Synthesis of Group 4 Organometallic Complexes That Contain the Bis(borylamide) Ligand $[Mes_2BNCH_2CH_2NBMes_2]^{2-}$

Timothy H. Warren, Richard R. Schrock,* and William M. Davis

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Titanium and zirconium derivatives of the new chelating bis(borylamido) ligand $[Mes_2BNCH_2CH_2NBMes_2]^{2-}$ ($[Ben]^{2-}$) are prepared by treating $MCl_4(THF)_2$ (M = Ti, Zr) with $(Ben)Mg(THF)_2$. Nitrogen−boron π-interactions in $(Ben)TiCl_2$ and $(Ben)ZrCl_2(THF)$ result in one mesityl group in each $BMes_2$ unit occupying space roughly above and below the MCl_2 plane. $(Ben)TiCl_2$ is smoothly alkylated by Grignard reagents in dichloromethane to give (Ben)Ti(R)Cl ($R = CH_2Ph$, CH_2CMe_3) and $(Ben)TiR_2$ (R = Me, CH_2Ph), while unstable $(Ben)ZrMe_2$ can be prepared from $(Ben)ZrCl_2(THF)$ and methyllithium in toluene. An X-ray study of $(Ben)Ti(CH_2Ph)Cl$ confirms the proposed ligand conformation and features a highly distorted "η^2" benzyl ligand with a $Ti-C_\alpha-C_{ipso}$ angle of only 87.0(5)°. $(Ben)MMe_2$ complexes cleanly decompose by metalation of the ortho methyl groups from mesityl rings on different borons at room temperature (for Zr) or upon heating (for Ti). An X-ray crystal structure of (TwistBen)Zr shows it to be a dimer in which the two zirconium centers are bridged by two mesityl *o*-methylene groups. $B(C_6F_5)_3$ binds to a methyl group in $(Ben)MMe_2$ complexes in dichloromethane, but such compounds show little polymerization activity toward ethylene at 25 °C and 1−2 atm as a consequence of strong anion binding.

Introduction

The bent metallocene is one of the most important types of early-transition-metal complexes in which reactive sites are structurally defined and sterically protected.[1] Consequently, complexes that contain only one cyclopentadienyl group or even no cyclopentadienyl groups that support a variety of "metallocene-like" chemistry at the remaining coordination sites are receiving increasing attention. In the former category are amido/cyclopentadienyl ligands,[2−6] and in the latter category are some recently reported tridentate diamido ligands.[7] The chelating bis(borylamido) ligand $[Mes_2BNCH_2CH_2NBMes_2]^{2-}$ would be a structurally and electronically unusual bidentate diamido ligand, since two mesityl groups should define and sterically protect two or three coordination sites in a plane roughly perpendicular to the NCCN ligand backbone as a consequence of N−B π-bonding. Furthermore, the strongly π-accepting boryl groups should attenuate the ability of the nitrogen atoms to donate π-electron density to the metal center and therefore should yield complexes in which the metal is more electrophilic than in more traditional alkyl and arylamide complexes.[3,5,8−19]

A relatively small number of borylamide complexes have been reported. For example, hydrozirconation of (*tert*-butylimino)(2,2,6,6-tetramethylpiperidino)borane resulted in zirconium−nitrogen bond formation as well as a β-agostic B−H−Zr interaction.[20] Addition of $t\text{-Bu}(Me_3Si)NB{\equiv}N\text{-}t\text{-Bu}$ across one M−C bond of the group 4 benzyne complexes $Cp_2M(C_6H_4)$ (M = Ti, Zr) gave five-membered metalacycles containing the M−N−B unit,[21] while a related four-membered metalacycle resulted from the 2 + 2 cycloaddition of $i\text{-BuN}{\equiv}B\text{-}i\text{-Bu}$ with the Ta=C double bond of $CpTaCl_2(CHCMe_3)$.[22] For later first-row metals a series of two-coordinate complexes of the type $M(NArBMes_2)_2$ (Ar = Ph, Mes; M = Cr−Ni) could be prepared.[23−25] The π-acceptor ability

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of the boryl substituent is probably an important factor in stabilizing *mono*meric, low-coordinate structures, since analogous complexes containing other bulky amides such as $N(SiMe_3)_2$ are *dimeric*.[26-28] Therefore, a combination of N−B π-bonding and the steric bulk of the $BMes_2$ group should play a significant role in the chemistry of group 4 complexes containing the $[Mes_2BNCH_2CH_2NBMes_2]^{2-}$ ligand. In this paper we describe the synthesis of the $[Mes_2BNCH_2CH_2NBMes_2]^{2-}$ ($[Ben]^{2-}$) ligand and several titanium and zirconium derivatives.

Results

The bis(borylamine) $Mes_2BNHCH_2CH_2NHBMes_2$ (H_2(Ben)) was prepared from lithium ethylenediamide (generated *in situ*) and 2 equiv of dimesitylboron fluoride (eq 1). Deprotonation of H_2(Ben) with butyllithium in the presence of $MgBr_2$(ether) affords (Ben)$Mg(THF)_2$ (eq 2). Both H_2(Ben) and (Ben)$Mg(THF)_2$ are white crystalline solids that were prepared in 80−90% yield on a scale of typically 30 and 10 g, respectively.

$$H_2NCH_2CH_2NH_2 \xrightarrow[(2)\ 2Mes_2BF]{(1)\ 2LiBu/THF} Mes_2BNHCH_2CH_2NHBMes_2 \quad (1)$$

$$H_2Ben \xrightarrow[THF]{2LiBu,\ MgBr_2(ether)} (Ben)Mg(THF)_2 \quad (2)$$

Addition of $MCl_4(THF)_2$ (M = Ti, Zr) to a dichloromethane solution of (Ben)$Mg(THF)_2$ produces yellow-orange (Ben)$TiCl_2$ (**1**) or colorless (Ben)$ZrCl_2$(THF) (**2**) (eq 3) in 81% and 71% yields, respectively. Room-temperature proton NMR spectra of both **1** and **2** exhibit a single sharp resonance for the methylene protons in the backbone as well as two sets of resonances due to inequivalent mesityl groups. Inequivalent mesityl groups within each $BMes_2$ unit are to be expected, since N−B π-bonding[29,30] should favor a structure in which one mesityl ring of each dimesitylboron unit lies above or below the MCl_2 plane and the other flanks the NCCN backbone (Figure 1). When a sample of (Ben)$TiCl_2$ is warmed to 90 °C, the six mesityl proton resonances (*m*-H, *o*-Me, *p*-Me) coalesce to give three signals as a consequence of rotation about the N−B bond. The value of $\Delta G^{\ddagger}_{rot}$ (17.4(2) kcal/mol) in **1** is significantly lower than the value of ~25 kcal/mol found for other (dimesitylboryl)amines such as $MeNHBMes_2$, $PhNHBMes_2$,[31] and H_2(Ben). (The fact that no coalescence of the closely spaced *m*-H, *o*-Me, and *p*-Me resonances of H_2(Ben) was observed by ^1H NMR spectroscopy in C_6D_5Br at 150 °C allowed us to estimate a lower limit of 23 kcal/mol for the barrier to N−B bond rotation in H_2(Ben).) The decreased barrier to N−B bond rotation observed in **1** may be ascribed to competition between empty metal d orbitals and boron p orbitals for nitrogen lone pair electron density. (The d^0 borylamides $Ti(NHBMes_2)_3Cl$, $Zr(NHBMes_2)_4$, and $Cp_2Zr(NHBMes_2)Cl$ also exhibit substantially reduced barriers to N−B bond rotation ($\Delta G^{\ddagger}_{rot}$ = 15.3(2), 15.2(2), and 16.2(2) kcal/mol, respectively) relative to other (dimesitylboryl)amines, whereas $Sn(NHBMes_2)_3Cl$ does not ($\Delta G^{\ddagger}_{rot} > 22$ kcal/mol).[32]) The fact that **2** binds THF, while **1** does not, is consistent with the larger size of Zr and its often higher coordination number in otherwise analogous Ti and Zr complexes. On the basis of X-ray structures of Ben derivatives to be described later, we assume that the THF in **2** is bound to the metal in the $ZrCl_2$ plane between the two chlorides.

