioned above, while this work was in progress, Reetz and Brümmer reported the synthesis of C_5H_4-

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(16) (a) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156. (b) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118. (c) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426. (d) Winter, C. H.; Zhou, X. X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210. (e) Martin, A.; Mena, M.; Palacios, F. *J. Organomet. Chem.* **1994**, *480*, C10.

(17) Helm, S.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1331.

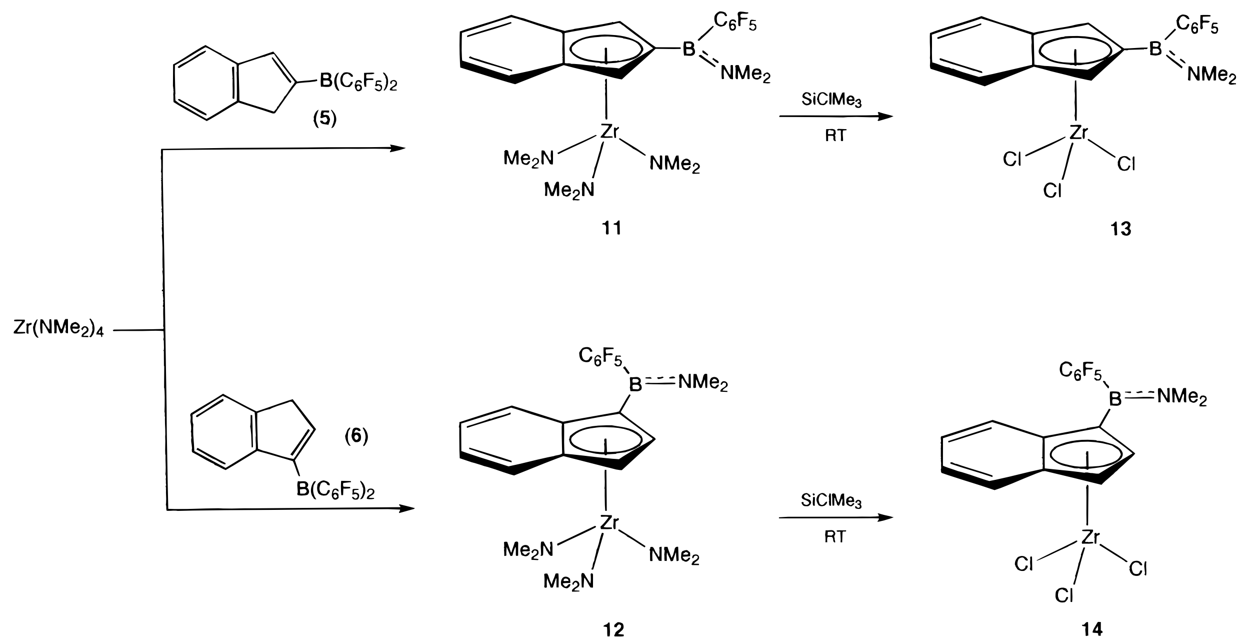
(18) Amor, F.; Okuda, J. *J. Organomet. Chem.* **1996**, *520*, 245.

(19) (a) Since $SnMe_3$ compounds are known for their reactivity toward metal halides, the synthesis of tin analogues of **9** and **10** was envisaged. Attempts to introduce the trimethylstannyl group to the indenylborane with trimethyltindiethylamide following a procedure similar to Abel's synthesis of Ind$(SnMe_3)_2$[19b] led to incomplete reaction and a variety of ill-defined products containing coordinated Et_2NH. The dehalostannylation reaction between bis(trimethylstannyl)indene and **1** also failed to afford a single clean product. (b) Orrell, K. G.; Sik, V.; Dunster, M. O.; Abel, E. W. *J. Chem. Soc., Faraday* **1975**, *71*, 631.

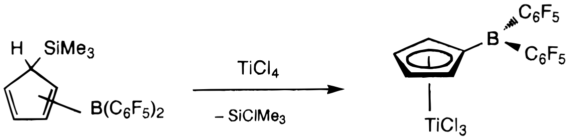
(20) Chandra, G.; Lappert, M. F. *J. Chem. Soc.* **1968**, 1940.

(21) (a) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (b) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030. (c) Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038. (d) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045. (e) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572. (f) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (g) Herrmann, W. A.; Morawietz, M. J. A. *J. Organomet. Chem.*, **1994**, *482*, 169.

Scheme 5



$(SiMe_3)B(C_6F_5)_2$ via the dehalostannylation reaction between 1,1-$C_5H_4(SnMe_3)SiMe_3$ and $(C_6F_5)_2BBr$, although by this route the compound could not be completely freed of the tin byproduct.[9,22] We have prepared $C_5H_4(SiMe_3)B(C_6F_5)_2$ (**17**) from Li[$C_5H_4SiMe_3$] and **1** in good yield on a large scale and with high purity (by ^1H NMR and elemental analysis). Dechlorosilylation of **17** with $TiCl_4$ proceeds smoothly at room temperature in dichloromethane to give $\{C_5H_4B(C_6F_5)_2\}TiCl_3$ (**18**) (eq 3). The compound is highly soluble in nonpolar solvents.

