Synthesis, Fluxionality, and Propene Insertion Reactions of Zirconium Boryldiene Complexes with Sterically Undemanding Cp Ligands

Marco M. Corradi, Gerardo Jiménez Pindado, Mark J. Sarsfield, Mark Thornton-Pett, and Manfred Bochmann*

School of Chemistry, University of Leeds, Leeds, U.K. LS2 9JT

Received October 26, 1999

The reduction of $Cp^RZrCl_3(dme)$ (Cp^R = Cp (**a**), $C_5H_4SiMe_3$ (**b**), C_5H_4Me (**c**), Ind (**d**)) with sodium amalgam in the presence of isoprene, followed by the addition of allylmagnesium chloride, gives the diene complexes $Cp^RZr(\eta^3\text{-allyl})(\eta^4\text{-isoprene})$ (**2a**−**d**). The preparations are conveniently carried out as one-pot reactions. The reaction of **2a**−**d** with $B(C_6F_5)_3$ in toluene solution at −78 °C proceeds quantitatively to give the thermally unstable zwitterionic complexes $Cp^RZr(\eta^3\text{-allyl})\{\eta^1{:}\eta^3\text{-}CH_2CMeCHCH_2B(C_6F_5)_3\}$ (**3a**−**d**), which on warming decompose under C−H activation and propene elimination to give $Cp^RZr(C_6F_5)\{\eta^4\text{-}CH_2\text{-}CMeCHCHB(C_6F_5)_2\}$ (**4a**−**d**). The complexes are stabilized by the coordination of one *o*-F atom of a boryl−C_6F_5 ring to the metal center. Compounds **4** are fluxional. The rotation of the Zr−C_6F_5 ligand is influenced by the steric demand of the Cp ligands ($\Delta G^‡$ = 43−49 kJ mol^{-1}), while there is little variation in the rotational barriers of the B−C_6F_5 substituents ($\Delta G^‡$ = ca. 47 kJ mol^{-1}). Recrystallization of **4a** from diethyl ether affords the 16-electron complex **4a**·OEt_2, in which fluorine coordination is replaced by an ether ligand. The structure of this complex has been determined; unlike its C_5Me_5 and $C_5H_3(SiMe_3)_2$ congeners, it shows the boryldiene moiety to occupy a prone (endo) conformation. Propene inserts into the CH_2 terminus of the boryldiene ligand under ambient conditions to give the metallacycles $Cp^RZr(C_6F_5)\{\eta^1{:}\eta^3\text{-}CH_2CH(Me)-CH_2C(Me)CHCHB(C_6F_5)_2\}$ (**5a**−**d**), with complete regioselectivity and very high stereoselectivity. The insertion process is reversible; propene extrusion occurs via β-alkyl elimination from the major chair conformation isomer.

We have recently reported the reaction of diene half-sandwich complexes of group 4 metals with $B(C_6F_5)_3$ to give zwitterionic bis(allylic) complexes of type **A**.[1,2] These electron-deficient compounds may be regarded as stabilized analogues of the 14-electron $[CpZr(allyl)_2]^+$ cation[3] and show good activity for the polymerization of ethene to high-molecular-weight polymers.[1a,b] With bulky cyclopentadienyl ligands (e.g., Cp″ = 1,3-$C_5H_3(SiMe_3)_2$) and methyl substituents on the dienyl moiety, the zwitterions **A** are readily isolable as crystalline solids; they are, however, sufficiently reactive to undergo well-defined decomposition reactions to boryldiene complexes **B** and, subsequently, to borole complexes **C** (Scheme 1).[4] We now report the reactions of $B(C_6F_5)_3$ with the analogous diene complexes $Cp^RZr(\eta^3\text{-allyl})(\eta^4\text{-diene})$,[5,6] which have sterically less demanding cyclopentadienyl ligands (Cp^R = C_5H_5 (Cp), $C_5H_4SiMe_3$ (Cp′), C_5H_4Me (Cp^{Me}), indenyl (Ind)).

Results and Discussion

Reduction of the trichloride complexes $Cp^RZrCl_3(dme)$ (**1**; Cp^R = Cp (**a**), Cp′ (**b**), Cp^{Me} (**c**), Ind (**d**)) with sodium amalgam in the presence of isoprene, followed by the addition of allylmagnesium chloride, gives the diene complexes $Cp^RZr(\eta^3\text{-allyl})(\eta^4\text{-isoprene})$ (**2a**−**d**) as dark red to maroon crystalline solids (**2a,b,d**) or a maroon oil (**2c**) in good yields. The preparations are conveniently carried out as one-pot reactions. The reactions of **2a**−**d** with $B(C_6F_5)_3$ in toluene solution at −78 °C proceed quantitatively to give the thermally unstable zwitterionic complexes $Cp^RZr(\eta^3\text{-allyl})\{\eta^1{:}\eta^3\text{-}CH_2CMeCHCH_2B(C_6F_5)_3\}$ (**3a**−**d**), which were characterized by ^1H and ^{13}C NMR spectroscopy (Scheme 2).[7,8] In contrast to the Cp″ analogue reported earlier,[1a] the new compounds **2a**−**d** are thermally very sensitive; they were generated

(1) (a) Jiménez Pindado, G.; Thornton-Pett, M.; Bouwkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358. (b) Jiménez Pindado, G.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115. (c) Jiménez Pindado, G.; Thornton-Pett, M.; Hursthouse, M. B.; Coles, S. J. *J. Chem. Soc., Dalton Trans.* **1999**, 1663.

(2) Bochmann, M. *Top. Catal.* **1999**, *7*, 9.

(3) For related hafnium systems see: Hessen, B.; van der Heijden, H. *J. Organomet. Chem.* **1997**, *534*, 237.

(4) Jiménez Pindado, G.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816.