$$(Ben)Mg(THF)_2 + MCl_4(THF)_2 \xrightarrow{CH_2Cl_2} (Ben)MCl_2(THF)_x \quad (3)$$

1: M = Ti, $x = 0$
2: M = Zr, $x = 1$

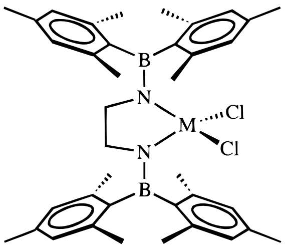

Figure 1. Proposed geometry of (Ben)MCl_2 complexes.

Monoalkyl- and dialkyltitanium derivatives can be prepared by treating (Ben)$TiCl_2$ in dichloromethane at −40 °C with Grignard reagents (eqs 4 and 5). Proton NMR spectra of unsymmetrically substituted **3a**,**b** show four *meta* and six mesityl methyl resonances, consistent with mirror symmetry and no rotation about B−N or mesityl B−C_{ipso} bonds on the NMR time scale. The AA′BB′ pattern ascribed to the ethylene backbone protons is also consistent with the low symmetry of **3a**,**b**. NMR spectra of **4a**,**b**, on the other hand, are consistent with C_{2v} symmetry. The ortho proton resonances of the benzyl ligands in both **3a** and **4a** are shifted upfield (to 5.756 and 6.101 ppm, respectively, in C_6D_6), which suggests that the phenyl π-systems may be interacting with the titanium center.[33,34] (The *o*-Ph ^1H resonances of the benzyl ligands in **3a** and **4a** could be shifted upfield also as a consequence of the ring current of the mesityl rings flanking the coordination wedge.) Rotation of the *N*-dimesitylboryl units in **4a**,**b** is qualitatively slower than in **1**, presumably as a

$$(Ben)TiCl_2 + RMgCl \xrightarrow{CH_2Cl_2} (Ben)Ti(R)Cl \quad (4)$$

3a: R = CH_2Ph
3b: R = CH_2CMe_3

$$(Ben)TiCl_2 + 2RMgCl \xrightarrow{CH_2Cl_2} (Ben)TiR_2 \quad (5)$$

4a: R = CH_2Ph
4b: R = Me

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Table 1. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters

	(Ben)Ti(CH_2Ph)Cl	[(TwistBen)Zr]$_2$·3C_6H_6
empirical formula	$C_{43}H_{51}B_2N_2ClTi$	$C_{76}H_{92}B_4N_4Zr_2$·3C_6H_6
fw	700.86	1521.60
cryst color, habit	red, plate	pale yellow, parallelepiped
cryst dimens (mm)	0.25 × 0.12 × 0.50	0.32 × 0.38 × 0.21
cryst syst	triclinic	monoclinic
no. of rflns used for unit cell determn (2θ range (deg))	20 (15.0–30.0)	25 (15.0–23.0)
a (Å)	13.949(6)	30.775(2)
b (Å)	16.633(7)	11.935(1)
c (Å)	9.136(4)	27.435(3)
α (deg)	106.00(3)	
β (deg)	96.84(3)	125.34(3)
γ (deg)	88.38(3)	
V (Å^3)	2023(3)	8220(5)
space group	$P\bar{1}$	$C2/c$
Z	2	4
ϱ(calc) (g/cm^3)	1.150	1.229
collecn temp (°C)	−80 ± 1	−86 ± 1
F_{000}	744	6416
μ(Mo Kα) (cm^{-1})	3.04	2.94
scan mode	$\omega-2\theta$	ω
total no. of unique rflns	7132	7601
no. of observs with $I > 3.00\sigma(I)$	3589	4130
no. of variable params	460	470
R	0.079	0.076
R_w	0.086	0.069
goodness of fit indicator	2.48	1.62

consequence of both the increased steric demands of alkyl ligands in the coordination wedge and the less electrophilic nature of the metal in **4a** or **4b** and consequently reduced competition for the nitrogen's electron pairs.

The structure of **3a** was determined in an X-ray study (Table 1). A drawing can be found in Figure 2 and relevant distances and angles in Table 2. The Ben ligand nearly symmetrically chelates the titanium center (Ti–N distances 1.894(6) and 1.912(6) Å) to form a puckered five-membered ring with a "bite" angle (N–Ti–N) of 89.2(2)°. The Ti–N distances are comparable to those found in other four-coordinate amido complexes,[8,9,13,17,21] which are in the 1.882–1.940 Å range. The coordination geometry at both B and N is trigonal planar, and the dihedral angle between the planes containing B and N is small (e.g., the dihedral angle C(2)–N(1)–B(2)–C(21) is 13°), consistent with substantial B–N π-bonding. A significant degree of N–B π-bonding is also suggested by N–B distances of 1.419(9) and 1.43(1) Å. Note, however, that these N–B distances are longer than N–B distances (1.36–1.41 Å) generally found in structurally characterized monoborylamines and metalloborylamides,[20,21,23–25,29,30,35,36] perhaps as a consequence of titanium's competing with the boryl groups for the nitrogen lone pairs. Puckering of the ethylene backbone and maintenance of the N–B π-interactions causes the mesityl rings to be not symmetrically oriented directly above and below the remaining two coordination sites but rather "off-center".

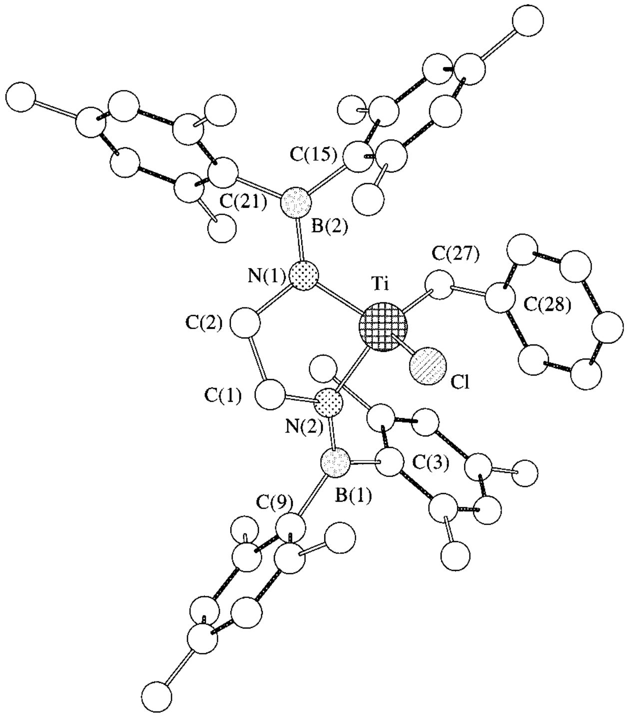

Figure 2. Chem 3D drawing of the molecular structure of **3a**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3a

