New Examples of Half-Sandwich (Borylcyclopentadienyl)titanium Trichloride Complexes and an X-ray Structural Characterization of the Homobimetallic Complex $[TiCl_3\{\eta^5\text{-}C_5H_4\}]_2BPh$

Scott A. Larkin,[†] Jeffery T. Golden,[†] Pamela J. Shapiro,[*,†] Glenn P. A. Yap,[‡]
David Ming Jin Foo,[†] and Arnold L. Rheingold[‡]

*Departments of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, and
University of Delaware, Newark, Delaware 19716*

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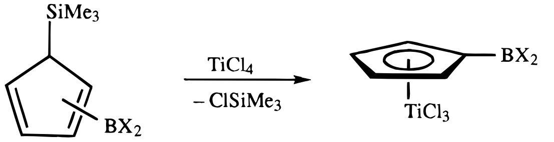
A new series of half-sandwich (borylcyclopentadienyl)titanium trichloride complexes have been prepared which include the boryl substituents $[1,2\text{-}(C_6H_4O_2)]B-$, $Ph(Cl)B-$, Ph_2B- and a $(PhB<)$-bridged bimetallic complex. No correlation was found between the ^1H and ^{13}C NMR chemical shifts of the cyclopentadienyl ring in these complexes and the Lewis acidity of the attached boryl group. The crystal structure of the phenylboron-bridged bimetallic complex $PhB\{(\eta^5\text{-}C_5H_4)TiCl_3\}_2$ was determined. The cyclopentadienyltitanium units of the molecule are twisted away from each other, forming an angle of 41° between the cyclopentadienyl ring planes. Each cyclopentadienyl ring is twisted out of the trigonal plane of the boron by 24°. Preliminary results concerning the Ti-alkylation of some of these complexes are described.

Introduction

Lewis-acidic main-group compounds are essential components of a variety of transition-metal-mediated catalytic processes. They have gained particular prominence for their use as cocatalysts for Ziegler−Natta olefin polymerization.[1] Other noteworthy, Lewis-acid-dependent processes include nickel-catalyzed olefin hydrocyanation,[2] nickel-catalyzed olefin dimerization,[3] and olefin metathesis by classical rhenium and tungsten catalysts.[4]

Impressed by the ability of the Lewis acid to activate the transition metal in these examples, we have embarked on a program to incorporate group 13 moieties directly within the ligand framework of organotransition-metal complexes in order to accomplish this activation intramolecularly. In addition, we expect to develop new modes of cooperation between the main-group Lewis acid and the transition metal.

In this paper we describe the preparation of a variety of new half-sandwich (borylcyclopentadienyl)titanium trichloride compounds which we plan to further modify in order to study their potential for catalysis. The synthetic approach to these complexes was based on a method reported briefly by Jutzi and Seufert in 1979, in which they prepared (borylcyclopentadienyl)titanium trichloride complexes through a dehalodesilylation reaction between various (borylcyclopentadienyl)trimethylsilane compounds and titanium tetrachloride (eq 1).[5]



(1)

Since then, no further chemistry involving these titanium complexes nor any additional applications of this approach to introducing borylcyclopentadienyl rings onto transition metals has been described.[6]

Various methods for covalently attaching group 13 moieties to the ancillary ligands of group 4 transition metals have been pursued by others.[7] In some instances, these have led to active, single-component olefin polymerization catalysts. The success of these systems lends support to our goal of attaching the Lewis acid directly to the cyclopentadienyl ligand framework of transition metals in order to promote intramolecular activation of the metal. By extending the chemistry pioneered by Jutzi, we have introduced additional examples of boryl-derivatized, half-sandwich titanium

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[†] University of Idaho.

[‡] University of Delaware.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.

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complexes, and we report the first X-ray crystal structure of one of these complexes, that of the homonuclear, bimetallic complex $PhB\{(\eta^5\text{-}C_5H_4)TiCl_3\}_2$. Absolute assignments of the ^1H and ^{13}C NMR chemical shifts of the cyclopentadienyl rings of these complexes were made through a combination of variable-temperature ^1H NMR studies and $^1H/^{13}C$ HETCOR analyses. Although the ^{11}B NMR chemical shifts of these (borylcyclopentadienyl)titanium complexes reflect the Lewis acidity of the boron, no correlation between the ^1H and ^{13}C NMR chemical shifts of the cyclopentadienyl ring on the titanium and the Lewis acidity of the attached boryl group was found.