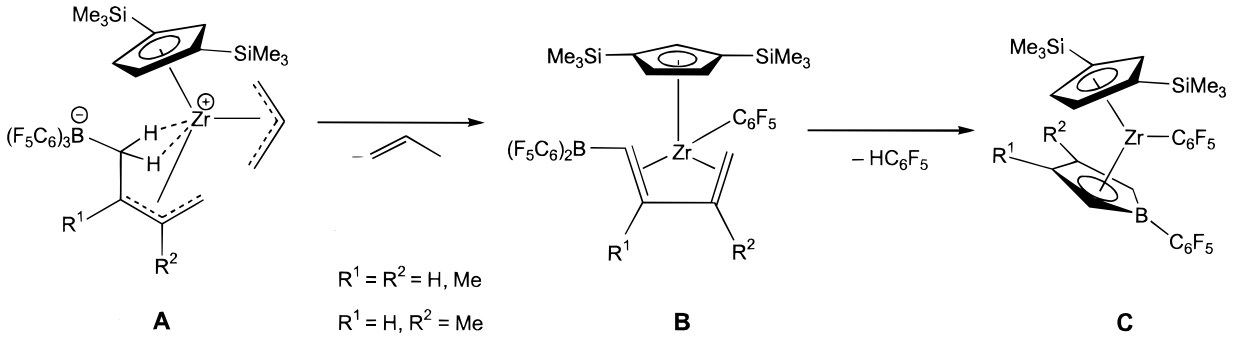
(5) Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Chem. Ber.* **1985**, *118*, 1383.

(6) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

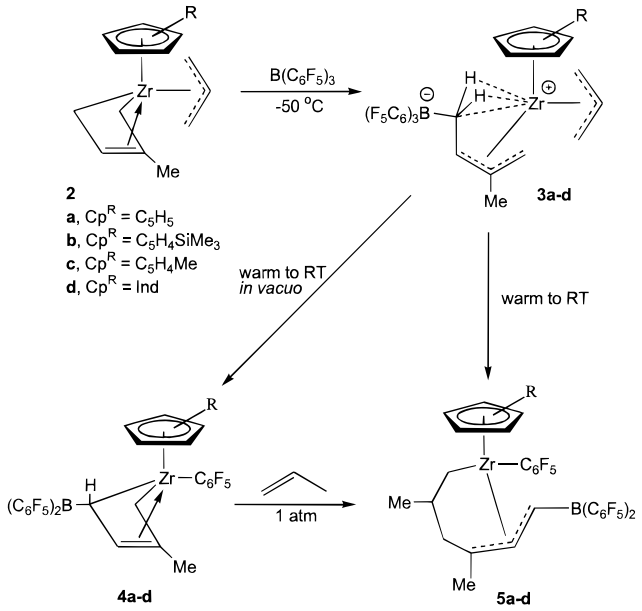
(7) For related complexes see: (a) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem.* **1995**, *107*, 1867; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (b) Temme, B.; Karl, J.; Erker, G. *Eur. J. Chem.* **1996**, *2*, 919. (c) Karl, J.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **1997**, *535*, 59. (d) Karl, J.; Erker, G. *Chem. Ber.* **1997**, *130*, 1261. (e) Karl, J.; Erker, G.; Fröhlich, R.; Zippel, F.; Bickelhaupt, F.; Schreuder Goedheijt, M.; Akkerman, O. S.; Binger, P.; Stannek, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2771. (f) Karl, J.; Dahlmann, M.; Erker, G.; Bergander, K. *J. Am. Chem. Soc.* **1998**, *120*, 5643.

10.1021/om990859t CCC: $19.00
Publication on Web 02/24/2000

Scheme 1



Scheme 2

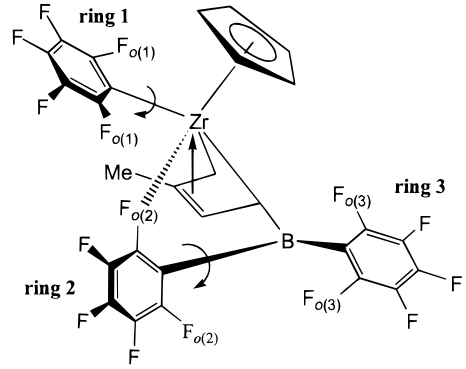


and handled in solution at temperatures below −50 °C but could not be isolated. The ^{1}H and ^{13}C NMR spectroscopic data of all new compounds are collected in Table 1.

When they are warmed to room temperature, **3a**−**d** undergo a clean decomposition reaction, consisting of activation of a C−H bond of the B−CH_2 moiety and elimination of a molecule of propene, with the simultaneous migration of one of the B−C_6F_5 groups from boron to the metal center, to give the complexes **4a**−**d** as red to maroon crystalline solids (Scheme 2).

These complexes are stable up to ca. 70 °C in solution. We have reported earlier that boryldiene complexes with Cp″ ligands undergo a rearrangement to give borole complexes of type **C** (Scheme 1). However, this reaction appears to be restricted to bulky cyclopentadienyl compounds;[9] although the decomposition reactions of **4a**,**b** in toluene solution were followed by NMR spectroscopy under a number of reaction conditions, there was no evidence for detectable amounts of borole products.

Complexes **4a**−**d** are highly fluxional in solution. Two of the three C_6F_5 rings (structure **D**, rings 1 and 2) show



hindered rotation, and therefore the appearance of up to 13 ^{19}F NMR resonances could be expected. At room temperature, the ^{19}F NMR spectrum of **4a** exhibits 7 distinct ^{19}F signals, whereas at −75 °C, this number has increased to 11, 2 of which overlap and represent two F atoms.

The nature of the fluxionality exhibited by **4a** is conveniently elucidated by variable-temperature ^{19}F NMR spectroscopy. At −75 °C in toluene-d_8, the *o*-F atoms of the Zr−C_6F_5 ligand (ring 1, *o*(1)) are observed at relatively high frequencies, δ −108.4 and −122.9. The *o*(2) ^{19}F resonances of ring 2 are also observed at this temperature as two magnetically distinct environments at δ −131.6 and −171.0. The high-field shift of δ −171.0 is consistent with the coordination of one *o*-F atom of ring 2 to the metal center; rotation of this ring is therefore highly hindered. Ring 3, by contrast, still exchanges rapidly at −75 °C, as shown by the single *o*(3)-F resonance at δ −130.2. Cooling to −90 °C is required to slow the rotation of ring 3 about the B−C_6F_5 bond sufficiently to give two extremely broad, overlapping *o*(3) ^{19}F resonances at δ −130.2 and −131.7.