	Distances		
Ti–N(1)	1.894(6)	Ti–N(2)	1.912(6)
Ti–C(27)	2.106(8)	Ti–C(28)	2.500(8)
Ti–Cl	2.325(3)	C(27)–C(28)	1.46(1)
N(1)–B(2)	1.43(1)	N(2)–B(1)	1.419(9)
	Angles		
N(1)–Ti–N(2)	89.2(2)	Ti–C(27)–C(28)	87.0(5)
C(27)–Ti–C(28)	35.8(3)	C(27)–Ti–Cl	125.5(2)
N(1)–Ti–C(27)	110.7(3)	N(2)–Ti–C(27)	113.9(3)
N(1)–Ti–Cl	110.3(2)	N(2)–Ti–Cl	100.9(2)
N(1)–C(2)–C(1)	109.2(6)	N(2)–C(1)–C(2)	107.8(6)
Ti–N(1)–B(2)	127.4(5)	Ti–N(2)–B(1)	137.6(5)
Ti–N(1)–C(2)	108.8(2)	Ti–N(2)–C(1)	100.2(4)
B(2)–N(1)–C(2)	122.3(6)	B(1)–N(2)–C(1)	121.0(6)
N(2)–B(1)–C(9)	121.0(7)	N(1)–B(2)–C(21)	118.7(7)
N(2)–B(1)–C(3)	117.7(6)	N(1)–B(2)–C(15)	118.4(7)
C(9)–B(1)–C(3)	121.3(6)	C(21)–B(2)–C(15)	122.9(7)

The chloride and benzyl ligands complete the pseudotetrahedral coordination geometry in **3a**. It is clear from the acute Ti–C(27)–C(28) angle (87.0(5)°) as well as the short Ti–C(28) distance (2.500(8) Å) that the π-system of the benzyl ligand is interacting in a symmetrical manner with the titanium center. For comparison, the most distorted benzyl ligand in Ti(CH_2Ph)$_4$ has a Ti–C_α–C_{ipso} angle of 88(2)° and a Ti–C_{ipso} distance of 2.61(3) Å.[37,38]

Close examination of proton NMR spectra of **3a** suggests that a second isomer is present in small amounts (<10%) in solution. Two sets of benzyl *o*-Ph resonances at δ 5.756 and 5.363 ppm and two sets of backbone resonances centered at δ 4.063 and 4.086 ppm are observed in C_6D_6 for the major and minor isomers, respectively. In view of the solid-state structure of **3a** we speculate that the minor isomer may be one in which

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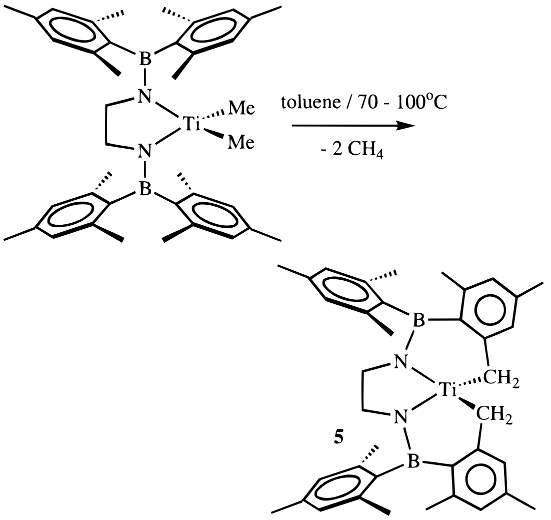
the benzyl group is rotated by 180°; i.e., the Ti−CH$_2$ bond is now in the "central" coordination position, and the phenyl ring is bound to the metal in an "outside" position. In this orientation the phenyl group of the benzyl ligand would interact to a greater degree sterically with the mesityl groups flanking the coordination wedge, and this isomer therefore should be significantly less favored than the one found in the solid state.

Thermolysis of (Ben)TiMe$_2$ (**4b**) in benzene follows first-order kinetics (k_{obs} = 1.8(2) × 10^{-4} s^{-1} at 79 °C) and yields deep red, C_2-symmetric (TwistBen)Ti (**5**) and methane (eq 6). We believe two pathways for this reaction to be most plausible. The first is a stepwise σ-bond metathesis[18,39−43] involving opposing *o*-Me C−H bonds and Ti−Me groups. The second is initial loss of methane via α-abstraction followed by 1,2-addition of a C−H bond in one ortho methyl group across the Ti=CH$_2$ bond; a second α-abstraction followed by C−H addition to the resulting Ti=C bond would yield **5**.[44,45] Thermolysis of (Ben)Ti(CD$_3$)$_2$ (**4b**-d_6) yields only CD$_3$H, according to ^{2}H NMR, consistent with the σ-bond metathesis pathway. (α-Abstraction requires that both CD$_4$ and CD$_2$CH$_2$ are formed.) A small inverse secondary isotope effect (k_H/k_D = 0.84(3)) is found at 79 °C.



(6)

(Ben)ZrMe$_2$ may be prepared from **2** and 2 equiv of methyllithium in toluene at −78 °C. However, it is much less stable thermally than (Ben)TiMe$_2$ and converts readily to the yellow dicyclometalated (TwistBen)Zr (**6**) and methane. Under conditions where (Ben)ZrMe$_2$ is synthesized, only mixtures of (Ben)ZrMe$_2$ and **6** can be obtained; significant conversion of (Ben)ZrMe$_2$ to **6** occurs even during crystallization of (Ben)ZrMe$_2$ at −40 °C. A rate constant could be obtained for conversion of (Ben)ZrMe$_2$ to **6** in mixtures of the two (k_{obs} = 8.4(2) × 10^{-4} s^{-1} at 43 °C). Derivatives that contain more sterically demanding alkyl derivatives are even less stable. For example, the reaction between (Ben)ZrCl$_2$(THF) and 2 equiv of LiCH$_2$SiMe$_3$ yields only **6** (62% yield) and tetramethylsilane (eq 7).

$$\mathrm{BenZrCl_2(THF) + 2LiCH_2SiMe_3 \xrightarrow[-2SiMe_4]{toluene} \mathbf{6}} \quad (7)$$

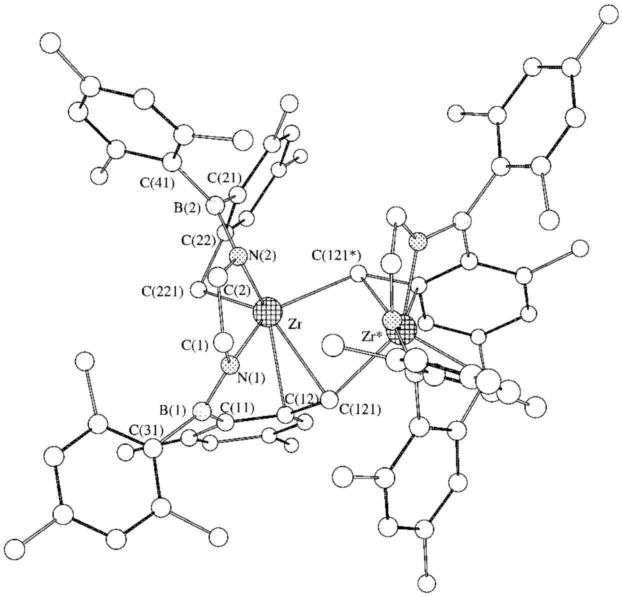


Figure 3. Chem 3D drawing of the molecular structure of 6 viewed almost down the crystallographic C_2 axis.