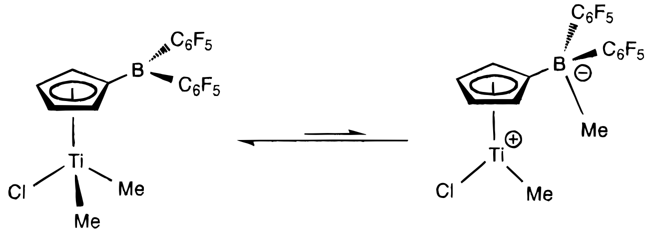


(17) (18) (3)

X-ray quality crystals were grown from a CH_2Cl_2/light petroleum mixture at 5 °C. A similar synthetic procedure has recently been used by Shapiro et al. to prepare a series of related catecholboryl- and phenylboryl-substituted titanium trichloride complexes.[3d]

In order to test the ability of a (pentafluorophenyl)boryl substituent to abstract an alkyl group from the metal center and thus act as an internal activator for olefin polymerizations (cf. Scheme 2), a solution of **14** in toluene was treated with 5 equiv of $AlEt_3$ under 1 bar ethene at 20 °C. The catalyst produces polyethene with an activity of 3.2×10^3 g of polymer $(mol{\cdot}bar{\cdot}h)^{-1}$. Under these conditions, borane-free $IndZrCl_3/AlEt_3$ mixtures produce, at best, traces of polymer. Similarly, toluene solutions of **18** (50 μmol) when treated with 5 equiv of $AlEt_3$ at -20 °C were found to be active even at low temperature. No attempt was made to optimize the temperature or the Ti/Al ratio; the optimum conditions would balance the requirement for full alkylation of the metal against possible heterodinuclear complex formation, reduction, or thermal decomposition. Temperatures of >0 °C lead to the slow reduction of titanium. The unsubstituted $(C_5H_5)TiCl_3/AlEt_3$ system is inactive under these conditions, even at substantially higher catalyst concentrations. By contrast, complexes with less Lewis acidic boryl substituents $(C_5H_4BR_2)TiCl_3$ (R_2 = Ph_2, PhCl or $O_2C_6H_4$)[3d] and related zirconocene derivatives[9,22] show no catalytic activity or do not undergo alkylation reactions cleanly.

Scheme 6



(19) (20)

To elucidate the interaction of aluminium alkyls with boryl complexes, the reaction of **18** with 5 equiv $AlMe_3$ in toluene-d_8 was followed by variable-temperature NMR. Alkylation begins slowly at about -50 °C to give a variety of unidentified species. At -20 °C only one organometallic product is evident, identified as $\{C_5H_4B(C_6F_5)_2\}TiMe_2Cl$ (**19**) by ^1H and ^{13}C NMR (Ti−Me, δ 71.4) in comparion with $Cp^*TiMeCl_2$ (Ti−Me, δ 78.2) and Cp^*TiMe_2Cl (Ti−Me, δ 68.0)[23] and by the ^{11}B chemical shift of δ 72.5, consistent with a trigonal $B(C_6F_5)_2$ group (Scheme 6). Although the formation of a catalytically active species would require an equilibrium involving an alkyl transfer to boron and formation of a $B(C_6F_5)_2Me$ borato zwitterion **20**, the concentration of any such species is evidently below the NMR detection limits. This observation is consistent with the comparatively modest catalyst activities observed. Further studies of this system are in progress.

X-ray Crystallography. The structures of **7** (Figure 1), **9** (Figure 2), and **18** (Figure 3) were determined by

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(22) Brümmer, H. Ph.D. Thesis, University of Düsseldorf, 1995.

(23) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 479. Martín, A.; Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2117.

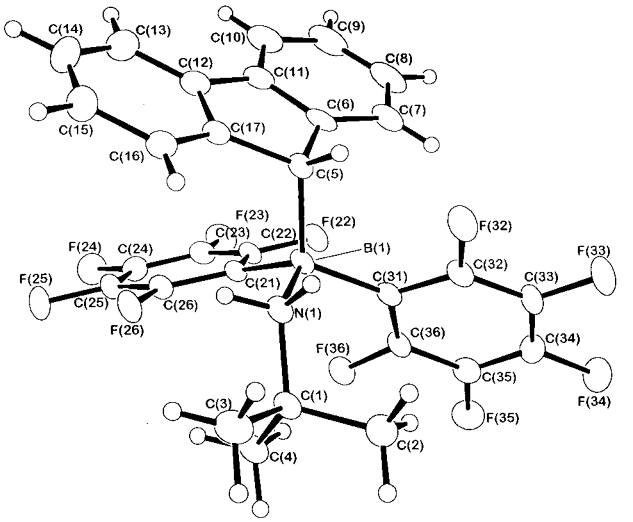

Figure 1. Crystal structure of (Flu)$B(C_6F_5)_2{\cdot}NH_2CMe_3$ (**7**), showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability.