The observation of hindered rotation of the Zr−C_6F_5 unit (ring 1) may be explained as the result of steric interaction between C_6F_5 and the Cp ligand. *o*-F coordination, analogous to that of Zr···$F_{o(2)}$, seems unlikely due to geometry constraints at the metal center, and

(8) For other examples of zwitterionic complexes of early transition metals containing borato ligands see: (a) Braunschweig, H.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1613. (b) Bochmann, M.; Lancaster, S. L.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081. (c) Bohra, R.; Hitchcock, P. B.; Lappert, M. F.; Au-Leung, S. F.; Leung, W. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2999. (d) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. (e) Song, X.; Bochmann, M. *J. Organomet. Chem.* **1997**, *545*−*546*, 597. (f) Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132. (g) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829. (h) Ahlers, W.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **1998**, 889. (i) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13, (j) Piers, W. E.; Sun, Y.; Lee, L. W. M. *Top. Catal.* **1999**, *7*, 133, and references therein.

(9) C_5Me_5 derivatives are converted to borole complexes in a reaction similar to the Cp″ analogues: Hessen, B. Personal communication.

Table 1. ^{1}H and ^{13}C NMR Spectroscopic Data for New Zirconium Half-Sandwich Complexes

	^{1}H NMR		^{13}C NMR	
complex	δ	assgnt	δ	assgnt
Cp′Zr(η-C_3H_5)(η^4-C_4H_5Me-2)	−0.64 (d, 1H, J = 7.4 Hz)	=CH_2 *anti*	0.4	$SiMe_3$
(2b) (C_6D_6)	−0.57 (t, 1H, J = 8.8 Hz)	=CH_2 *anti*	26.4	diene Me
	0.26 (s, 9H)	$SiMe_3$	46.1, 50.6	Zr−CH_2
	1.28 (d, 1H, J = 14.7 Hz)	anti CH of C_3H_5	57.0, 59.3	CH_2 of C_3H_5
	1.59 (d, 1H, J = 14.6 Hz)	*anti* CH of C_3H_5	110.1	diene CH
	1.60 (m, 1H)	*syn* CH of C_3H_5	111.9	$C^{2,5}$ of C_5H_4
	1.89 (s, 3H)	diene Me	116.6	$C^{3,4}$ of C_5H_4
	2.01 (m, 3H)	*syn* CH of C_3H_5 & 2 =CH_2 *syn*	117.4 123.5	C^1 of C_5H_4 diene CMe
	5.14 (t, 1H, J = 9.9 Hz)	diene CH	125.3	CH of C_3H_5
	5.99 (m, 3H)	CH of C_3H_5 & 2,5 Cp H		
	6.50 (m, 2H)	3,4 Cp H		
Cp^{Me}Zr(η-C_3H_5)(η^4-C_4H_5Me-2)	−0.67 (d, 1H, J = 7.8 Hz)	=CH_2 *anti*	15.6	Cp Me
(2c) (C_6D_6)	−0.61 (d, 1H, J = 8.8 Hz)	=CH_2 *anti*	26.1	diene Me
	1.18 (d, 1H, J = 14.7 Hz)	anti CH of C_3H_5	46.0, 50.2	Zr−CH_2
	1.46 (d, 1H, J = 14.7 Hz)	*anti* CH of C_3H_5	57.2, 59.4	CH_2 of C_3H_5
	1.56 (d, 1H, J = 9.1 Hz)	*syn* CH of C_3H_5	108.0	$C^{2,5}$ of C_5H_4
	1.82 (s, 3H)	diene Me	108.7	C^1 of C_5H_4
	1.86 (m, 2H)	=CH_2 *syn*	109.8	$C^{3,4}$ of C_5H_4
	1.96 (s, 3H)	Cp Me	110.7	diene CH
	2.00 (m, 1H)	*syn* CH of C_3H_5	123.8	diene CMe
	5.07 (t, 1H, J = 9.8 Hz)	diene CH	125.5	CH of C_3H_5