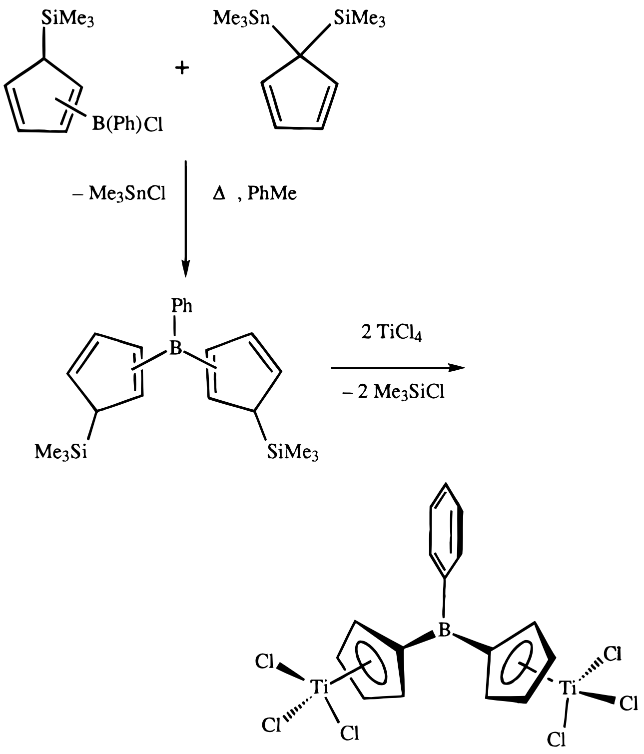
Results and Discussion

Synthesis of (Borylcyclopentadienyl)titanium Trichloride Complexes. From the work of Jutzi and Seufert, cyclopentadienyltitanium trichloride complexes with rings derivatized with $-BCl_2$, $-BBr_2$, $-B(OC_2H_5)_2$, and $-B(CH_3)_2$ groups were known.[5] We have expanded this list to include the $-BPh_2$, $-B(Cl)Ph$, and $-B(Cat)$ ($Cat = 1,2\text{-}(C_6H_4O_2)^{2-}$) derivatives and the PhB-bridged bimetallic complex. While in all cases the cyclopentadienyl ligands were introduced onto the titanium *via* a dehalodesilylation reaction between a trimethylsilyl-substituted ligand precursor and $TiCl_4$, a variety of approaches were used to introduce the boryl groups onto the rings in the synthesis of the (borylcyclopentadienyl)trimethylsilane ligand precursors. These ligand precursors consist of a mixture of regioisomers in which the boryl group generally occupies vinylic positions on the cyclopentadiene ring.[8] Due to the presence of multiple isomers, and due to the fluxionality of the isomers with an allylic silyl group, the ^1H NMR signals for the cyclopentadienyl ring protons in the room-temperature spectra are generally broad and weak. Since we were primarily interested in the titanium complexes derived from these molecules, no effort was made to establish their isomer distribution or to further characterize their fluxional properties.

Our reasons for preparing additional examples of (borylcyclopentadienyl)titanium trichloride complexes were multifold. Foremost was our desire to have boryl substituents with a range of Lewis acidities in order to examine the effect of the Lewis acidity of the ring substituent on the electronic properties and reactivity of the titanium center. We also wanted boryl substituents which were easily introduced onto the ring and which would not interfere with further ligand substitution at the titanium center.

Synthesis of $TiCl_3\{\eta^5\text{-}C_5H_4(BCat)\}$ (2). $(Cat)B-C_5H_4SiMe_3$ (**1**) is prepared straightforwardly by reacting $Li\{C_5H_4(SiMe_3)\}$ directly with (Cat)BCl in the manner described by Grundke and Paetzold for the synthesis of *B*-cyclopentadienylcatecholborane.[9] This ligand was attractive to us since its synthesis involves fewer reaction steps than the synthesis of the diethoxyboryl ligand,[8b] and it is also readily purified either by distillation or by recrystallization from petroleum ether. The corresponding ((catecholboryl)cyclopentadienyl)titanium trichloride complex is prepared in the usual manner by reacting **1** with $TiCl_4$.

Scheme 1



Syntheses of $TiCl_3\{\eta^5\text{-}C_5H_4(BPh_2)\}$ (3) and $TiCl_3\{\eta^5\text{-}C_5H_4(BPhCl)\}$ (4). Whereas boron trihalides readily replace the silyl substituents of silyl-substituted cyclopentadienyl rings, the more labile stannyl substituent is necessary when introducing boryl groups containing non-halide substituents such as alkoxy or, in this case, aryl substituents. Thus, the reaction of $[C_5H_4(SiMe_3)(SnMe_3)]$ with Ph_2BBr and $PhBCl_2$ afforded the corresponding ((diphenylboryl)cyclopentadienyl)- and ((chlorophenylboryl)cyclopentadienyl)trimethylsilane ligand precursors with the elimination of trimethyltin halide. Efforts to purify these ligand precursors by distillation resulted in decomposition; therefore, the crude materials were reacted directly with $TiCl_4$ to form the half-sandwich complexes.