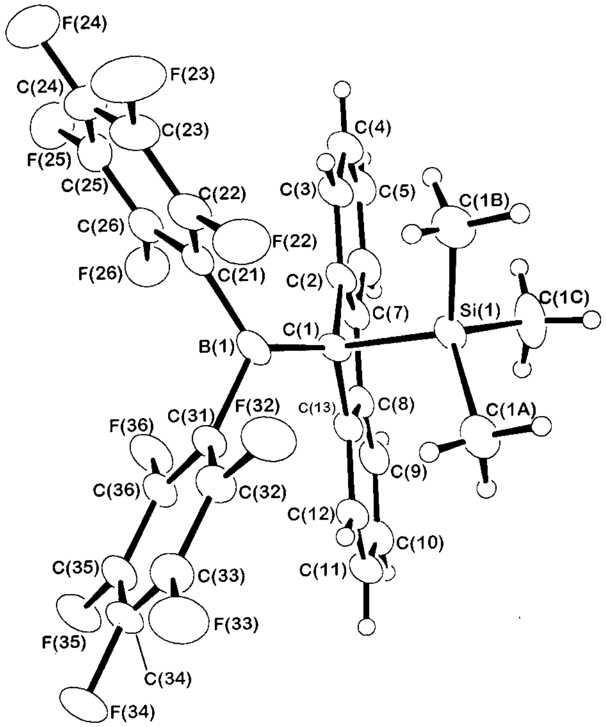

Figure 2. Crystal structure of $(FluSiMe_3)B(C_6F_5)_2$ (**9**), showing the atomic numbering scheme.

single-crystal X-ray diffraction. Crystal data are collected in Table 2, selected bond lengths and angles in Table 3.

The structure of the amine adduct **7** shows a distorted tetrahedral environment about the central boron atom. B–N bond lengths for $BX_3{\cdot}NR_3$ adducts typically lie in the range 1.50–1.60 Å. The B–N bond distance in **7** of 1.643(3) Å lies at the top end of this range but is slightly shorter than that in $Me_3B{\cdot}NHMe_2$ [1.656(4) Å];[24] by comparison the B–N distance in $(CF_3)_2BF{\cdot}NHMe_2$ is only 1.584(7) Å.[25] The B–C_6F_5 distances 1.649(4) Å for [B(1)–C(31)] and 1.652(4) Å for [B(1)–C(21)] are slightly longer than the average bond distance of 1.629 Å in $B(C_6F_5)_3{\cdot}PH_3$.[26] The corresponding bond lengths in the three-coordinate borane $B(C_6F_5)_2Cl$ (1.552 and 1.566 Å) are significantly shorter.[27] The crystal structures of several fluorenylboranes and diboranes have been determined.[28] The B(1)–C(5) bond distance at 1.670(3) Å is only slightly longer than the B–fluorenyl bond lengths observed by Meller et al.[28a] and Nöth et al.[28b] in (amino)(fluorenyl)boranes.

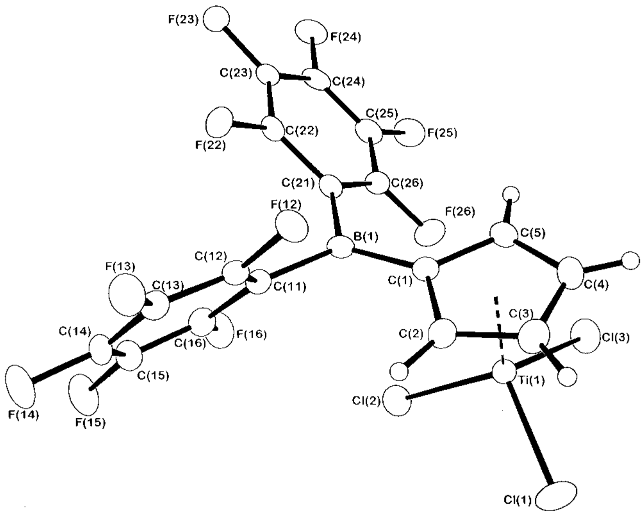

Figure 3. Crystal structure of $\{C_5H_4B(C_6F_5)_2\}TiCl_3$ (**18**), showing the atomic numbering scheme.

The boron environment in **9** is trigonal-planar. The two C_6F_5 rings are almost perpendicular to the C(21)–B–C(31) plane to reduce steric interactions, with dihedral angles of 100.7 and −96.7°. The B–C_6F_5 distances at 1.588(5) and 1.592(4) Å are shorter than those in the four-coordinate **7** but slightly longer than in **18** [1.577(3) and 1.575(3) Å] and $B(C_6F_5)_2Cl$,[27] presumably as a result of steric crowding. The B–fluorenyl bond length of 1.549(5) Å is considerably shorter than that of **7** or in (aminofluorenyl)boranes,[28] without approaching that of (tetramethylpiperidino)(9-fluorenylidene)-borane, 1.424(3), which has extensive B–C double bond character.[28b] The fluorenyl–Si bond distance of 1.990(3) Å is slightly longer than those found by Schubert for silyl-substituted fluorenes, the longest of which was 1.97(2) Å for the Me_3Si–C bond in [9-(trimethylsilyl)fluorenyl]bis(trimethylsilyl)bromosilane.[29]

Complex **18** is monomeric and shows the familiar piano stool geometry. The $C_5H_4TiCl_3$ moiety shows no unusual features, with an average Ti–Cl bond distance of 2.2240(7) Å and a Ti–Cp centroid distance of 2.02 Å.[30] The environment around boron in **18** is approximately trigonal-planar (angle sum, 359.4°). The $B(C_6F_5)_2$ substituent is almost coplanar with the cyclopentadienyl ring and shows a dihedral angle between

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Table 2. Crystal Data for Compounds 7, 9, and 18