	5.88 (t, 2H, J = 2.5 Hz)	2,5 Cp H		
	5.91 (tt, 1H, $J_{c,a}$ = 14.7, $J_{c,s}$ = 9.1 Hz)	CH of C_3H_5		
	6.04 (m, 2H)	3,4 Cp H		
(Ind)Zr(η-C_3H_5)(η^4-C_4H_5Me-2)	−0.42 (d, 1H, J = 7.4 Hz)	=CH_2 *anti*	26.1	diene Me
(2d) (C_6D_6)	−0.37 (d, 1H, J = 7.4 Hz)	=CH_2 *anti*	45.4, 49.2	Zr−CH_2
	−0.03 (d, 1H, J = 14.7 Hz)	*anti* CH of C_3H_5	62.5, 64.2	CH_2 of C_3H_5
	0.39 (d, 1H, J = 14.6 Hz)	*anti* CH of C_3H_5	96.4, 96.7	$C^{2,4}$ of C_5H_3
	1.66 (d, 1H, J = 9.3 Hz)	*syn* CH of C_3H_5	109.7	diene CH
	1.77 (m, 2H)	=CH_2 *syn*	115.8	C^3 of C_5H_3
	1.79 (s, 3H)	diene Me	123.2, 123.3	$C^{6,9}$ of C_6 ring
	2.13 (d, 1H, J = 9.3 Hz)	*syn* CH of C_3H_5	123.6, 123.7	$C^{1,5}$ of C_6 ring
	4.98 (t, 1H, J = 9.7 Hz)	diene CH	125.3, 125.4	$C^{7,8}$ of C_6 ring
	5.90 (tt, 1H, $J_{c,a}$ = 14.6, $J_{c,s}$ = 9.3 Hz)	CH of C_3H_5	126.2	CH of C_3H_5
	6.67 (m, 2H), 6.78 (m, 1H)	Cp H		
	6.87 (m, 2H)	C_6 ring		
	7.30 (m, 2H)	C_6 ring		
CpZr(η-C_3H_5){η^3-CH_2CMeCH-$CH_2B(C_6F_5)_3$} (**3a**) (C_7D_8, −50 °C)	−1.63 (d, 1H, J = 13.8 Hz)	B−CH_2 *anti*	25.2	diene Me
	−1.33 (s, 1H)	B−CH_2 *syn*	28.2 (br)	B−CH_2
	0.79 (m, 1H)	Zr−CH_2 *anti*	59.7	Zr−CH_2
	0.95 (m, 2H)	*anti* & *syn* CH_2 of C_3H_5	64.0, 70.5	CH_2 of C_3H_5
	1.08 (s, 3H)	diene Me	103.7	diene CH
	2.30 (d, 1H, J = 6.3 Hz)	Zr−CH_2 *syn*	112.2	Cp
	2.45 (m, 2H)	*anti* & *syn* CH_2 of C_3H_5	135.4	CH of C_3H_5
	4.62 (d, 1H, J = 14.4 Hz)	diene CH		
	5.56 (s, 5H)	Cp		
	5.58 (m, 1H)	CH of C_3H_5		
Cp′Zr(η-C_3H_5){η^3-CH_2CMeCH-$CH_2B(C_6F_5)_3$} (**3b**) (C_7D_8, −50 °C)	−1.51 (d, 1H, J = 14.3 Hz)	B−CH_2 *anti*	−0.94	$SiMe_3$
	−1.35 (s, 1H)	B−CH_2 *syn*	24.1	diene Me
	−0.07 (s, 9H)	$SiMe_3$	27.7 (br)	B−CH_2
	0.90 (m, 3H)	Zr−CH_2 *anti* and *anti* & *syn* CH_2 of C_3H_5	60.1 64.0, 71.7	Zr−CH_2 CH_2 of C_3H_5
	0.99 (s, 3H)	diene Me	104.4	diene CH
	2.36 (d, 1H, J = 6.9 Hz)	Zr−CH_2 *syn*	112.9, 116.6, 120.0	Cp
	2.55 (m, 2H)	*anti* & *syn* CH_2 of C_3H_5	121.7	
	4.62 (d, 1H, J = 14.7 Hz)	diene CH	135.5	CH of C_3H_5
	5.42, 5.80, 6.04, 6.33 (m, 1H each)	Cp H		
	5.70 (m, 1H)	CH of C_3H_5		
Cp^{Me}Zr(η-C_3H_5){η^3-CH_2CMeCH-$CH_2B(C_6F_5)_3$} (**3c**) (C_7D_8, −50 °C)	−1.55 (d, 1H, J = 14.7 Hz)	B−CH_2 *anti*	14.9	Cp Me
	−1.20 (s, 1H)	B−CH_2 *syn*	25.2	diene Me
	0.81 (m, 3H)	Zr−CH_2 *anti* and *anti* & *syn* CH_2 of C_3H_5	26.5 (br) 59.5	B−CH_2 Zr−CH_2
	0.99 (s, 3H)	diene Me	64.3, 71.2	CH_2 of C_3H_5
	1.45 (s, 3H)	Cp Me	103.8	diene CH
	2.10 (d, 1H, J = 6.6 Hz)	Zr−CH_2 *syn*	111.2, 112.0,	Cp
	2.43 (d, 1H, J = 15.0 Hz)	*anti* CH_2 of C_3H_5	112.7, 112.9	
	2.60 (d, 1H, J = 8.1 Hz)	*syn* CH_2 of C_3H_5	135.6	CH of C_3H_5
	4.63 (d, 1H, J = 14.7 Hz)	diene CH		
	5.35 (m, 2H), 5.56 (m, 2H)	Cp H		
	5.69 (m, 1H)	CH of C_3H_5		