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

Distances			
Zr−N(1)	2.106(6)	Zr−N(2)	2.088(6)
Zr−Zr*	3.251(2)	Zr−C(121*)	2.449(8)
Zr−C(121)	2.464(8)	Zr−C(12)	2.549(8)
Zr−C(221)	2.252(8)	Zr−C(22)	2.703(8)
N(1)−B(1)	1.38(1)	N(2)−B(2)	1.43(1)
Angles			
N(1)−Zr−N(2)	73.3(2)	C(121)−Zr−C(121*)	82.8(2)
Zr−C(121)−C(12)	69.7(4)	Zr−C(221)−C(22)	90.6(5)
N(1)−Zr−C(221)	108.0(3)	N(2)−Zr−C(221)	96.1(3)
Zr−N(1)−B(1)	109.3(5)	Zr−N(2)−B(2)	107.4(5)
Zr−N(1)−C(1)	119.6(5)	Zr−N(2)−C(2)	123.0(5)
B(1)−N(1)−C(1)	128.8(7)	B(2)−N(2)−C(2)	122.9(7)
N(1)−B(1)−C(11)	111.4(7)	N(2)−B(2)−C(21)	115.0(7)
N(1)−B(1)−C(31)	124.8(8)	N(2)−B(2)−C(41)	123.1(8)
C(11)−B(1)−C(31)	123.8(7)	C(21)−B(2)−C(41)	121.9(8)

^{1}H and ^{13}C NMR spectroscopy demonstrate that the solution structures of **5** and **6** are significantly different. The titanium complex is C_2-symmetric, while the zirconium analog appears to lack any symmetry on the NMR time scale, even at 100 °C. Furthermore, the four Zr−CH$_2$ $^1J_{CH}$ coupling constants range from 112 to 145 Hz, suggesting there are significant differences between the bonding modes of each methylene.

An X-ray diffraction study shows that **6** is dimeric and possesses crystallographically imposed C_2 symmetry (Figure 3; Table 3). Two methylene groups nearly symmetrically bridge the two zirconium centers (Zr−C(121) = 2.464(8) Å, Zr−C(121*) = 2.449(8) Å), Zr···Zr = 3.251(2) Å). The ipso carbon from one mesityl group (e.g., C(12)) also strongly interacts with the zirconium center from which it originates (Zr−C(12) = 2.549(8) Å). These structural parameters should be compared with the nonbridging mesityl methylene group in which the

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Zr–C(221) distance is 2.252(8) Å. However, the Zr–C(22) distance of 2.703(8) Å and the Zr–C(221)–C(22) angle of 90.6(5)° demonstrate that the ipso carbon of even the nonbridging mesityl ring also weakly interacts with the zirconium center. The N(1)–Zr–N(2) angle (73.3(2)°) for the five-membered ring is more acute than that (89.2(2)°) found in the structure of **3a**. The contraction is due in part to the larger size of zirconium relative to titanium as well as perhaps to the decreased steric demands of the mesityl rings upon metalation. The Zr–N distances (2.088(6) and 2.106(6) Å) are comparable to those found in other four- and psuedo-four-coordinate zirconium–amido complexes.[3,5,8,9,12,16,18–20] Borylamide N–B π-interactions are maintained in the metalated structure according to N–B distances (1.38(1) and 1.43(1) Å) and the small dihedral angles C(2)–N(2)–B(2)–C(41) (9°) and C(1)–N(1)–B(1)–C(31) (3°).

The (Ben)MMe_2 complexes react with the strong Lewis acid $B(C_6F_5)_3$ in dichloromethane to give what we presume on the basis of analogous studies in metallocene chemistry[46–49] to be the "zwitterionic" complexes [(Ben)MMe][$MeB(C_6F_5)_3$], in which a methyl group is partially abstracted by the triarylborane (eq 8). The

$$\underset{M\,=\,Ti,\ Zr}{(Ben)MMe_2} + B(C_6F_5)_3 \xrightarrow{CD_2Cl_2} \underset{\substack{\mathbf{7}:\ M\,=\,Ti \\ \mathbf{8}:\ M\,=\,Zr}}{[(Ben)MMe][MeB(C_6F_5)_3]} \quad (8)$$

symmetry of **7** and **8**, according to NMR spectra, is the same as the symmetry of **3a**,**b**. All of these data, along with the demonstrated strong B–N π-bonding, would seem to eliminate the possibility that $B(C_6F_5)_3$ binds to a lone pair on nitrogen. We have also eliminated the possibility that (Ben)MMeCl complexes form (along with free $[MeB(C_6F_5)_3]^-$ ion) by chloride abstraction from dichloromethane by showing that characteristic resonances for (Ben)MMeCl can be observed by NMR in the presence of $[MeB(C_6F_5)_3]^-$ (as a tetraalkylammonium salt). Therefore, it would appear that the interaction between "$[MeB(C_6F_5)_3]^-$" and the metal is relatively strong. Unfortunately, we have not been able to isolate either of these adducts and so have not been able to confirm their identity via X-ray studies. Strong binding of $[MeB(C_6F_5)_3]^-$ to the metal would help explain why dichloromethane solutions of **7** and **8** do not polymerize ethylene readily at 25 °C and 1–2 atm.

Discussion and Conclusion

On the basis of the results presented here, we believe that the concept of using N–B π-bonding to enforce a desirable orientation of the mesityl groups in complexes that contain the Ben ligand is a valid one and that Ben complexes have some characteristics that are reminiscent of metallocenes. The N–B π-interaction also is likely to be responsible for what appears to be a relatively electron-deficient nature of the metal in Ben complexes. The short $M-C_{ipso}$ contacts and acute $M-C_\alpha-C_{ipso}$ angles seen in the solid-state structures of **3a** and **6** are of the magnitude commonly seen in actinide[50] and *cationic* group 4 complexes.[33,34,51] The electrophilic nature of the metal is also evidenced by facile conversion of (Ben)MMe_2 complexes to (Twist-Ben)M complexes, one that is consistent with attack by a coordinatively unsaturated, electrophilic metal center on a CH bond with concerted abstraction of a proton by the leaving methyl group.[39,40] The fact that **7** and **8** do not react with ethylene is also consistent with the relatively high electrophilicity of the metal center and strong binding of the $[MeB(C_6F_5)_3]^-$ ion to the metal.[46]

A disadvantage of the present Ben ligand, however, is the lack of sufficient steric protection to prevent dimerization via bridging methylenes (to give **6**) or to expel the $[MeB(C_6F_5)_3]$ anion in **7** and **8** in the presence of ethylene. Some flexibility in the ethylene bridge between the two amido nitrogens may exacerbate to some degree what we perceive to be insufficient "lateral" steric protection. Nevertheless, the similarity between the basic coordination geometry of the Ti and Zr Ben complexes and typical metallocene coordination geometries, in particular the presence of three coordination sites in a plane perpendicular to the MN_2 plane, is unmistakable. Future efforts will be aimed at a further exploration of these similarities and differences and the construction of a more crowded Ben ligand that would not only resist metalation but would provide a more crowded environment in which a boron-based anion would be bound more weakly than observed here.

Experimental Section

General Procedures. All experiments were performed under nitrogen in a Vacuum Atmospheres drybox or under argon using standard Schlenk techniques. All solvents were purified by standard techniques, while deuterated NMR solvents were dried and stored over 4-Å molecular sieves before use.