	7	**9**	**18**
formula	$C_{29}H_{20}BF_{10}N$	$C_{28}H_{17}BF_{10}Si \cdot {}^1/_2C_7H_8$	$C_{17}H_4BCl_3F_{10}Ti$
fw	583.27	628.38[a]	563.26
cryst dimens, mm	0.65 × 0.48 × 0.40	0.55 × 0.50 × 0.40	0.68 × 0.53 × 0.38
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	13.677(2)	7.8748(8)	10.1617(6)
b, Å	9.7230(12)	8.6936(9)	19.0088(11)
c, Å	19.898(2)	20.896(2)	10.3960(8)
α, deg		96.057(10)	
β, deg	108.908(9)	98.008(10)	104.342(6)
γ, deg		98.856(9)	
V, Å^3	2503.4(5)	1387.9(2)	1945.5(2)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.548	1.504	1.923
λ, Å	1.541 84	1.541 84	0.710 73
μ, mm^{-1}	1.249	1.562	0.949
$F(000)$	1184	638	1096
max, min transmsn factors	0.700, 431	0.581, 0.486	0.867, 0.726
θ range, deg	$6.92 \le 2\theta \le 129.02$	$4.3 \le 2\theta \le 129.0$	$4.28 \le 2\theta \le 49.96$
index range	$-16 \le h \le 14$, $0 \le k \le 11$, $0 \le l \le 23$	$-9 \le h \le 9$, $-9 \le k \le 9$, $0 \le l \le 24$	$-12 \le h \le 12$, $-22 \le k \le 22$, $-12 \le l \le 12$
no. of reflns collected	3872	4402	6612
no. of unique reflns, n	3872	4402	3419 ($R_{int} = 0.0164$)
no. of reflns with $F_c^2 > 2.0\sigma(F_c^2)$	3774	4186	3003
no. of parameters, p	374	409	290
goodness of fit on F^2, s[b]	1.136	1.095	1.090
R_1[c]	0.0434	0.0578	0.0258
wR_2[d]	0.1164	0.1448	0.0668
weighting params a, b[e]	0.0364, 3.9857	0.0515, 2.6793	0.0246, 1.6255
extinction param[f]	0.00004(10)		0.0017(4)
largest diff, peak and hole, e Å^{-3}	0.249, −0.200	0.575, −0.550	0.277, −0.265

[a] Includes solvate molecule. [b] $s = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{-1/2}$. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [e] $w = [\sigma^2(F_o^2) + (aP)2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [f] $F_c' = kF_c\{1 + 0.001F_c^2\lambda^3/\sin(2\theta)\}^{-1/4}$.

the C5 and the C(11)−B−C(21) planes of 167.4°. The two C_6F_5 rings are twisted out of the BC_2 plane by a significantly lesser degree than in **9**, with dihedral angles between C(11)−B−C(21) and the planes through the phenyl rings of 119.2 and −40.1°, respectively. Although the boryl group adopts a conformation that would allow some π-interaction between boron and the cyclopentadienyl ring, there is no evidence from the B−C (Cp) bond distance of 1.545(3) Å for a fulvene-type resonance structure.[3c] The B−C(1) bond length is very similar to those found for B−C(Flu) in **9** [1.549(5) Å] and B−C(Cp) [1.55(2) Å] in $\{PhB(\eta^5\text{-}C_5H_4)_2\}(TiCl_3)_2$.[3d] The structural features are in agreement with significant Lewis acidic character of the $B(C_6F_5)_2$ substituent.

Conclusions

Cyclopentadienyl-, indenyl-, and fluorenylbis(pentafluorophenyl)boranes are readily accessible from $(C_6F_5)_2BF\cdot OEt_2$. The compounds form stable adducts with amines, although their Lewis acid character is less pronounced than that of $B(C_6F_5)_3$, and adducts with Et_2O are very labile. The reaction of $(C_6F_5)_2BF\cdot OEt_2$ with indenyllithium includes the unexpected formation of a 2-substituted regioisomer in good yield. The compounds are a source of boryl−Cp ligands for group 4 metals. Treatment of $IndB(C_6F_5)_2$ with $Zr(NMe_2)_4$ not only leads to the anticipated formation of a half-sandwich tris(amido) complex but is accompanied by the exchange of one C_6F_5 substituent for NMe_2. Dehalosilylation of $C_5H_4(SiMe_3)B(C_6F_5)_2$ with $TiCl_4$ proceeds smoothly to give $\{C_5H_4B(C_6F_5)_2\}TiCl_3$ which, in the presence of 5 equiv of $AlEt_3$, acts as a “self-activating” ethene polymerization catalyst.

Experimental Section

General Considerations. All manipulations were performed under a dinitrogen atmosphere using Schlenk techniques. Solvents were distilled under N_2 over sodium benzophenone (THF), sodium (toluene), Na/K alloy [diethyl ether, light petroleum (bp 40−60 °C)], or CaH_2 (dichloromethane). NMR solvents were dried over activated 4 Å molecular sieves (C_6D_6, CD_2Cl_2, pyridine-d_5, $CDCl_3$, THF-d_8). NMR spectra were recorded on Bruker ARX250 and DPX300 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C NMR) or external $BF_3\cdot OEt_2$ (^{11}B). $Zr(CH_2Ph)_2$[31] and $Zr(NMe_2)_4$[32] were prepared according to literature procedures.