Synthesis of $[TiCl_3]_2\{(\eta^5\text{-}C_5H_4)_2BPh\}$ (6). Selective attachment of a single (trimethylsilyl)cyclopentadiene ring to the boron in the reaction of $PhBCl_2$ with $[C_5H_4(SiMe_3)(SnMe_3)]$ was achieved at room temperature. More forcing conditions were required to attach a second ring to the boron. This was accomplished by reacting $PhBCl_2$ with 2 equiv of $[C_5H_4(SiMe_3)(SnMe_3)]$ in refluxing toluene to form $[C_5H_4(SiMe_3)]_2BPh$ (**5**) (Scheme 1). Apart from their role in transferring the borylcyclopentadienyl ligand to titanium, the trimethylsilyl substituents also appeared to stabilize the cyclopentadienylboranes against polymerization, since efforts to prepare $PhB(C_5H_5)_2$ by an analogous route afforded insoluble polymer.

We were able to introduce two titanium atoms onto $(C_5H_4SiMe_3)_2PhB$ to form the phenylborane-bridged cyclopentadienyltitanium bimetallic complex, **6** (Scheme 1). Single crystals suitable for an X-ray structure determination were obtained, affording the first solid-state structure of one of these systems (*vide infra*).

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Table 1. ^1H,^{13}C, and^{11}B NMR Chemical Shifts (ppm) for Boryl−CpTiCl$_3$

boryl group	^1H		^{13}C		
	2,5-Cp	3,4-Cp	2,5-Cp	3,4-Cp	^{11}B
Cl$_2$B−	6.64	6.04	130	126	32[a]
Me$_2$B−	6.63	6.22	130	127	54[a]
Ph(Cl)B−	7.06	6.21	131	127	38[b]
Ph$_2$B−	6.80	6.35	134	128	41[b]
[TiCp]PhB−	7.07	6.14	134	128	c
(Cat)B−	6.92	6.11	129	126	12[b]

[a] C$_6$D$_6$ solution. [b] CDCl$_3$ solution. [c] Sample was not soluble enough to obtain a ^{11}B NMR spectrum.

NMR Characterization of (Borylcyclopentadienyl)titanium Trichloride Complexes. In the ^1H NMR spectra of the boryl-CpTiCl$_3$ complexes, the signals for the 2,5- and 3,4-protons of the cyclopentadienyl rings appear as two pseudotriplets corresponding to an AA′BB′ system. An unequivocal assignment of these ring protons cannot be made by a simple consideration of electron-acceptor effects of the boron. The relative shielding of the protons can change from one system to another as a consequence of magnetic anisotropy effects from the metal. Siebert and co-workers illustrated this situation by showing that the relative order of the chemical shifts of the 2,5- and 3,4-cyclopentadienyl ring protons in ferrocenylborane complexes were opposite from their ordering in cymantrenylborane complexes.[10] The relative order of the ^{13}C chemical shifts of the ring carbons is consistent with that of the protons. Siebert and co-workers were able to make absolute assignments for the ring carbon and proton signals in the ferrocene and cymantrene complexes by demonstrating a decoalescence at low temperature of the ^1H NMR signal for the 2,5-protons upon freezing out the rotation of an unsymmetrically substituted boryl substituent. We used this same method to make definitive assignments for the ring protons α and β to the boryl substituent of our cyclopentadienyltitanium trichloride complexes. Examination of the low-temperature ^1H NMR behavior of complexes **3** and **6** allowed us to assign the α-protons of the ring as the low-field triplet, which decoalesced with cooling. The upfield triplet assigned to the β-protons exhibited only a loss of definition with cooling. Assignment of the ring carbon signals in the ^{13}C NMR spectra was accomplished by using (H,C)-HETCOR spectra. In all cases, as with the 2,5-protons, the lower field signal corresponded to the 2,5-carbons.