Magnesium bromide etherate, butyllithium, methyllithium, methyllithium-d_3, methylmagnesium chloride, and benzylmagnesium chloride were used as received. Ethylenediamine containing 0.6% water was stored over 4-Å molecular sieves before use. $MCl_4(THF)_2$ (M = Ti, Zr),[52] Mes_2BF,[23] $B(C_6F_5)_3$,[53] and neopentylmagnesium chloride in ether[54] were prepared according to literature proceedures.

^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra usually were recorded at 300, 75.4, 282, and 96.2 MHz, respectively. Proton spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. Carbon spectra were referenced internally relative to the ^{13}C signal of the NMR solvent relative to tetramethylsilane. Fluorine and boron spectra were referenced externally to neat $CFCl_3$ and BF_3 etherate, respectively. All *J* values are given in Hz. IR spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratories.

$Mes_2BNHCH_2CH_2NHBMes_2$ (H_2(Ben)). Butyllithium (52 mL, 131 mmol, 2.5 M in hexane) was added to a solution of ethylenediamine (3.74 g, 62.1 mmol) in THF (500 mL) at –40

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°C. A white flocculent precipitate formed almost immediately, and the color of the solution changed to dark purple. After 5 h the purple had faded and the slurry was chilled to −40 °C. Solid dimesitylboron fluoride (35.0 g, 131 mmol) was added to the chilled solution over 10 min. The flocculent white precipitate dissolved almost immediately to yield a light yellow solution with suspended LiF. After the solution was stirred overnight, the solvents were removed in vacuo and the residue was extracted with warm dichloromethane (800 mL). The extract was filtered through Celite, concentrated, and cooled to −40 °C. Fluffy white needles were collected by filtration, washed liberally with pentane, and dried in vacuo for 12 h to afford 30.50 g (84% yield) of the product as a dichloromethane solvate (1 part dichloromethane to 3 parts H_2(Ben)). An analytical sample of H_2(Ben) (as a solvate containing 0.5 equiv of benzene) was obtained by recrystallization from warm benzene: ^{1}H NMR ($CDCl_3$) δ 6.756 (s, 4, *m*-H), 6.735 (s, 4, *m*-H), 4.478 (br s, 2, NH), 3.092 (pseudo t, 4, NCH_2), 2.267 (s, 6, *p*-Me), 2.236 (s, 6, *p*-Me), 2.205 (s, 12, *o*-Me), 2.109 (s, 12, *o*-Me); ^{13}C{^{1}H} NMR δ 140.8, 140.1 (C_o), 137.3, 136.9 (C_p), 128.3, 127.6 (C_m), 46.4 (NCH$_2$), 22.8, 22.1 (*o-Me*), 21.1, 21.0 (*p-Me*); ^{11}B NMR δ 45.3 (width 1170 Hz); IR (Nujol/KBr) 3367, 3356 ν(NH) cm^{-1}. Anal. Calcd for $C_{41}H_{53}N_2B_2$: C, 82.70; H, 8.96; N, 4.71. Found: C, 83.03; H, 9.02; N, 4.70.

(Ben)Mg(THF)$_2$. Butyllithium (22.5 mL, 56.2 mmol, 2.5 M in hexane) was added to a solution of H_2(Ben) (8.93 g, 16.1 mmol) and $MgBr_2$ (ether) (4.75 g, 18.4 mmol) in THF (250 mL) at −40 °C. The solution was warmed to room temperature and stirred overnight. Dichloromethane (100 mL) was added, and the mixture was stirred for 6 h, after which the solvents were removed in vacuo to give a yellow oil. The oil was extracted with CH_2Cl_2/pentane (150 mL, 50/50). The extract was filtered and concentrated to an oil. When the residue was stirred with a mixture of pentane (100 mL) and THF (10 mL), a white solid formed and was collected by filtration. The white solid was redissolved in dichloromethane (100 mL), and the mixture was filtered and concentrated again to an oil. The oil was triturated with pentane (100 mL) to give white crystals. The mixture was chilled to −40 °C for 2 h, and the crystals were collected by filtration, washed liberally with pentane, and thoroughly dried in vacuo to afford 9.51 g (77%) of the product as a 2/3 pentane clathrate which contained ~5% H_2(Ben). Repeated recrystallization failed to remove the H_2(Ben) impurity: ^{1}H NMR (pyridine-d_5) δ 6.897 (s, 4, *m*-H), 6.551 (s, 4, *m*-H), 3.782 (s, 4, NCH_2), 3.647 (m, 8, THF), 2.592 (s, 12, *o*-Me), 2.375 (s, 12, *o*-Me), 2.262 (s, 6, *p*-Me), 2.123 (s, 6, *p*-Me), 1.609 (m, 8, THF); ^{13}C{^{1}H} NMR δ 141.0, 140.5 (C_o), 134.6 (C_p), 128.3, 127.9 (C_m), 67.9 (THF), 54.8 (NCH$_2$), 34.2 (CH$_2$), 23.6, 23.4 (*o-Me*), 22.5 (CH$_2$), 21.2, 20.9 (*p-Me*), 14.2 (THF).

(Ben)TiCl$_2$ (1). $TiCl_4(THF)_2$ (3.40 g, 10.2 mmol) was added slowly to a solution of (Ben)Mg(THF)$_2$(pentane)$_{2/3}$ (7.84 g, 10.2 mmol) in dichloromethane (100 mL) at −40 °C. The solution quickly turned orange. A copious amount of white precipitate had formed after 1 h. After 3 h the solution was filtered and the extracts were concentrated to dryness. The residue was crystallized from dichloromethane/ether at −40 °C to yield 5.52 g (81%) of fluffy orange solid. An analytical sample was obtained by double recrystallization from dichloromethane/pentane: ^{1}H NMR ($CDCl_3$) δ 6.802 (s, 4, *m*-H), 6.745 (s, 4, *m*-H), 4.409 (s, 4, NCH_2), 2.402 (s, 12, *o*-Me), 2.333 (s, 12, *o*-Me), 2.251 (s, 6, *p*-Me), 2.193 (s, 6, *p*-Me); ^{13}C{^{1}H} NMR δ 145.7 (C_o), 140.9 (C_o), 140.4 (C_p), 138.3 (C_p), 128.9, 128.3 (C_m), 59.5 (CH$_2$), 23.6, 22.8 (*o-Me*), 21.3, 21.0 (*p-Me*). Anal. Calcd for $C_{38}H_{48}N_2B_2Cl_2Ti$: C, 67.80; H, 7.18; N, 4.16. Found: C, 67.55; H, 7.13; N, 3.95.

(Ben)ZrCl$_2$(THF) (2). $ZrCl_4(THF)_2$ (3.25 g, 8.61 mmol) was added slowly to a stirred solution of (Ben)Mg(THF)$_2$(pentane)$_{0.22}$ (6.05 g, 8.61 mmol) in dichloromethane (100 mL) at −40 °C. The solution was warmed to room temperature. After it stood overnight, the solution was filtered and the extracts were concentrated to dryness in vacuo. The residue was extracted with toluene (75 mL) and the extract concentrated to ~20 mL. Layering with pentane followed by cooling the solution overnight afforded white crystals, which were collected by filtration, washed with pentane, and dried in vacuo to give 4.84 g (71%) of the product. An analytical sample of (Ben)ZrCl$_2$(THF)·CH_2Cl_2 was obtained by recrystallization from dichloromethane/pentane: ^{1}H NMR (C_6D_6) δ 6.816 (s, 4, *m*-H), 6.618 (s, 4, *m*-H), 4.129 (s, 4, NCH_2), 3.197 (m, 4, THF), 2.694 (s, 12, *o*-Me), 2.513 (s, 12, *o*-Me) 2.189 (s, 6, *p*-Me), 1.945 (s, 6, *p*-Me), 1.058 (m, 4, THF); ^{13}C{^{1}H} NMR δ 147.2, 140.8, 140.0, 137.3 (C_o and C_p), 129.6, 128.6 (C_m), 73.4 (THF), 55.8 (NCH$_2$), 25.4, 25.3, 23.5, 21.1 (Ar−*Me*). Anal. Calcd for $C_{43}H_{58}N_2B_2Cl_4OZr$: C, 59.12; H, 6.69; N, 3.21. Found: C, 58.84; H, 6.83; N, 2.92.