Experimental Procedures. $(C_6F_5)_2BBr$. This compound was made by a modification of a literature procedure.[13b] To a solution of $(C_6F_5)BBr_2$ (11.0 g, 32.5 mmol) in toluene (80 mL) was added C_6F_5HgBr (14.5 g, 32.5 mmol). The mixture was refluxed for 2 d. The $HgBr_2$ precipitate was filtered off and the solvent removed in vacuo, leaving a light yellow oily residue. This was extracted with light petroleum and filtered. Evaporation of the volatiles gave $(C_6F_5)_2BBr$ as a sticky white solid (4.8 g, 113 mmol, 35%). ^{11}B NMR ($CDCl_3$, 20 °C): δ 61.2. ^{13}C NMR ($CDCl_3$, 20 °C): δ 147.4 (d, J_{CF} = 250 Hz), 144.7 (d, J_{CF} = 262 Hz), 137.6 (d, J_{CF} = 258 Hz), 114.0 (br, *ipso*-C of C_6F_5).

$(C_6F_5)_2BF\cdot OEt_2$ (1). A solution of C_6F_5MgBr in diethyl ether (100 mL, 1.0 M, 0.1 mol) was added at 0 °C to a solution of $BF_3\cdot OEt_2$ (6.15 mL, 0.05 mol) in diethyl ether (100 mL). After the volatiles were removed, the product was extracted with 400 mL of a 4:1 petroleum/toluene mixture. Removal of the solvents gave a brownish oil which slowly crystallized to a grey/tan solid. Crude yield, 30 g (70 mmol, 70%). Recrystallization from petroleum afforded an analytically pure sample in ca. 30% yield. ^{19}F NMR (C_6D_6, 20 °C, 282.4 MHz):

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 7, 9, and 18

	Compound **7**		
B(1)−N(1)	1.643(3)	B(1)−C(31)	1.649(4)
B(1)−C(21)	1.652(4)	B(1)−C(5)	1.670(3)
N(1)−C(1)	1.542(3)	C(5)−C(6)	1.516(4)
C(5)−C(17)	1.520(3)	C(6)−C(7)	1.385(4)
C(6)−C(11)	1.399(4)	C(7)−C(8)	1.397(4)
C(8)−C(9)	1.388(5)	C(9)−C(10)	1.375(5)
C(10)−C(11)	1.395(4)	C(11)−C(12)	1.460(4)
N(1)−B(1)−C(31)	105.8(2)	N(1)−B(1)−C(21)	111.9(2)
C(31)−B(1)−C(21)	115.1(2)	N(1)−B(1)−C(5)	104.0(2)
C(31)−B(1)−C(5)	113.8(2)	C(21)−B(1)−C(5)	105.7(2)
C(1)−N(1)−B(1)	128.8(2)	C(6)−C(5)−C(17)	101.5(2)
C(6)−C(5)−B(1)	112.5(2)		
	Compound **9**		
C(1a)−Si(1)	1.853(4)	Si(1)−C(1)	1.990(3)
C(1)−C(13)	1.521(4)	C(1)−C(2)	1.525(4)
C(1)−B(1)	1.549(5)	C(2)−C(3)	1.391(5)
C(2)−C(7)	1.394(5)	C(3)−C(4)	1.396(4)
C(4)−C(5)	1.377(5)	C(5)−C(6)	1.385(5)
C(6)−C(7)	1.398(4)	C(7)−C(8)	1.460(5)
B(1)−C(21)	1.588(5)	B(1)−C(31)	1.592(4)
C(1b)−Si(1)−C(1)	111.7(2)	C(1a)−Si(1)−C(1)	111.94(14)
C(1c)−Si(1)−C(1)	104.8(2)	C(13)−C(1)−C(2)	102.3(2)
C(13)−C(1)−B(1)	117.9(2)	C(2)−C(1)−B(1)	118.1(3)
C(13)−C(1)−Si(1)	103.8(2)	C(2)−C(1)−Si(1)	103.0(2)
B(1)−C(1)−Si(1)	109.9(2)	C(1)−B(1)−C(21)	123.3(3)
C(1)−B(1)−C(31)	120.9(3)	C(21)−B(1)−C(31)	115.4(3)
	Compound **18**		
Ti(1)−Cl(3)	2.2204(7)	Ti(1)−Cl(1)	2.2227(7)
Ti(1)−Cl(2)	2.2288(7)	Ti(1)−C(2)	2.307(2)
Ti(1)−C(1)	2.331(2)	Ti(1)−C(5)	2.364(2)
Ti(1)−C(3)	2.370(2)	Ti(1)−C(4)	2.390(2)
C(1)−C(5)	1.426(3)	C(1)−C(2)	1.441(3)
C(1)−B(1)	1.545(3)	C(2)−C(3)	1.400(3)
C(3)−C(4)	1.410(3)	C(4)−C(5)	1.405(3)
B(1)−C(21)	1.575(3)	B(1)−C(11)	1.577(3)
Cl(3)−Ti(1)−Cl(1)	102.20(3)	Cl(3)−Ti(1)−Cl(2)	106.27(3)
Cl(1)−Ti(1)−Cl(2)	102.11(3)	Cl(3)−Ti(1)−C(1)	118.03(5)
Cl(1)−Ti(1)−C(1)	134.33(5)	Cl(2)−Ti(1)−C(1)	87.24(6)
C(5)−C(1)−C(2)	105.5(2)	C(5)−C(1)−B(1)	130.0(2)
C(2)−C(1)−B(1)	124.5(2)	B(1)−C(1)−Ti(1)	122.01(14)
C(1)−B(1)−C(21)	123.4(2)	C(1)−B(1)−C(11)	117.7(2)
C(21)−B(1)−C(11)	118.3(2)		

δ −134.48 (4 F, *o*-C_6F_5), −149.95 (1 F, B−F), −154.50 (2 F, *p*-C_6F_5), −163.01 (4 F, *m*-C_6F_5). Anal. Calcd for $C_{16}H_{10}BF_{11}O$: C, 43.87; H, 2.30; F, 47.71. Found: C, 43.55; H, 2.65; F, 48.0.