The ^1H, ^{13}C, and ^{11}B NMR chemical shifts of a series of (borylcyclopentadienyl)titanium trichlorides, including the dichloro- and dimethylboryl derivatives reported by Jutzi, are tabulated in Table 1. Although the ^{11}B NMR chemical shifts are clearly sensitive to the electron-accepting ability of the boron,[11] the ^1H and ^{13}C NMR chemical shifts of the cyclopentadienyl ring appear to be unaffected by the nature of the boryl substituent. Indeed, the relative ring proton chemical shifts for the different complexes are inconsistent with the trends indicated by ^{11}B NMR chemical shifts. The ^{13}C NMR chemical shifts of the cyclopentadienyl ring carbons likewise do not reflect the Lewis acidity of the attached boryl group. In their discussion of their boryl-CpTiCl$_3$ complexes, Jutzi and Seufert correctly assumed that the resonances of the ring protons α to the boryl substituent of the titanium complexes occurred downfield of the β protons. The authors also claimed a dependence of the ring proton chemical shifts on the Lewis acidity of the boryl substituent, yet examination of their data fails to reveal any regular pattern among the different boryl derivatives, with the exception of the diethoxyboryl derivative, for which the ^1H NMR chemical shifts occur upfield of the corresponding shifts in the more Lewis-acidic dichloroboryl, dibromoboryl, and dimethylboryl derivatives. In contrast, greater electron-withdrawing character of the boryl substituent has a noticeable electron deshielding effect on the ^1H and ^{13}C NMR chemical shifts of the cyclopentadienyl rings of cymantrenylborane and ferrocenylborane complexes.[10,12] Apparently, the Lewis-acidic titanium places a greater demand on the π-electrons of the cyclopentadienyl ring than the boryl substituents.

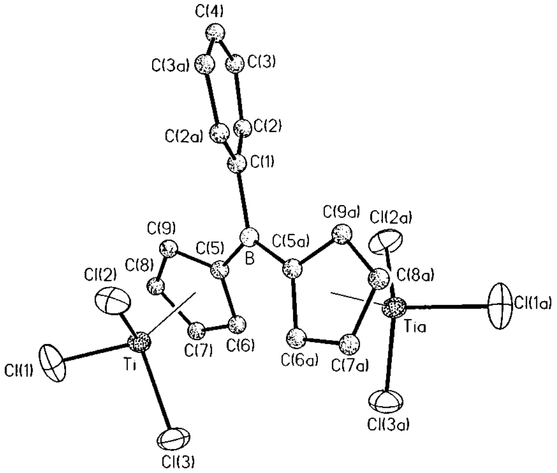

Figure 1. Molecular structure of PhB{(η^5-C$_5$H$_4$)TiCl$_3$}$_2$, (**6**), with the atom-labeling scheme. Thermal ellipsoid plots are given for titanium and chloride atoms at 35% probability. Carbon and boron atoms were refined isotropically.

Description of the Molecular Structure of [TiCl$_3$]$_2${(η^5-C$_5$H$_4$SiMe$_3$)$_2$BPh} (6). An ORTEP view of the molecular structure of **6** is shown in Figure 1. A summary of the crystal data and structure refinement is presented in Table 2. Selected bond lengths and angles are listed in Table 3.

There are four dimers per unit cell, each residing on a 2-fold rotational axis passing through the central phenylboron bridge. Thus, the cyclopentadienyltitanium units are pointed in opposite directions from the trigonal plane formed by the boron and C(1), C(5), and C(5a). The torsion angle between the planes of the cyclopentadienyl rings is 41°. Each cyclopentadienyl ring is twisted out of the trigonal plane of the boron by 24°, thereby reducing the amount of conjugation possible between the π-system of the cyclopentadienyl rings and the formally empty p orbital on the boron. It is difficult to assess the presence of multiple bonding from the B−C(ring) bond distance of 1.55(2) Å, which is within the range observed for B−C single bonds in other three-

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Table 2. Crystallographic Data for $C_{16}H_{13}BCl_6Ti_2$ (6)

	(a) Crystal Parameters		
formula	$C_{16}H_{13}BCl_6Ti_2$	Z	4
fw	524.57	cryst dimens, mm	0.1 × 0.2 × 0.4
cryst syst	orthorhombic	D(calc), g cm^{-3}	1.684
space group	Pbcn	μ(Mo Kα), cm^{-1}	15.44
a, Å	15.223(3)	temp, K	256
b, Å	11.328(4)	T(max)/T(min)	1.2
c, Å	11.997(2)		
	(b) Data Collection		
diffractometer	Siemens P4	data collected (h,k,l)	−6,+13,+14
monochromator	graphite	no. of rflns collected	1158
radiation	Mo Kα (λ = 0.710 73 Å)	no. of indpt rflns	830
2θ scan range, deg	4.0−50.0	no. of indpt obsd rflns, $F_o \geq 4\sigma(F_o)$	702
	(c) Refinement[a]		
$R(F)$, %	6.56	$\Delta(\rho)$, e Å^{-3}	0.771, −0.448
$R(wF^2)$, %	16.66	N_o/N_v	11.5
Δ/σ (max)	0.8	GOF	1.09