(Ben)Ti(CH$_2$Ph)Cl (3a). Benzylmagnesium chloride (0.256 mL, 0.446 mmol, 1.74 M in THF) was added to a solution of (Ben)TiCl$_2$ (0.300 g, 0.446 mmol) in dichloromethane (10 mL) at −40 °C. The solution immediately turned deep red, and a fine precipitate formed. The solution was kept at −40 °C for 3 h and was filtered through Celite. The solvents were removed from the filtrate in vacuo, and the residue was recrystallized from a mixture of toluene and pentane to afford 0.144 g (32%) of red plates in three crops. ^{1}H NMR(C_6D_6): δ 6.915−6.70 (m, Ar), major isomer: 5.756 (dd, 2, *o*-Ph), 4.160 (AA′BB′, 2, NCH_2), 3.965 (AA′BB′, 2, NCH_2), 3.208 (s, 2, CH_2Ph), 2.545 (br s, 6, Ar−*Me*), 2.511 (s, 6, Ar−*Me*), 2.483 (br s, 6, Ar−*Me*), 2.320 (s, 6, Ar−*Me*), 2.172 (s, 6, Ar−*Me*), 2.122 (s, 6, Ar−*Me*); minor isomer, δ 5.363 (br d, 2, *o*-Ph), 4.086 (br m, 4, NCH_2), 3.279 (s, 2, CH_2Ph), 2.584 (s, Ar−*Me*), 2.496 (s, Ar−*Me*), 2.390 (s, Ar−*Me*); corresponding integrals and remaining Ar−*Me* resonances are obscured by the methyl resonances of the major isomer. ^{13}C NMR (major isomer): δ 144.2, 142.5, 140.8, 139.9, 139.6, 138.3, 137.8, 130.7, 129.6, 129.5, 129.3, 128.9, 128.5, 126.8 (C_{aryl}), 100.9 ($^1J_{CH}$ = 134, CH$_2$Ph), 54.5 ($^1J_{CH}$ = 142, NCH$_2$), 24.1, 23.3, 23.1, 21.2, 21.1 (Ar−*Me*). Anal. Calcd for $C_{45}H_{55}N_2B_2ClTi$: C, 74.15; H, 7.61; N, 3.84. Found: C, 73.91; H, 7.83; N, 3.64.

(Ben)Ti(CH$_2$CMe$_3$)Cl (3b). Neopentylmagnesium chloride (0.495 mL, 1.34 mmol, 2.7 M in ether) was added to a solution of (Ben)TiCl$_2$ (0.750 g, 1.11 mmol) in dichloromethane (20 mL) at −40 °C. The mixture was warmed to room temperature, allowed to stand overnight at room temperature, and filtered through Celite. The solvents were removed from the filtrate in vacuo, and the residue was recrystallized from pentane at −40 °C to afford 0.586 g (74%) of orange crystals in two crops. An analytical sample was obtained by double-recrystallization from dichloromethane/pentane: ^{1}H NMR (C_6D_6) δ 6.834 (s, 2, *m*-H), 6.808 (s, 2, *m*-H), 6.756 (s, 2, *m*-H), 6.741 (s, 2, *m*-H), 3.963 (AA′BB′, 2, NCH_2), 3.674 (AA′BB′, 2, NCH_2), 2.628 (s, 6, Ar−*Me*), 2.574 (s, 6, Ar−*Me*), 2.487 (s, 6, Ar−*Me*), 2.432 (s, 2, CH_2CMe$_3$), 2.357 (s, 6, Ar−*Me*), 2.169 (s, 6, Ar−*Me*), 2.116 (s, 6, Ar−*Me*), 0.586 (s, 9, CH$_2$CMe_3); ^{13}C{^{1}H} NMR δ 143.24, 141.84, 140.67, 139.89, 139.22, 137.74, 129.63, 129.30, 128.82, 128.56 (C_{aryl}), 53.79 (NCH$_2$), 39.08 (Ti−CH$_2$), 31.65 (CMe_3), 31.52 (CMe$_3$), 24.08, 23.36, 23.17, 23.04, 21.12 (Ar−*Me*). Anal. Calcd for $C_{43}H_{59}N_2B_2ClTi$: C, 72.85; H, 8.39; N, 3.95. Found: C, 72.31; H, 8.55; N, 3.81.

(Ben)Ti(CH$_2$Ph)$_2$ (4a). Benzylmagnesium chloride (1.11 mL, 1.93 mmol, 1.74 M in THF) was added to a solution of (Ben)TiCl$_2$ (0.620 g, 0.921 mmol) in dichloromethane (20 mL) at −40 °C. The solution immediately turned deep red, and a fine precipitate formed. After the solution stood at −40 °C for 1.5 h, 1,4-dioxane (0.100 g, 1.12 mmol) was added and the solution was filtered through Celite. The solvents were removed in vacuo, and the residue was recrystallized from pentane at −40 °C to afford 0.382 g (53%) of red crystals: ^{1}H NMR (C_6D_6) δ 7.003 (t, 4, *m*-Ph), 6.836 (t, 2, *p*-Ph), 6.839 (s, 4, *m*-Mes), 6.788 (s, 4, *m*-Mes), 6.101 (d, 4, *o*-Ph), 3.776 (s, 4, NCH_2), 2.790 (s, 4, CH_2Ph), 2.516 (s, 12, *o*-Me), 2.249 (s, 12, *o*-Me), 2.194 (s, 6, *p*-Me), 2.184 (s, 6, *p*-Me); ^{13}C{^{1}H} NMR δ 146.2 (Ph_i), 142.4, 140.6 (Mes_o), 138.9, 137.5 (Mes_p), 129.3 (Ph_m), 128.74, 128.65 (C_m), 127.0 (Ph_o), 124.0 (Ph_m), 99.7 (CH$_2$Ph), 52.1 (NCH$_2$), 23.9, 23.3 (*o-Me*), 21.13, 21.07 (*p-Me*). Anal.

Calcd for $C_{52}H_{62}N_2B_2Ti$: C, 79.61; H, 7.96; N, 3.57. Found: C, 79.30; H, 8.14; N, 3.38.