$(C_6F_5)_2$BOEt (2). A solution of C_6F_5MgBr in Et_2O (500 mL, 1.0 M, 0.5 mol) was added at 0 °C to a solution of $BF_3{\cdot}OEt_2$ (31 mL, 0.25 mol) in Et_2O (400 mL). The reaction was allowed to warm slowly to room temperature and stirred overnight. The volatiles were removed in vacuo, leaving a sticky dark brown residue. The residue was heated (100−200 °C) in vacuo to release the crude product. Distillation of the oil at 120−130 °C(5 mmHg) afforded **2** as a low-melting (mp 25−28 °C) solid (40 g, 0.1 mol, 40%). MS: *m/z* 390 (M^+), 346 [$(C_6F_5)_2B^+$], 223 ($C_6F_5BOEt^+$), 195 ($C_6F_5BO^+$), 167 ($C_6F_5^+$).

Li[$(C_6F_5)_2$B(OEt)(IndH)]·2THF (3). To a suspension of indenyllithium (IndLi, 1.9 g, 15.6 mmol) in Et_2O (100 mL) at −78 °C was added **2** (6.0 g, 15.6 mmol) and the mixture warmed to room temperature and stirred for 1 h. After the addition of THF (5 mL, 63 mmol), the volatiles were removed in vacuo leaving a light yellow oil. After a period of several weeks, **3** slowly crystallized (9.2 g, 15.0 mmol, 90%). Anal. Calcd for $C_{31}H_{28}BF_{10}LiO_3$: C, 56.73; H, 4.30. Found: C, 57.25; H, 3.85.

$(C_6F_5)_2$B(FluH) (4). A solution of **1** (90 mmol) in 400 mL of Et_2O was cooled to −78 °C, and fluorenyllithium (FluLi, 15.2 g, 88 mmol) was added. The mixture was slowly warmed to room temperature and stirred for 3 h. The volatiles were evaporated, leaving a sticky, dark brown gum. The product was extracted with hot petroleum (2 × 500 mL). Concentration of the filtrate and cooling to −18 °C gave **4** as a cotton wool-like solid (17 g, 33 mmol, 38%). Recrystallization from Et_2O yielded **4**·Et_2O as colorless crystals. Anal. Calcd for $C_{29}H_{19}BF_{10}O$: C, 59.62; H, 3.28 Found: C, 60.15; H, 3.45.

Ether-free **4**: The Et_2O adduct (4.96 g) was placed under vacuum and heated to 60 °C for 4 h. Anal. Calcd for $C_{25}H_9BF_{10}$: C, 58.86; H, 1.78 Found: C, 58.85; H, 1.75.

$(C_6F_5)_2$B(2-IndH) (5) and $(C_6F_5)_2$B(1-IndH) (6). A solution of **1** in Et_2O (400 mL, 256 mmol) was treated with 256 mmol of IndLi as described for **4**. The solvent was removed, leaving a sticky brown foam which was extracted with petroleum (1.2 L) at 50 °C. Cooling to 5 °C yielded 9 g of yellow crystals as the first fraction. Concentration to ca. 500 mL and cooling to 5 °C gave a second fraction of yellow cubic crystals (11 g). Both fractions were identified as the 2-indenylborane **5** by ^{1}H NMR (combined yield 20 g, 16.9%). Concentration of the remaining solution and cooling to −16 °C gave the 1-indenylborane **6** as a mass of pale orange needle cushions (yield 45 g, 38%). Anal. Calcd for $C_{21}H_7BF_{10}$: C, 54.82; H, 1.53. Found for **5**: C, 54.91; H, 1.60. Found for **6**: C, 55.05; H, 1.90.

$(C_6F_5)_2$B(FluH)·H_2NCMe_3 (7). To a solution of **5** (6.0 g, 11.8 mmol) in light petroleum (50 mL) was added *tert*-butylamine (1.2 mL, 11.8 mmol) at room temperature. The mixture was shaken and left overnight at room temperature, giving **7** as colorless crystals (4.2 g, 7.2 mmol, 61%). Recrystallization from dichloromethane afforded crystals of **7** suitable for X-ray diffraction. Anal. Calcd for $C_{29}H_{20}BF_{10}N$: C, 59.72; H, 3.46; N, 2.40. Found: C, 57.75; H, 3.40; N, 1.95.

$(C_6F_5)_2$B(IndH)·H_2NCMe_3 (8). The compound was made as described for **7** from **6** (2.3 g, 5 mmol) and *tert*-butylamine (1 mL, 10 mmol) giving **8** (1.3 g, 2.1 mmol, 43%) as colorless crystals which were recrystallized from dichloromethane. Anal. Calcd for $C_{25}H_{18}BF_{10}N$: C, 56.31; H, 3.40; N, 2.63. Found: C, 56.15; H, 3.35; N, 2.5.