[a] Quantity minimized: $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6

Ti−Cl(1)	2.211(6)	Ti−Cnt	2.000
Ti−Cl(2)	2.219(3)	B−C(1)	1.57(2)
Ti-Cl(3)	2.218(4)	B−C(5)	1.55(2)
Ti−C(5)	2.355(11)	C(5)−C(6)	1.439(12)
Ti−C(6)	2.342(13)	C(5)−C(9)	1.42(2)
Ti-C(7)	2.315(11)	C(6)−C(7)	1.43(2)
Ti−C(8)	2.340(13)	C(7)−C(8)	1.40(2)
Ti−C(9)	2.321(9)	C(8)-C(9)	1.40(2)
Cl(1)−Ti−Cl(2)	104.5(2)	C(5)−Ti−C(6)	35.7(3)
Cl(1)−Ti−Cl(3)	101.4(2)	C(5)−Ti−C(9)	35.4(5)
Cl(2)−Ti−Cl(3)	103.7(2)	C(6)−Ti−C(7)	35.7(6)
C(5)−B−C(5a)	127.0(11)	C(7)−Ti−C(8)	34.9(4)
C(5)−B−C(1)	116.5(6)	C(8)−Ti−C(9)	34.8(4)

coordinate boron species.[13] The phenyl ring is also twisted out of conjugation with the boron p orbital by 47°, exhibiting a B−C bond length of 1.55(7) Å. The $CpTiCl_3$ units are unremarkable; the Ti−Cl bond distances are normal at 2.211(6)-2.219(3) Å,[14] and the Ti−ring centroid distance of 2.000 Å is comparable to that of other cyclopentadienyltitanium trichloride complexes.[15]

Whereas there are numerous examples of chelated metallocene complexes of titanium,[16] there are relatively few reported examples of cyclopentadienyltitanium complexes in which the bridged rings span two titanium atoms.[17] As in the structure of **6** reported here, whenever the cyclopentadienyltitanium units are free to rotate about the bridging group, they adopt a *trans* arrangment in the solid state in order to minimize steric interactions.

Preliminary Investigations into the Reactivity of the Half-Sandwich (BorylCyclopentadienyl)titanium Trichloride Complexes. Preliminary efforts to alkylate the titanium centers of the (borylcyclopentadienyl)titanium trichloride complexes have revealed that these systems are unstable toward a variety of organometallic alkylating reagents, including alkyllithium, Grignard, and alkylaluminum reagents. The decomposition of (Cat)B−$CpTiCl_3$ in the presence of these reagents appears to be due to the vulnerability of the catechol group. For instance, Me_2B−$CpTiCl_3$ was the only species isolated (in approximately 10% yield) from the reaction of (Cat)B−$CpTiCl_3$ with trimethylaluminum. (Cat)B−$CpTiCl_3$ does, however, react cleanly with dimethylzinc, which is generally a milder alkylating agent. The monoalkylation product (Cat)B−$CpTiCl_2$(Me) (**7**) is formed exclusively, even when the reaction is carried out in the presence of 5 equiv of dimethylzinc. Similar reactivity with dimethylzinc has been reported for the parent complex $CpTiCl_3$[18] and has been confirmed by us.

All efforts to form the metallocene (Cat)B−Cp(C_5H_5)$TiCl_2$ were unsuccessful. Ill-defined polymeric material, presumably due to cleavage of the catechol group on the boron, was obtained upon reacting **2** with LiCp, Cp_2Mg, or $C_5H_5SnMe_3$ in toluene. As expected,[19] no reaction was observed between **2** and $C_5H_5SiMe_3$. There was no reaction between Cp_2Zn and CpTl and **2** at room temperature; decomposition resulted when the reaction mixtures were heated. We were, however, able to prepare the (dimethylboryl)- and (diphenylboryl)titanocene dichloride complexes *via* salt-elimination reactions between the corresponding half-sandwich complexes $\{\eta^5\text{-}(R_2B)C_5H_4\}CpTiCl_2$ (R = Me, Ph), and lithium cyclopentadienide.[20] Efforts to prepare additional derivatives, particularly Ti−alkyl derivatives of the boryl-substituted half-sandwich and bent-metallocene complexes, are underway.

Summary and Conclusions

By expanding upon Jutzi's method for attaching boryl-substituted cyclopentadienyl rings to titanium, we have