(Ben)TiMe$_2$ (4b). Methylmagnesium chloride (1.50 mL, 4.51 mmol, 3.0 M in THF) was added to a solution of (Ben)TiCl$_2$ (1.38 g, 2.05 mmol) in dichloromethane (75 mL) at −40 °C. The solution immediately turned yellow, and a fine precipitate formed. After the mixture stood at −40 °C for 1.5 h, 1,4-dioxane (0.400 g, 4.51 mmol) was added and the solution was filtered through Celite. The solvents were removed in vacuo, and the residue was recrystallized from dichloromethane/ether at −40 °C to afford 0.876 g (67%) of fluffy yellow needles in two crops. An analytical sample was obtained by recrystallization from dichloromethane/pentane: ^1H NMR (C_6D_6) δ 6.822 (s, 4, *m*-H), 6.744 (s, 4, *m*-H), 3.860 (s, 4, NCH_2), 2.527 (s, 12, *o*-Me), 2.427 (s, 12, *o*-Me), 2.193 (s, 6, *p*-Me), 2.084 (s, 6, *p*-Me), 0.858 (s, 6, Ti−CH_3); ^{13}C NMR δ 144.2, 140.3 (C_o), 139.5, 137.5 (C_p), 137.0, 136.2 (C_i), 129.3, 128.6 (C_m), 67.3 ($^1J_{CH}$ = 121.5, Ti-CH_3), 53.8 (NCH_2), 23.8, 22.9 (*o-Me*), 21.2 (*p-Me*). Anal. Calcd for $C_{40}H_{54}N_2B_2Ti$: C, 75.98; H, 8.60; N, 4.43. Found: C, 75.71; H, 8.55; N, 4.16.

(Ben)Ti(CD$_3$)$_2$ (**4b**-d_6) was prepared analogously, employing 2 equiv of LiCD$_3$·LiI in toluene: ^2H NMR (C_6H_6) δ 0.738.

(Ben)ZrMe$_2$. Methyllithium (1.10 mL, 1.64 mmol, 1.5 M in ether) was added to a solution of (Ben)ZrCl$_2$(THF) (0.707 g, 0.821 mmol) in toluene at −78 °C. After 1 h, the solution became cloudy as it was warmed to −40 °C. The solution was further warmed to 0 °C, and the volatile components were removed in vacuo. The oily, yellow residue was extracted with pentane, and the extract was concentrated and cooled to −40 °C to give 0.212 g (56%) of white crystals after 1 day. Subsequent crops consisted largely of (TwistBen)Zr. Recrystallization and elemental analysis of (Ben)ZrMe$_2$ were not attempted due to its thermal instability. ^1H NMR (C_6D_6): δ 6.844 (s, 4, *m*-H), 6.703 (s, 4, *m*-H), 3.911 (s, 4, NCH_2), 2.461 (s, 12, *o*-Me), 2.407 (s, 12, *o*-Me), 2.213 (s, 6, *p*-Me), 2.020 (s, 6, *p*-Me), −0.015 (s, 6, Zr−CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ 146.48, 141.15, 140.00, 136.88, 129.78, 127.72 ($C_{aromatic}$), 54.51 (NCH_2), 47.57 (Zr−*Me*), 23.90, 22.34, 21.19, 20.95 (Ar−*Me*).

(TwistBen)Ti (5). (Ben)TiMe$_2$ (0.200 g, 0.316 mmol) in toluene (4 mL) was heated to 70 °C in a Teflon-sealed tube for 36 h. The solution was filtered, and the volatile components were removed in vacuo. The resulting red solid was triturated with dichloromethane to give 0.148 g (79%) of the product. An analytical sample was crystallized from toluene at −40 °C: ^1H NMR (C_6D_6) δ 6.951 (br s, 2, *m*-H), 6.702 (br s, 2, *m*-H), 6.628 (s, 2, *m*-H), 6.568 (s, 2, *m*-H), 4.344 (AA′BB′, 2, NCH_2), 4.175 (AA′BB′, 2, NCH_2), 2.811 (d, $^1J_{HH}$ = 5.7, 2, Ti−CH_2), 2.530 (s, 6, Ar−Me), 2.257 (s, 6, Ar−Me), 2.195 (s, 6, Ar−Me), 2.136 (s, 6, Ar−Me), 2.071 (s, 6, Ar−Me), 2.247 (d, $^1J_{HH}$ = 5.7, 2, Ti−CH_2); $^{13}C\{^1H\}$ NMR 149.18, 148.34, 140.94, 140.78 (br), 137.80, 131.82, 128.60 (br), 128.32 (C_{aryl}), 75.97 (Ti−CH_2), 60.00 (NCH_2), 23.15, 22.45 (br), 21.18, 21.11 (Ar−*Me*). Anal. Calcd for $C_{38}H_{46}N_2B_2Ti$: C, 76.03; H, 7.72; N, 4.67. Found: C, 76.17; H, 8.04; N, 4.31.

(TwistBen)Zr (6). (a) From (Ben)ZrMe$_2$. A sample of (Ben)ZrMe$_2$ was allowed to stand in benzene-d_6 overnight. **6** was formed quantitatively, according to ^1H NMR, along with methane.

(b) From Reaction of (Ben)ZrCl$_2$(THF) with LiCH$_2$SiMe$_3$. A solution of LiCH$_2$SiMe$_3$ (0.056 g, 0.608 mmol) in toluene (2 mL) at −40 °C was added to a solution of (Ben)ZrCl$_2$(THF) (0.240 g, 0.304 mmol) in toluene (10 mL). After 15 min the cloudy, light yellow solution solution was filtered through Celite and the solvents were removed in vacuo to give a yellow oil. The oil was extracted with pentane (10 mL) and immediately filtered through Celite. Yellow needles formed from the filtrate upon standing. The mother liquor was removed after 1 day, and the needles were washed with pentane. Concentrating and cooling the mother liquor to −40 °C afforded a second crop; yield 0.122 g (62%). An analytical sample was obtained by recrystallization from benzene/pentane: ^1H NMR (CD_2Cl_2) δ 6.982 (s, 1, *m*-H), 6.807 (s, 1, *m*-H), 6.771 (s, 1, *m*-H), 6.712 (s, 2, *m*-H), 6.683 (s, 1, *m*-H), 6.251 (s, 1, *m*-H), 6.154 (s, 1, *m*-H), 4.288 (m, 1, NCH_2), 3.941 (m, 1, NCH_2), 3.657 (m, 1, NCH_2), 3.451 (m, 1, NCH_2), 2.527 (d, $^2J_{HH}$ = 9.2, 1, Zr−CH_2), 2.481 (d, $^2J_{HH}$ = 7.0, 1, Zr−CH_2), 2.410 (s, 3, Ar−*Me*), 2.353 (s, 3, Ar−*Me*), 2.242 (s, 3, Ar−*Me*), 2.226 (s, 3, Ar−*Me*), 2.149 (s, 3, Ar−*Me*), 2.101 (s, 3, Ar−*Me*), 2.083 (s, 3, Ar−*Me*), 1.900 (s, 3, Ar−*Me*), 1.881 (s, 3, Ar−*Me*), 1.866 (s, 3, Ar−*Me*), 1.041 (d, $^2J_{HH}$ = 9.2, 1, Zr−CH_2), −0.121 (d, $^2J_{HH}$ = 7.0, 1, Zr−CH_2); ^{13}C NMR δ 151.96, 145.50, 145.23, 143.25, 142.73, 142.06, 140.58, 140.31, 139.53, 137.26, 136.85, 130.71, 130.42, 128.23, 127.77, 127.65, 127.24 (C_{aryl}), 71.78 ($^1J_{CH}$ = 145 and 133, Zr-CH_2), 58.92 ($^1J_{CH}$ = 135 and 112, Zr−CH_2), 57.61 ($^1J_{CH}$ = 134, NCH_2), 52.54 ($^1J_{CH}$ = 136, NCH_2), 23.67, 23.52, 23.03, 22.56, 22.44, 22.36, 21.48, 21.25, 21.19, 21.16 (Ar−*Me*). Anal. Calcd for $C_{38}H_{46}N_2B_2Zr$: C, 70.92; H, 7.20; N, 4.35. Found: C, 71.18; H, 7.57; N, 3.99.