$(C_6F_5)_2$B(FluSiMe_3) (9). To a solution of **1** in Et_2O (100 mL, 1.0 M, 0.1 mol) was added Li[FluSiMe_3] (0.1 mol) in a procedure analogous to that for **4**. On addition, the solution became a dark green. The mixture was slowly warmed to room temperature and stirred for 6 h. Removal of the volatiles left a sticky dark brown gum which was extracted with a 1:1 toluene/petroleum mixture (600 mL) at 50 °C. Cooling the solution yielded colorless crystals of **9**·0.5 $C_6H_5CH_3$ (15 g, 24 mmol, 24%). Anal. Calcd for $C_{31.5}H_{21}BF_{10}Si$: C, 60.20; H, 3.38. Found: C, 60.5; H, 3.45.

Recrystallization from diethyl ether yielded **9**·Et_2O. The ether dissociates in chlorinated solvents, and the NMR is identical to that of **9** above. Anal. Calcd for $C_{32}H_{27}BF_{10}OSi$: C, 58.55; H, 4.15 Found: C, 58.25; H, 3.85.

$(C_6F_5)_2$B(IndSiMe_3) (10). As described for **4**, **1** (100 mmol) in Et_2O was treated with 100 mmol of Li[IndSiMe_3]. The reaction was allowed to warm slowly to room temperature and stirred for 4 h. Removing the solvent from the very deep orange solution gave a foam which was extracted with light petroleum (500 mL) at 40 °C. Stripping the solvent gave **10** as a red-orange oil which eventually crystallized as a mixture of regioisomers (25 g, 47%). Anal. Calcd for $C_{24}H_{15}BF_{10}Si$: C, 54.16; H, 2.84; F, 35.69. Found: C, 55.45; H, 3.05; F, 34.2.

{**2-(C_6F_5)(Me_2N)B(Ind)**}**Zr(NMe_2)$_3$ (11).** Solid **5** (0.71 g, 1.54 mmol) and Zr(NMe_2)$_4$ (0.41 g, 1.54 mmol) were combined, and toluene (10 mL) was added. The reaction was stirred overnight at room temperature while a slow stream of nitrogen was bubbled over the solution. Solvent removal left a viscous orange-brown oil. The yield was quantitative by NMR.

{**1-(C_6F_5)(Me_2N)B(Ind)**}**Zr(NMe_2)$_3$ (12).** A mixture of **6** (4.37 g, 9.52 mmol) and Zr(NMe_2)$_4$ (2.54, 9.5 mmol) was dissolved in toluene (20 mL). A small exotherm was noted along with a slight darkening of the solution to red-orange. The reaction was treated in the same fashion as for **11**. Removal of the volatiles gave a brownish viscous oil in quantitative yield (by NMR).

{2-(C_6F_5)(Me_2N)B(Ind)}$ZrCl_3$ (13). To a solution of **11** (4.18 g, 7.47 mmol) in toluene (20 mL) at −30 °C was added $SiClMe_3$ (7.3 g, 5.8 mL, 67.2 mmol) slowly via syringe. The reaction was warmed to room temperature and stirred for 6 h. Removal of the solvents gave **13** as a yellow foam, yield 90% by NMR.

{1-(C_6F_5)(Me_2N)B(Ind)}$ZrCl_3$ (14). To a solution of **12** (4.90 g, 8.76 mmol) in 20 mL of toluene and was added $SiClMe_3$ (8.56 g, 6.81 mL, 78.8 mmol). The mixture lightened in color and became slightly warm. The solution was stirred for 6 h before the solvent was stripped off to give a golden yellow foam. The crude yield was ca. 90% by NMR. The crude material readily dissolved in CH_2Cl_2 from which a microcrystalline solid precipitated on standing at room temperature. ^{19}F NMR (THF-d_8, 20 °C): δ −130.2 (m, 1 F, *o*-F), −131.3 (m, 1 F, *o*-F), −154.7 (m, 1 F, *p*-F), −164.0 (m, 2 F, *m*-F). Anal. Calcd for $C_{17}H_{12}BCl_3F_5NZr$: C, 39.42; H, 1.73; N, 2.00; F, 27.11; Cl, 15.18. Found: C, 38.2; H, 2.6; N, 2.2; F, 28.5; Cl, 17.85. MS (EI): *m*/*z* 533 (M^+), 336 $[C_9H_6B(C_6F_5)(NMe_2)]^+$, 291 $[C_9H_6B(C_6F_5)]^+$, 114 ($C_9H_7^+$), 163 ($ZrCl_2^+$).

{2-(C_6F_5)(Me_2N)B(Ind)}$ZrCl_3$·DME (15). To a suspension of **13** (3.73 g, 7.0 mmol) in petroleum (30 mL) was added dimethoxyethane (0.63 g, 0.73 mL, 7.0 mmol). After stirring for 4 h, a pale yellow powder had precipitated. Filtration and drying in vacuo at 20 °C for 6 h afforded **15** (4.0 g, 6.41 mmol, 92%). Anal. Calcd for $C_{21}H_{22}BCl_3F_5NO_2Zr$: C, 40.44; H, 3.56; N, 2.25; Cl, 17.05. Found: C, 39.55; H, 3.80; N, 2.20; Cl, 18.75.