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prepared new examples of half-sandwich boryl−CpTiCl$_3$ complexes and have prepared the first example of a boron-bridged cyclopentadienyl−homobimetallic complex, which we have crystallographically characterized. Comparison of the cyclopentadienyl ring ^{1}H and ^{13}C NMR chemical shifts of a variety of these complexes did not reveal any correlation with the Lewis acidity of the attached boryl group. Further experiments are necessary to assess the possible influence of the boryl substituents on the electronic properties of the titanium. We are currently examining the redox properties of these complexes by electrochemical methods. We are also in the process of preparing the perfluorinated analog of our diphenylboryl derivative (i.e. $(C_5F_6)_2B-CpTiCl_3$), which should exhibit the greatest influence, if any, of the boryl substituent on the electronic properties of the titanium center. Various avenues for replacing the chlorine ligands on the titanium center in these complexes with more reactive groups such as alkyl groups are also being explored.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques. All solvents were distilled under nitrogen over sodium benzophenone ketyl (toluene, ethyl ether, THF) or CaH$_2$ (petroleum ether, methylene chloride). The solvents were then stored in line-pots, from which they were either vacuum-transferred from sodium benzophenone ketyl or cannulated directly. The NMR solvents benzene-d_6 and CDCl$_3$ were dried over activated 4 Å molecular sieves. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4 Å molecular sieves. NMR spectra were recorded on an IBM NR-300 (300.13 MHz, ^{1}H; 75.46 MHz, ^{13}C; 75.46 and 96.27 MHz, ^{11}B) and an IBM NR-200 (200.13 MHz, ^{1}H; 50.32 MHz, ^{13}C; 64.20 MHz, ^{11}B). All chemical shifts are reported in ppm and referenced to solvent (^{13}C, ^{1}H) or B(OH)$_3$ (^{11}B, external reference, δ 0 ppm). Mass spectra were obtained on a VG 7070-HS GC/MS instrument with a heated direct-insertion probe for solid samples. Elemental analyses were determined by Desert Analytics and the University of Idaho analytical facilities. Bromodiphenylborane[21] and (trimethylsilyl)(trimethylstannyl)cyclopentadiene[22] were prepared as described in the literature.

Procedures. $(\{SiMe_3\}C_5H_4)(C_6H_4O_2)B$ (1). Toluene (100 mL) was added to a mixture of (Me$_3$SiC$_5$H$_4$)Li (5.6 g, 39 mmol), and *B*-chlorocatecholborane (6.0 g, 39 mmol) and the reaction mixture was heated at reflux for 12 h. LiCl was removed by filtration, and the filtrate was evaporated under reduced pressure to afford a gummy, off-white residue which was dissolved in 20 mL of petroleum ether. Cooling of this solution to −78 °C afforded **1** as a white precipitate (yield: 4.6 g, 46%). The product may also be isolated as a pale yellow oil which solidifies over time by distillation from the residue under reduced pressure (160 °C, 2×10^{-2} Torr). ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.7 (br, Cp *H*), 7.2−7.0 (m, arene *H*), 6.9−6.7 (m, arene *H*), 6.6 (br, Cp *H*), 3.3 (br, Cp *H*), 0.1 (s, $Si(CH_3)_3$), −0.1 (s, $Si(CH_3)_3$). ^{11}B NMR (CDCl$_3$): δ 11.3. MS (EI): *m/z* 256 (M$^+$, 59.37), 240 (M$^+$ − CH$_3$ − H, 59.37), 149 ($C_5H_4BSiMe_3^+$ + H, 22.90), 136 ($C_5H_4SiMe_3^+$ − H, 10.66), 73 (Me_3Si^+, 18.43), 64 ($C_5H_4^+$, 21.65). Anal. Calcd for $C_{14}H_{17}BO_2Si$: C, 65.60; H, 6.68. Found: C, 65.59; H, 6.50.

$[\{C_6H_4O_2\}B(\eta^5\text{-}C_5H_4)]TiCl_3$ (2). TiCl$_4$ (0.73 g, 3.8 mmol) was added dropwise to a solution of **1** (1.0 g, 3.8 mmol) in 40 mL of methylene chloride at room temperature, and the reaction mixture was stirred for 12 h. Removal of the volatiles under reduced pressure afforded a dark red tar, which yielded **2** as a brick red precipitate upon addition of 10 mL of methylcyclohexane (yield 0.80 g, 62%). ^{1}H NMR (C$_6$D$_6$): δ 6.98−7.03 (m, 2H, Cat *H*), 6.92 ($\sim$t, $J \approx$ 2Hz, 2H, Cp *H*), 6.73−6.78 (m, 2H, Cat *H*), 6.11 ($\sim$t, $J \approx$ 2 Hz, 2H, Cp *H*). ^{13}C NMR (C$_6$D$_6$): δ 128.6, 125.6 ($CatB(C_5H_4)$), 123.4, 112.9 ($C_6H_4O_2B$). ^{11}B NMR (CDCl$_3$): δ 11.5. MS (EI): *m/z* 338 (M$^+$, 24.4), 336 (M$^+$ − 2H, 22.6), 183 ($[C_6H_4O_2]B(C_5H_4)^+$, 100), 157 ($BC_5H_3\text{-}TiCl^+$, 18.4). Anal. Calcd for $C_{11}H_8BCl_3O_2Ti$: C, 39.18; H, 2.39. Found: C, 39.53; H, 2.31.