Table 1. (Continued)

	^{1}H NMR		^{13}C NMR	
comp lex	δ	assgnt	δ	assgnt
(Ind)Zr(η-C_3H_5){η^3-CH_2CMeCH-$CH_2B(C_6F_5)_3$} (**3d**) (C_7D_8, −50 °C)	−1.14 (d, 1H, J = 14.7 Hz)	B−CH_2 *anti*	22.5 (br)	B−CH_2
	−0.93 (s, 1H)	B−CH_2 *syn*	25.1	diene Me
	−0.13 (d, 1H, J = 13.2 Hz)	*anti* CH_2 of C_3H_5	58.0	Zr−CH_2
	0.12 (d, 1H, J = 15.0 Hz)	*anti* CH_2 of C_3H_5	70.5, 78.8	CH_2 of C_3H_5
	0.92 (m, 1H)	Zr−CH_2 *anti*	97.0, 99.2, 117.6	C of C_5 ring
	1.01 (s, 3H)	diene Me	108.8	diene *C*Me
	1.30 (m, 1H)	*syn* CH_2 of C_3H_5	124.7, 124.9, 125.4,	C of C_6 ring
	2.09 (d, 1H, J = 6.6 Hz)	Zr−CH_2 *syn*	125.8, 126.0, 126.9	
	2.80 (d, 1H, J = 8.1 Hz)	*syn* CH_2 of C_3H_5	137.7	diene *C*H
	4.65 (d, 1H, J = 14.7 Hz)	diene CH		
	5.70 (m, 1H)	CH of C_3H_5		
	5.82, 6.14, 6.27 (s, 1H each)	H of C_5 ring		
	6.61 (m, 3H)	H of C_6 ring		
	7.42 (d, 1H, J = 8.1 Hz)	H of C_6 ring		
$CpZr(C_6F_5)${η^4-CH_2CMeCH-$CH_2B(C_6F_5)_2$} (**4a**) (C_6D_6)	0.06 (d, 1H, J = 9.7 Hz)	Zr−CH_2 *anti*	26.4	diene Me
	1.37 (s, 3H)	diene Me	72.8	Zr−CH_2
	2.13 (d, 1H, J = 10.8 Hz)	Zr−CH_2 *syn*	98.4	B−CH
	2.90 (d, 1H, J = 12.0 Hz)	B−CH	114.0	Cp
	5.89 (d, 1H, J = 11.9 Hz)	diene CH	115.2	diene *C*Me
	6.09 (s, 5H)	Cp	121.6	diene *C*H
Cp′$Zr(C_6F_5)${η^4-CH_2CMeCH-$CH_2B(C_6F_5)_2$} (**4b**) (C_6D_6)	−0.10 (s, 9H)	$SiMe_3$	−2.1	$SiMe_3$
	0.28 (d, 1H, J = 9.4 Hz)	Zr−CH_2 *anti*	26.9	diene Me
	1.36 (s, 3H)	diene Me	71.3	Zr−CH_2
	2.13 (d, 1H, J = 9.0 Hz)	Zr−CH_2 *syn*	97.1	B−CH
	3.03 (d, 1H, J = 12.0 Hz)	B−CH	114.3, 116.3,	Cp
	5.65 (m, 1H)	Cp H	118.6, 121.8	
	5.89 (d, 1H, J = 12.3 Hz)	diene CH	120.2	diene *C*H
	6.43, 6.55, 7.23 (m, 1H each)	Cp H		
$Cp^{Me}Zr(C_6F_5)${η^4-CH_2CMeCH-$CH_2B(C_6F_5)_2$} (**4c**) (C_6D_6)	0.06 (d, 1H, J = 10.5 Hz)	Zr−CH_2 *anti*	14.0	Cp Me
	1.35 (s, 3H)	diene Me	26.5	diene Me
	1.56 (s, 3H)	Cp Me	73.2	Zr−CH_2
	2.12 (d, 1H, J = 9.6 Hz)	Zr−CH_2 *syn*	97.7	B−CH
	2.96 (d, 1H, J = 11.8 Hz)	B−CH	112.3, 112.5,	Cp
	5.84 (m, 3H)	diene CH & 2 Cp-H	114.4, 115.2	
	6.04, 6.07, 6.25 (m, 1H each)	Cp H	120.8	diene *C*H
(Ind)Zr(C_6F_5){η^4-CH_2CMeCH-$CH_2B(C_6F_5)_2$} (**4d**) (C_6D_6)	−0.62 (d, 1H, J = 9.3 Hz)	Zr−CH_2 *anti*	26.6	diene Me
	1.12 (s, 3H)	diene Me	76.8	Zr−CH_2
	1.43 (d, 1H, J = 9.2 Hz)	Zr−CH_2 *syn*	94.1	Zr−CH
	3.23 (d, 1H, J = 12.0 Hz)	Zr−CH	97.2, 105.2	C_5 ring
	5.53 (d, 1H, J = 11.7 Hz)	diene CH	115.6, 118.8	C_5−C_6 bridge
	5.98 (m, 1H), 6.20 (m, 1H)	C_5 ring	120.9	diene *C*H
	6.41 (t, 1H, J = 7.2 Hz)	C_6 ring	121.8	C_5 ring
	6.59 (t, 1H, J = 7.2 Hz)	C_6 ring	124.8, 124.9	C_6 ring
	6.88 (d, 1H, J = 8.1 Hz)	C_6 ring	126.8, 128.5	C_6 ring
	7.07 (m, 1H)	C_5 ring		
	7.43 (d, 1H, 8.1)	C_6 ring		

no evidence for such an interaction has been found in the crystallographically characterized 1,3-$C_5H_3(SiMe_3)_2$ and C_5Me_5 analogues.[1a,b] Further information regarding the dynamic processes was obtained through a line-shape analysis study. Warming a solution of **4a** in toluene-d_8 from −75 to +60 °C results in the broadening, coalescence, and finally sharpening of both the *o*(1) and *o*(2) ^{19}F resonances. Thus, the two *o*(1) ^{19}F signals at δ −108.4 and −122.9 coalesce at −25 °C, and further warming results in the formation of a single, sharp resonance signal at δ −117.7. A similar, albeit slower, process is observed for the *o*(2) resonances, which coalesce at higher temperature (+10 °C) and at 60 °C give a broad ^{19}F signal at δ −148.1. This signal sharpens on warming above 60 °C, although a large amount of decomposition is also observed.

Compounds **4b**−**d** exhibit behavior identical with that of **4a**. The ^{19}F NMR chemical shifts for all four complexes at both high and low temperatures are almost identical (Table 2).

Rate constants for the fluxional processes in compounds **4a**−**d** were measured by full line-shape treatment over the temperature range −75 to +60 °C. The resulting thermodynamic parameters are shown in Table 3.

The activation barriers in **4a**−**d** for the rotation of the B−C_6F_5 bonds, as derived from analysis of the coalescence of the *o*(2) ^{19}F resonance signals, are quite similar to one another, with $\Delta G^{\ddagger}$ values of ca. 46 kJ mol^{-1}, and a corresponding similarity in the coalescence temperatures, T_c (Table 3). From the *o*-fluoride interchange in the 18-electron bis-Cp system Cp_2Zr{η^3-CH_2-$CHCHCH_2B(C_6F_5)_3$}, Erker et al.[10] have estimated the strength of the Zr−F interaction to be in the region of 35 kJ mol^{-1}. The higher interchange barrier found here for **4** suggests rather stronger Zr−F coordination, in agreement with the greater electron deficiency of these 16-electron complexes.

The rotational barriers of the Zr−C_6F_5 bonds vary to a much greater extent. Given that the hindered rotation about the Zr−C_6F_5 axis arises through steric interaction between the cyclopentadienyl ring and the C_6F_5 moiety,

(10) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.

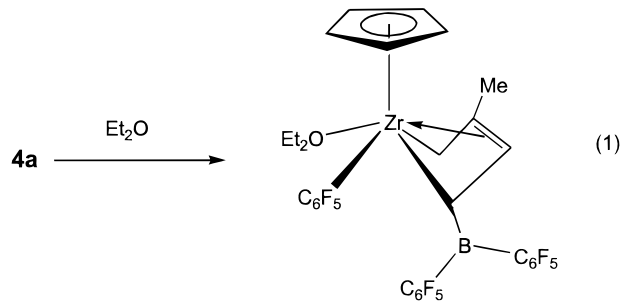
Table 2. ^{19}F NMR Spectroscopic Data for Zirconium Boryldiene Complexes at −75 and 60 °C (C_7D_8, 282.2 MHz)