{1-(C_6F_5)(Me_2N)B(Ind)}$ZrCl_3$·2THF (16). Compound **14** (3.73 g, 7.0 mmol) was dissolved in THF (3 mL) and the excess THF removed under vacuum. The resulting foam was recrystallized from a CH_2Cl_2/petroleum mixture at −16 °C, yielding bright yellow needle cushions (2.0 g, 2.95 mmol, 42%). Anal. Calcd for $C_{25}H_{28}BCl_3F_5NO_2Zr$: C, 44.30; H, 4.16; N, 2.07; Cl, 15.69. Found: C, 44.05; H, 4.5; N, 1.90; Cl, 17.8.

(C_6F_5)$_2$B($C_5H_4SiMe_3$) (17). Following the procedure described for **4**, a solution of **1** in Et_2O (200 mL, 1.0 M, 0.2 mol) was treated with Li[$C_5H_4SiMe_3$]. Removal of the volatiles left a golden brown foam which was extracted with petroleum (500 mL) to give a red solution. Removal of the solvent left **17** as a red-brown oil which slowly crystallized at 5 °C (55 g, 114 mmol, 57%). Anal. Calcd for $C_{20}H_{13}BF_{10}Si$: C, 49.82; H, 2.72. Found: C, 49.45; H, 2.65.

{$C_5H_4B(C_6F_5)_2$}$TiCl_3$ (18). To an orange solution of **17** (3.26 g, 6.76 mmol) in CH_2Cl_2 (40 mL) at −78 °C was added $TiCl_4$ (1.52 g, 0.88 mL, 8 mmol) via syringe. The reaction was allowed to warm to room temperature and stirred for 72 h. The color changed to green with a small amount of dark precipitate which was filtered off. The filtrate was concentrated to ca. 10 mL and left to crystallize at −20 °C overnight. Yellow-orange crystals of **18** formed (2.8 g, 4.97 mmol, 73.5%). X-ray quality crystals were grown from a CH_2Cl_2/petroleum solution at 5 °C. Anal. Calcd for $C_{17}H_4BCl_3F_{10}Ti$: C, 36.25; H, 0.72; Cl, 18.88. Found: C, 36.10; H, 0.85; Cl, 18.75.

Polymerizations. Ethene polymerization were carried out by saturating toluene (20 mL) with ethene (1 bar) at −20 °C. $AlEt_3$ (250 μmol) was injected, followed by 50 μmol of **18** in toluene (0.5 mL). The reaction was stopped by the injection of methanol (2 mL) after 1 h, giving 0.12 g of polyethene [productivity 2.4 × 10^3 g PE (mol of Ti·bar·h)$^{-1}$]. Under comparable conditions, no polymer was obtained from 50 to 250 μmol of $CpTiCl_3$. Simlarly, a solution of **14** (50 μmol) and $AlEt_3$ (250 μmol) in toluene (20 mL) was stirred under 1 bar ethene at 20 °C for 1 h, resulting in the recovery of 0.163 g of PE. An identical comparison experiment using $IndZrCl_3/AlEt_3$ at 20 °C gave only a faint trace of polymer.

NMR Reaction of 18 with $AlMe_3$. In an NMR tube, 0.41 mL of a 0.15 M solution of **18** (0.06 mmol) in toluene-d_8 was cooled to −78 °C. A 1.5 M solution of $AlMe_3$ (0.2 mL, 0.3 mmol) was then added via syringe. The solutions were mixed, and the sample was inserted into the spectrometer at −50 °C. At −20 °C, the formation of {$C_5H_4B(C_6F_5)_2$}$TiMe_2Cl$ (**19**) was evident as the only identifiable titanium species, together with a broad signal for excess $AlMe_3$ and $AlMe_2Cl$. ^{1}H NMR of **19** (300 MHz, toluene-d_8): δ 6.29 (t, 2 H, J = 2.31 Hz, 2,5-Cp^B), 6.03 (t, 2 H, J = 2.3 Hz, 3,4-Cp^B), 1.32 (s, 6 H, TiMe). ^{13}C NMR (75.47 MHz, toluene-d_8): δ 148.30 (d, J_{CF} = 233 Hz, *m*-C_6F_5), 140.10 (d, J_{CF} = 244 Hz, *p*-C_6F_5), 136.44 (d, J_{CF} = 226 Hz, *o*-C_6F_5), 121.59 (2,5-Cp^B), 119.60 (3,4-Cp^B), 71.42 (Ti-Me). ^{11}B NMR: δ 72.52.

X-ray Crystallography. Data for all three complexes were collected at 160 K on a Stoe STADI4 diffractometer operating in the $\omega-\theta$ scan mode. All three compounds were corrected for absorption empirically using azimuthal ψ-scans. Full details of crystal data, data collection, and structure refinement are given in Table 2.

The structures of all three compounds were solved by standard heavy-atom methods using SHELXS-86.[33] The asymmetric unit of **9** was found to contain a half molecule of toluene disordered across the center of symmetry at (−2 − *x*, −*y*, 1 − *z*). Refinement, by full-matrix least squares on F^2 using SHELXL-93,[34] was essentially the same for all three compounds. Non-hydrogen atoms (including those of the toluene solvate molecule of **9**) were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized positions using a riding model (with free rotation for methyl groups).

Complete atomic coordinates, anisotropic displacement parameters, and interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre. See Instructions for Authors, *Organometallics,* 1997, Issue 1.

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Supporting Information Available: Tables of full crystallographic data for **1**, **9**, and **18** (9 pages). Ordering information is given on any current masthead page.

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