$TiCl_3\{\eta^5\text{-}C_5H_4(BPhCl)\}$ (3). The ligand precursor, $\{(Me_3Si)C_5H_4\}B(Cl)Ph$, was prepared *in situ* by adding dichlorophenylborane (1.06 g, 6.65 mmol) dropwise to a solution of (trimethylsilyl)(trimethylstannyl)cyclopentadiene (2.00 g, 6.65 mmol) in 50 mL of toluene at room temperature. After 1 h, TiCl$_4$ (1.26 g, 6.65 mmol) was added dropwise to the reaction mixture. After it was stirred overnight at room temperature, the greenish yellow solution was dried under reduced pressure to yield a green oil. Trituration of the oil with petroleum ether caused **3** to precipitate as an olive green powder (yield 1.34 g, 65.8%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.86−7.90 (m, 2H, Ph *H*), 7.10−7.25 (m, 3H, Ph *H*), 7.06 ($\sim$t, $J \approx$ 2.7 Hz, 2H, Cp *H*), 6.21 ($\sim$t, $J \approx$ 2.7 Hz, 2H, Cp *H*). ^{13}C NMR (C$_6$D$_6$): δ 136.3, 133.8, 128.4 (C_6H_5B), 130.7, 126.6 (C_5H_4Ti). ^{11}B NMR (CDCl$_3$): δ 38. MS (EI): *m/z* 342 (M$^+$, 0.8), 305 (M$^+$ − H$_2$Cl, 11.1), 152 ($TiCl_3^+$, 100), 126 (44.6, $PhBClH_3^+$). Anal. Calcd for $C_{11}H_9BCl_4Ti$: C, 38.67; H, 2.65. Found: C, 38.95; H, 2.69.

$TiCl_3\{\eta^5\text{-}C_5H_4(BPh_2)\}$ (4). Bromodiphenylborane (2.34 g, 9.59 mmol) was added dropwise to a solution of (trimethylsilyl)(trimethylstannyl)cyclopentadiene (3.00 g, 9.59 mmol) in 25 mL of petroleum ether at room temperature. The reaction mixture was stirred overnight under a blanket of argon. The solvent was removed from the reaction mixture under reduced pressure, and the Me$_3$SnBr was removed by heating the residue to 120 °C under vacuum. The remaining crude $(\{SiMe_3\}C_5H_4)BPh_2$, an orange-red oil, was used in the next step without further purification. ^{1}H NMR (CDCl$_3$): δ 7.9−7.6 (m, Ph *H*), 7.6−7.4 (m, Ph *H*), 7.1 (br, Cp *H*), 6.7 (br, Cp *H*). ^{11}B NMR (CDCl$_3$): δ 45. MS (EI): *m/z* 302 (M$^+$, 23.6), 165 (Ph_2B^+, 65.3), 135 ($Me_3SiC_5H_2^+$, 22.8), 73 ($SiMe_3^+$, 100).

The titanium complex **4** was prepared by dissolving the crude $(\{SiMe_3\}C_5H_4)BPh_2$ in 25 mL of dichloromethane and adding TiCl$_4$ (2.00 g, 10.5 mmol) dropwise to the solution at room temperature. The solution turned immediately from bright orange to deep red and over time assumed a greenish tinge. The reaction mixture was stirred overnight, and the volatiles were removed under reduced pressure, leaving a green-black, oily residue. Trituration of the residue with petroleum ether afforded **4** as a lime green powder (yield 1.98 g, 54%). ^{1}H NMR (C$_6$D$_6$): 7.62−7.67 (m, 2H, Ph *H*), 7.16−7.27 (m, 3H, Ph *H*), 6.76 ($\sim$t, $J \approx$ 2.6 Hz, 2H, Cp *H*), 6.36 ($\sim$t, $J \approx$ 2.6 Hz, 2H, Cp *H*). ^{13}C NMR (C$_6$D$_6$): δ 138, 132, 128 ($[C_6H_5]_2B$), 128, 134 (C_5H_4Ti). ^{11}B NMR (CDCl$_3$): δ 41. MS (EI): *m/z* 382 (M$^+$, 32.8), 346 (M$^+$ − HCl, 26.4), 305 (M$^+$ − Ph, 49.3), 269 (M$^+$ − [Ph + HCl], 13.6), 228 ($C_5H_3BPh_2^+$, 100), 151 ($C_5H_3BPh^+$, 75.7), 126 ($C_5H_4BTiH_3^+$, 65.0), 100 (?, 64.3), 65 ($C_5H_5^+$, 71.4). Anal. Calcd for $C_{17}H_{14}BCl_3Ti$: C, 53.26; H, 3.68. Found: C, 53.05; H, 3.53.