(Ben)TiMe[MeB(C$_6$F$_5$)$_3$] (7) was generated in solution by dissolving (Ben)TiMe$_2$ (0.060 g, 0.094 mmol) and B(C$_6$F$_5$)$_3$ (0.060 g, 0.117 mmol) in CD$_2$Cl$_2$. The orange solution was analyzed by ^1H NMR. No solid product could be recovered from these solutions: ^1H NMR (CD_2Cl_2) δ 7.286 (s, 2, *m*-H), 7.254 (s, 2, *m*-H), 6.940 (s, 4, *m*-H), 4.507 (AA′BB′, 4, NCH_2), 2.471 (s, 6, Ar−Me), 2.443 (s, 6, Ar−Me), 2.308 (s, 6, Ar−Me), 2.275 (br, 12, Ar−Me), 2.229 (s, 6, Ar−Me), 0.710 (s, 3, Ti−CH_3), 0.497 (br, 3, Ti−CH_3−B(C$_6$F$_5$)$_3$); $^{13}C\{^1H\}$ NMR δ 156.6, 148.8 (C_o or C_p), 148.8 (m, $^1J_{CF}$ = 234, *o*-C$_6$F$_5$), 142.4, 141.5, 140.8 (C_o and C_p), 137.9 (m, $^1J_{CF}$ = 241, *p*-C$_6$F$_5$), 137.3 (C_m), 136.8 (m, $^1J_{CF}$ = 241, *m*-C$_6$F$_5$), 136.7 (C_m), 129.3 (C_m), 72.0 (Ti−CH_3), 64.6 (NCH_2), 26.2, 23.1, 22.9, 22.0, 21.3 (Ar−*Me* and *Me*−B(C$_6$F$_5$)); ^{19}F NMR δ −131.21 (d, $^3J_{FF}$ = 19.8, *o*-C$_6$F$_5$), −163.37 (t, $^3J_{FF}$ = 17.8, *p*-C$_6$F$_5$), −165.94 (m, $^3J_{FF}$(av) = 22.5, *m*-C$_6$F$_5$).

(Ben)ZrMe[MeB(C$_6$F$_5$)$_3$] (8) was generated by dissolving (Ben)ZrMe$_2$ (0.066 g, 0.098 mmol) and B(C$_6$F$_5$)$_3$ (0.050 g, 0.098 mmol) in CD$_2$Cl$_2$: ^1H NMR (CD_2Cl_2) δ 7.281 (s, 4, *m*-H), 6.903 (s, 4, *m*-H), 4.095 (AA′BB′, 2, NCH_2), 3.968 (AA′BB′, 2, NCH_2), 2.535 (s, 6, Ar−Me), 2.310 (s, 6, Ar−Me), 2.288 (s, 12, Ar−Me), 2.274 (s, 6, Ar−Me), 2.234 (s, 6, Ar−Me), 0.493 (br, 3, Zr−*Me*−B(C$_6$F$_5$)$_3$), 0.096 (s, 6, Zr−CH_3); partial $^{13}C\{^1H\}$ NMR δ 153.76, 148.10 (m, $^1J_{CF}$ = 236, *o*-C$_6$F$_5$), 146.88, 143.18, 141.38 (br), 140.70 (br), 139.68, 137.40 (m, $^1J_{CF}$ = 245, *p*-C$_6$F$_5$), 136.24 (m, $^1J_{CF}$ = 246, *m*-C$_6$F$_5$), 135.08, 132.84, 128.53, 131.58; ^{19}F NMR δ −131.63 (d, $^3J_{FF}$ = 18.6, *o*-C$_6$F$_5$), −163.80 (t, $^3J_{FF}$ = 21.2, *p*-C$_6$F$_5$), −166.37 (m, $^3J_{FF}$(av) = 21.3, *m*-C$_6$F$_5$).

Kinetic Measurements of Intramolecular C−H Activation. Teflon-sealed NMR tubes containing 30−90 mg of the dimethyl derivatives in 0.60 mL of toluene-d_8 (for **4b** and **4b**-d_6) or benzene-d_6 (for mixtures of (Ben)ZrMe$_2$ and **6**) were placed in a heated NMR probe. The probe temperature was calibrated before and after the measurements using ethylene glycol (for **4b** and **4b**-d_6) or methanol (for (Ben)ZrMe$_2$) and remained constant within ±0.5 °C. The reactions were monitored by ^1H NMR spectroscopy by integrating the N−CH_2 resonances of **4b** and **4b**-d_6 or the Zr−*Me* resonance in (Ben)ZrMe$_2$ relative to an internal benzene standard. In all cases the kinetics followed first-order behavior over 3 half-lives and the rate constants obtained were insensitive to the initial concentration of metal complex.

X-ray Structure of (Ben)Ti(CH$_2$Ph)Cl. Suitable deep red crystals of **3a** were grown from a concentrated benzene/pentane solution at room temperature. A crystal having approximate dimensions of 0.25 × 0.12 × 0.50 mm was mounted on a glass fiber. Data were collected at −80 ± 1 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range 15.00 < 2θ < 30.00°, corresponded to a triclinic cell with parameters a = 13.949(6) Å, b = 16.633(7) Å, c = 9.136(4) Å, α = 106.00(3)°, β = 96.84(3)°, γ = 88.38(3)°, V = 2023(3) Å^3, Z = 2, fw = 700.86, and ρ(calc) = 1.150 g/cm^3. On the basis of packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$.

A total of 7458 reflections were collected in the range $2\theta < 50.3°$, with 7132 being unique. An empirical absorption correction was applied, using the program DIFABS,[55] which resulted in transmission factors ranging from 0.84 to 1.18. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3589 observed reflections ($I > 3.00\sigma(I)$) and 460 variable parameters and converged with $R = 0.079$ and $R_w = 0.086$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.47 and -0.68 e/Å^3, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

X-ray Structure of [(TwistBen)Zr]$_2$·3C$_6$H$_6$. Suitable light yellow crystals of **6** containing 3 equiv of benzene were grown by allowing (Ben)ZrMe$_2$ to decompose in benzene solution at room temperature. A crystal having approximate dimensions of 0.32 × 0.38 × 0.21 mm was mounted on a glass fiber. Data were collected at -86 ± 1 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $15.00 < 2\theta < 23.00°$, corresponded to a monoclinic cell with parameters $a = 30.775(2)$ Å, $b = 11.935(1)$ Å, $c = 27.435(3)$ Å, $\beta = 96.84(3)°$, $V = 8220(5)$ Å^3, $Z = 4$, fw 1521.60, and ρ(calc) = 1.229 g/cm^3. On the basis of the systematic absences of hkl ($h + k \neq 2n$) and $h0l$ ($h, l \neq 2n$) as well as the successful solution and refinement of the structure, the space group was determined to be $C2/c$.

A total of 7758 reflections were collected in the range $2\theta < 49.9°$, with 7601 being unique. An empirical absorption correction was applied, using the program DIFABS, which resulted in transmission factors ranging from 0.80 to 1.28. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient 0.57539×10^{-7}). The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4130 observed reflections ($I > 3.00\sigma(I)$) and 470 variable parameters and converged with $R = 0.076$ and $R_w = 0.069$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.71 and -0.88 e/Å^3, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

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Supporting Information Available: Tables giving experimental details of the X-ray data collection and refinement, final positional parameters, and final thermal parameters and labeled ORTEP diagrams for (Ben)Ti(CH$_2$Ph)Cl and [(TwistBen)Zr]$_2$·3C$_6$H$_6$ (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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