	o(1)		*o*(2)		*o*(3)		*m*(1)		*m*(2)		*m*(3)		*p*(1)		*p*(2)		*p*(3)	
compd	−75	60	−75	60	−75	60	−75	60	−75	60	−75	60	−75	60	−75	60	−75	60
4a	−108.4	−117.7	−131.6	−148.1	−130.2	−130.8	−156.0	−159.5	−160.9	−161.7	−160.9	−161.7	−149.6	−151.4	−153.0	−153.6	−151.2	−153.1
	−122.9		−171.0				−160.2											
4b	−107.0	−117.3	−131.1	−147.5	−130.1	−130.3	−155.7	−159.2	−161.0	−161.9	−161.0	−161.6	−149.2	−151.2	−153.0	−153.8	−150.5	−152.7
	−123.5		−169.8				−160.1											
4c	−108.4	−118.3	−131.5	−147.1	−130.9	−130.6	−156.2	−159.7	−160.9	−161.9	−160.9	−161.7	−149.2	−151.4	−153.1	−153.8	−151.0	−153.1
	−123.1		−169.8				−159.9											
4d	−107.0	−118.2	−131.2	−146.3	−130.7	−130.1	−155.9	−159.6	−160.7	−161.8	−160.7	−161.8	−147.7	−150.6	−153.4	−153.0	−151.3	−154.0
	−123.1		−172.2				−159.8											

a higher activation barrier to rotation is observed for complexes with more sterically demanding cyclopentadienyl rings. Thus, for the least hindered compound **4a** the barrier to interconversion is $\Delta G^{\ddagger}(248\ \mathrm{K}) = 43$ kJ mol^{-1}, whereas compound **4b**, with arguably the most bulky ligand of the series (Cp′), has $\Delta G^{\ddagger}(273\ \mathrm{K}) = 49$ kJ mol^{-1}.

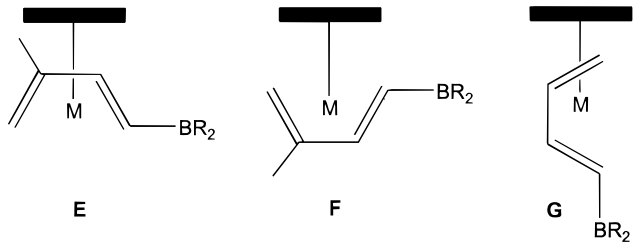
We found earlier that the Cp″ derivative Cp″Zr(C_6F_5){η^4-$CH_2CMeCHCHB(C_6F_5)_2$} exists as a mixture of two conformational isomers, resulting from prone (endo) and supine (exo) orientation of the diene ligand with respect to the cyclopentadienyl ring.[1b] The activation barrier for the prone/supine interchange has been calculated as $\Delta G^{\ddagger}(233\ \mathrm{K}) = 47$ kJ mol^{-1}. Analysis of the ^{19}F NMR spectra of the Cp′ complex **4b** affords evidence that this compound also exists as a mixture of two such isomers, with a coalescence temperature similar to that of the Cp″ derivative, although in this instance the relative amount of the second isomer is small (1:50).

Recrystallization of **4a** from diethyl ether afforded crystals of CpZr(C_6F_5){η^4-$CH_2CMeCHCHB(C_6F_5)_2$}-(OEt_2) (**4a**·OEt_2) (eq 1).



(1)

The structure was solved by X-ray diffraction (Figure 1). In contrast to the analogous Cp″ and C_5Me_5 complexes, which do not bind ether, the less hindered structure of **4a** allows the entry of a diethyl ether ligand into the coordination sphere of zirconium, to give a 16-electron complex with a distorted-octahedral environment. In consequence, there is no coordination to an *o*-F atom of one of the C_6F_5 substituents, as shown by the long Zr···*o*-F distances (Zr···F(7) = 3.700 Å, Zr···F(11) = 3.213 Å). The Zr−O bond of 2.3699(13) Å is significantly longer than that in the related cationic hafnium complex [Cp″Hf(η^4-$C_4H_4Me_2$-2,3)(OEt_2)]$^+$ (2.148(2) Å).[1c] Unlike Cp″Zr(C_6F_5){η^4-$CH_2CMeCHCHB(C_6F_5)_2$}, the boryldiene unit in **4a**·OEt_2 adopts a prone (endo) orientation (**E**). The diene conformations are most



probably a consequence of the steric requirements of the cyclopentadienyl ligands; in previous crystal structures of compounds of type **4** the supine conformation (**F**, for Cp″)[1c] and a diene orientation roughly perpendicular to the cyclopentadienyl ligand (**G**, for C_5Me_5)[1a] had been established.

Table 3. Thermodynamic Data for Zirconium Boryldiene Complexes

	T_c (°C)		$\Delta G^{\ddagger}$ at T_c (kJ mol^{-1})		$\Delta H^{\ddagger}$ (kJ mol^{-1})		$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	
compd	*o*(1)	*o*(2)	*o*(1)	*o*(2)	*o*(1)	*o*(2)	*o*(1)	*o*(2)
4a	−25	10	43	47	48	53	21	21
4b	0	10	49	47	49	58	2	39
4c	−15	12	45	45	46	57	5	42
4d	−2	5	48	46	44	55	−12	32

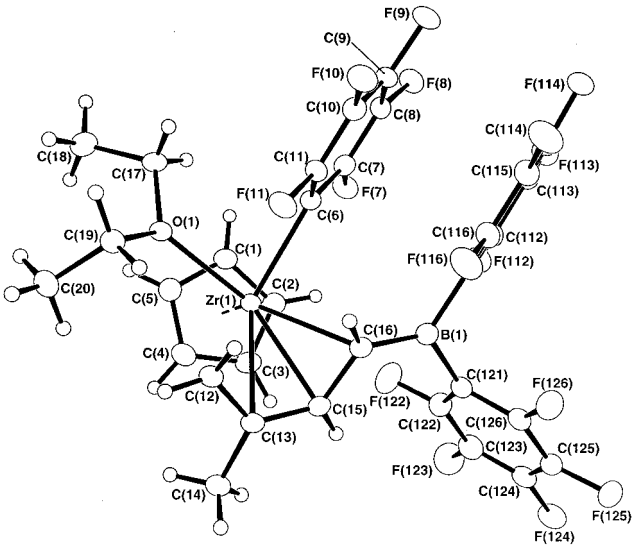
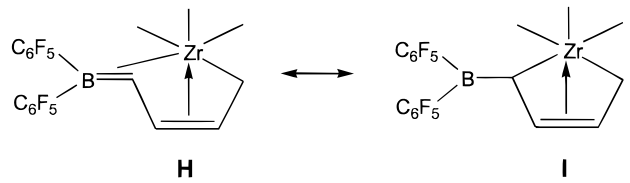