$(\{SiMe_3\}C_5H_4)_2BPh$ (5). Dichlorophenylborane (1.53 g, 9.62 mmol) was added to a solution of (trimethylsilyl)(trimethylstannyl)cyclopentadiene (5.69 g, 19.0 mmol) in 50 mL of toluene at room temperature. The reaction mixture was refluxed under a blanket of argon overnight. The volatiles were removed *in vacuo*, leaving 3.40 g (97.7% theoretical yield) of crude **5** as a viscous, red-orange oil. Attempts to purify the oil by distillation lead to apparent decomposition. ^{1}H NMR (CDCl$_3$): δ 7.6 (m, Ph *H*), 7.4 (m, Ph *H*), 7.2 (m, aryl *H*), 7.0 (br, Cp *H*), 6.7 (br, Cp *H*), −0.1 (br, $Si(CH_3)_3$). ^{11}B NMR (CDCl$_3$): δ 37. MS: *m/z* 362 (M$^+$, 5.6), 225 (M$^+$ − $Me_3SiC_5H_4$, 43.2), 152 (C_5H_4BPh, 13.4), 135 ($C_5H_2SiMe_3^+$, 13.6), 84 ($BSiMe_3^+$, 15.6), 73 ($SiMe_3^+$, 100).

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[$TiCl_3\{\eta^5$-$C_5H_4\}]_2BPh$ (6). An excess of $TiCl_4$ (2.8 g, 15 mmol) was vacuum-transferred to a solution of crude **5** (2.5 g, 6.8 mmol) in chloroform (50 mL) at −78 °C. When the reaction mixture was warmed to room temperature, compound **7** deposited as yellow-green crystals which were isolated by filtration (yield 2.2 g, 63%). ^{1}H NMR (C_6D_6): δ 7.45 (t, 1H, Ph *H*), 7.41 (d, 1H, Ph *H*), 7.31−7.16 (m, 3H, Ph *H*), 7.07 (t, $J \approx 2.4$ Hz, 4H, Cp *H*), 6.14 (t, $J \approx 2.4$ Hz, 4H, Cp *H*). ^{13}C NMR (CD_2Cl_2): δ 136.3, 132.3, 128.3 (C_6H_5B), 134.2, 128.8 ($(\mathit{C}_5H_4)_2$-Ti. Anal. Calcd for $C_{16}H_{13}BCl_6Ti$: C, 36.63; H, 2.50. Found: C, 36.58; H, 2.29.

[$\{C_6H_4O_2\}B$-(η^5-C_5H_4)]Ti(Me)Cl_2 (7). At room temperature, 1.4 mL (3.0 mmol) of a 2.14 M solution of dimethylzinc in toluene was added dropwise by syringe to a solution of **2** (1.0 g, 3.0 mmol) in 20 mL of toluene, and the reaction mixture was stirred for 12 h. The solution was filtered to remove the insolubles, and the filtrate was dried *in vacuo*, leaving a gummy, tan residue. Taking the residue up in 10 mL of petroleum ether afforded **3** as a yellowish tan precipitate (yield 0.250 g, 24.5%). ^{1}H NMR (C_6D_6): δ 7.00 (m, 2H, Cat *H*), 6.81 (~t, $J \approx 4$ Hz, 2H, Cp *H*), 6.72−6.77 (m, 2H, Cat *H*), 5.96 (~t, $J \approx 4$ Hz, 2H, Cp *H*), 1.86 (s, 3H, TiCH_3). ^{13}C NMR (C_6D_6): δ 123.8, 122.7 (CatB(C_5H_4)), 148.3, 123.4, 112.9 ($\mathit{C}_6H_4O_2B$), 82.6 (Ti$\mathit{C}H_3$). ^{11}B NMR (C_6D_6): δ 9. MS (EI): *m/z* 316 (M^+, 2.9), 300 (33.8), 184 (35.7), 134 (53.4), 69 (100). Anal. Calcd for $C_{12}H_{11}BCl_2O_2Ti$: C, 45.49; H, 3.50. Found: C, 45.71; H, 3.69.

Crystal Structure Determination of [$TiCl_3\{\eta^5$-$C_5H_4\}]_2$-BPh (6). Yellow-green crystals of **6** formed during the synthesis of the compound in chloroform. A suitable crystal was selected and mounted in a thin-walled, nitrogen-flushed glass capillary. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 24°).

The systematic absences in the diffraction data are uniquely consistent for space group *Pbcn*. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A semiempirical ellipsoid absorption correction was applied to the data set. The molecule is located on a 2-fold axis. The titanium and chlorine atoms were refined with anisotropic displacement coefficients. The boron and carbon atoms were refined isotropically. The hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Tables of crystallographic data collection and solution and refinement details, atomic coordinates, complete bond lengths and angles, and anisotropic displacement coefficients (5 pages). Ordering information is given on any current masthead page.

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