Figure 1. Molecular structure of $CpZr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}(OEt_2)$ (**4a**·OEt_2), showing the atomic numbering scheme. Ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Zr−C(6) = 2.379(2), Zr−O(1) = 2.3699(13), Zr−C(12) = 2.344(2), Zr−C(13) = 2.507(2), Zr−C(15) = 2.466(2), Zr−C(16) = 2.425(2), C(12)−C(13) = 1.421(3), C(13)−C(15) = 1.387(3), C(15)−C(16) = 1.441(3), C(16)−B(1) = 1.483(3), B(1)−C(111) = 1.591(3), B(1)−C(121) = 1.602(3); O(1)−Zr−C(6) = 78.78(5), O(1)−Zr−C(12) = 81.05(5), C(12)−Zr−C(6) = 123.84(7), C(12)−Zr−C(16) = 78.53(6), Zr−C(6)−C(7) = 131.36(14), Zr−C(6)−C(11) = 115.79(13), C(12)−C(13)−C(15) = 122.3(2), C(13)−C(15)−C(16) = 127.2(2), C(15)−C(16)−B(1) = 123.3(2), C(16)−B(1)−C(111) = 122.9(2), C(16)−B(1)−C(121) = 122.4(2).

Yamamoto et al.[11] pointed out that in the titanium complexes Cp*TiCl(η^4-diene) with a supine conformation the TiC_4 moieties are best described as σ^2,π-metallacyclopentenes, while complexes with a prone conformation have almost pure Ti(II) π-diene character. In contrast, the bond length distribution within the boryldiene ligand of the prone complex **4a**·OEt_2 is very similar to that found in supine zirconium and hafnium compounds, e.g. $Cp''Zr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$, and forms a σ^2,π-metallacyclopentene.

The Zr−C_6F_5 and one of the B−C_6F_5 rings are parallel to each other, in π-stacking fashion. The B−C(16) bond of 1.483(3) Å is significantly shorter than the B−C_6F_5 bond distances of 1.591(3) and 1.602(3) Å and is short also compared to other B−C(sp^2) distances such as in $\{C_5H_4\text{−}B(C_6F_5)_2\}TiCl_3$ (1.549(5) Å).[12] As indicated previously,[1a] this shortening may be explained by the contribution of a zwitterionic resonance structure with a partial B═C double bond (**H**) to the bonding of the metallacyclopentene unit (**I**).



H **I**

Propene Insertion Reactions. The reaction of **2a**−**d** with $B(C_6F_5)_3$ to give **4a**−**d** generates 1 equiv of propene as the byproduct. If the reaction proceeds in vacuo, this propene is removed as it is liberated, and complexes **4a**−**d** are isolated in high yields. On the other hand, if the propene is not removed, **4a**−**d** are converted slowly into new products, arising from the insertion of propene into the least hindered CH_2 terminus of the boryldiene ligand, to afford the metallacyclic complexes **5a**−**d** (Scheme 2).

The same complexes are also accessible from isolated **4a**−**d** and propene. Treatment of a toluene solution of $CpZr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ (**4a**) with ca. 1 equiv of propene at −30 °C, subsequent warming to room temperature, and further stirring for 2 days affords a pale yellow solution, containing the propene insertion complex $CpZr(C_6F_5)\{\eta^1\text{:}\eta^3\text{-}CH_2CH(Me)CH_2\text{-}CMeCHCHB(C_6F_5)_2\}$ (**5a**). Compound **5a** was purified by repeated recrystallizations as a pale yellow powder which was characterized spectroscopically. Repeated attempts to obtain crystalline material were unsuccessful. The assignment of the ^1H and ^{13}C NMR resonances (Table 4) was aided by the use of ^{13}C-INEPT ($^1J(^1H-^{13}C)$ couplings are listed in Table 4) and $^1H-^{13}C$ correlation NMR experiments.

The room-temperature ^{19}F NMR spectrum of **5a** exhibits nine resonance signals. The broad resonances at δ −123.1 and −133.3 sharpened on warming the sample from 24 to 54 °C. The former resonance was assigned as the *o*-F of the Zr−C_6F_5 moiety (cf. ring 1 in compound **4a**), while the latter is due to the *o*-F signal of the B−C_6F_5 unit coordinated to the Zr center (cf. ring 2 in compound **4a**).

The insertion of propene to give **5a** proceeds best on a small scale, preferably as an NMR tube reaction; e.g., the reaction of 70 mg of **4a** with propene in a 5 mm NMR tube is complete after ca. 7 h to give a clean sample of **5a**. Reactions on a larger scale, however, which require prolonged stirring under 1 bar of propene to achieve complete conversion of **4a**, were accompanied by the formation of side products which proved difficult to remove and required several recrystallization steps; these were identified mainly as propene oligomers. Thus, the reaction of a red solution of **4a** with a continuous stream of propene for ca. 3 h afforded a pale yellow solution, the $^{13}C\{^1H\}$ NMR spectrum of which exhibited numerous resonance signals, including those of atactic polypropylene (δ 18−21, 29−30, 45−47). There

(11) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105.

(12) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995.

(13) For single propene insertion reactions with cationic Zr complexes see: (a) Pellecchia, C.; Grassi, A.; Zambelli, A. *J. Chem. Soc., Chem. Commun.* **1993**, 947. (b) Pellecchia, C.; Immirzi, A.; Zambelli, A. *J. Organomet. Chem.* **1994**, *479*, C9. (c) Pellecchia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (d) Thorn, M. G.; Etheridge, Z. C.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1998**, *17*, 3636. (e) Dahlmann, M.; Erker, G.; Nissinen, M.; Fröhlich, R. *J. Am. Chem. Soc.* **1999**, *121*, 2820.

Table 4. ^{1}H and ^{13}C NMR Spectroscopic Data for CpZr(C_6F_5){$CH_2CH(Me)CH_2C(Me)CHCHB(C_6F_5)_2$} (5a-A)

$\delta(^1H)$	assgnt	$\delta(^{13}C)$	assgnt
−0.58 (1H, dd, ^2J = 15.0, ^3J = 12.2 Hz)	Zr−CH_aH$_b$CH(Me)CH$_2$−	26.1 ($^1J_{CH}$ = 126 Hz)	Zr−CH$_a$H$_b$CH(*Me*)CH$_2$−; Zr−CHB(C_6F_5)$_2$−HC(*Me*)−
0.74 (3H, d, ^3J = 6.17 Hz)	Zr−CH$_a$H$_b$-CH(*Me*)CH$_2$−	30.8 ($^1J_{CH}$ = 130 Hz)	Zr−CH$_a$H$_b$CH(Me)CH$_2$−
1.53 (3H, s)	Zr−CHB(C_6F_5)$_2$CHC(*Me*)−	44.0 ($^1J_{CH}$ = 129 Hz)	Zr−CH$_a$H$_b$CH(Me)CH$_2$−
1.60 (1H, m, br)	Zr−CH$_a$*H*$_b$CH(Me)CH$_2$−	87.9 ($^1J_{CH}$ = 122 Hz)	Zr−*C*H$_a$H$_b$CH(Me)CH$_2$−
1.71 (1H, m)	Zr−CH$_a$H$_b$C*H*(Me)CH$_2$−	100.5 ($^1J_{CH}$ = 130 Hz)	Zr-*C*HB(C_6F_5)$_2$CHC(Me)−
1.80 (2H, s)	Zr−CH$_a$H$_b$CH(Me)C*H*$_2$−	113.5 ($^1J_{CH}$ = 175 Hz)	*C*$_5$H$_5$
3.30 (1H, d, ^3J = 16.8 Hz)	Zr−C*H*B(C_6F_5)$_2$CHC(Me)−	128.3 ($^1J_{CH}$ = 155 Hz)	Zr−CHB(C_6F_5)*C*HC(Me)−
6.03 (5H, s)	C$_5$*H*$_5$	134.0−152.2	Zr−CHB(C_6F_5)$_2$; Zr−*C*$_6F_5$
6.18 (1H, d, ^3J = 16.8 Hz)	Zr−CHB(C_6F_5)$_2$C*H*C(Me)−	152.8	Zr−CHB(C_6F_5)$_2$CH*C*(Me)−

Table 5. ^{1}H NMR Spectroscopic Data for the Propene Insertion Complexes 5a-d

	$\delta(^1H)$			
assgnt	**5a**	**5b**	**5c**	**5d**
Zr−C*H*$_a$H$_b$CH(Me)CH$_2$−	−0.58 (dd, ^2J = 15.0, ^3J = 12.2 Hz)	−0.58 (dd, ^2J = 15.0, ^3J = 12.2 Hz)	−0.50 (dd, ^2J = 14.6, ^3J = 11.2 Hz)	−0.42 (dd, ^2J = 15.0, ^3J = 11.7 Hz)
Zr−CH$_a$*H*$_b$CH(Me)CH$_2$−	1.60	n/o	n/o	n/o
Zr−CH$_a$H$_b$C*H*(Me)CH$_2$−	1.71	n/o	n/o	n/o
Zr−CH$_a$H$_b$CH(*Me*)CH$_2$−	0.74 (d, ^3J = 6.2 Hz)	0.73 (d, ^3J = 5.7 Hz)	0.75 (d, ^3J = 6.2 Hz)	0.83 (d, ^3J = 6.2 Hz)
Zr−CH$_a$H$_b$CH(Me)C*H*$_2$−	1.80	n/o	n/o	n/o
Zr−C*H*B(C_6F_5)$_2$CHC(Me)−	3.30 (d, ^3J = 16.8 Hz)	3.24 (d, ^3J = 16.6 Hz)	3.31 (d, ^3J = 16.3 Hz)	3.27 (d, ^3J = 16.5 Hz)
Zr−CHB(C_6F_5)$_2$C*H*C(Me)−	6.18 (d, ^3J = 16.8 Hz)	6.22 (d, ^3J = 16.6 Hz)	6.18 (d, ^3J = 16.3 Hz)	6.20 (d, ^3J = 16.5 Hz)
Zr−CHB(C_6F_5)$_2$CHC(*Me*)−	1.53	1.66 (s)	1.58 (s)	1.62 (s)

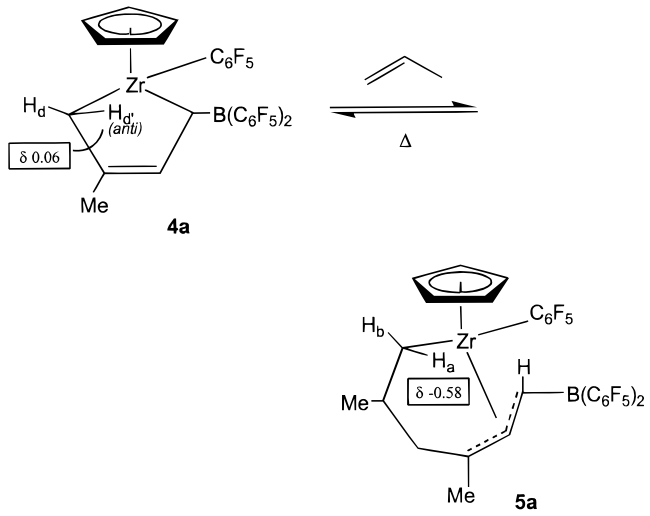
are a number of reports of stoichiometric propene insertions into M−R bonds of cationic group 4 complexes.[10,13] It has also been shown that neutral Zr−alkyl species, Cp*ZrR(diene), are capable of ethene oligomerization;[14] in this case, however, the insertion process involves the Zr−alkyl bond and not the diene ligand. On the other hand, ethene is capable of inserting into the M−CH_2 bonds of some titanium and zirconium diene complexes, and the titanium-catalyzed coupling reactions of dienes with 1-alkenes no doubt involve related seven-membered metallacyclic intermediates.[15]

The formation of propene oligomerization byproducts prevented the isolation of **5b**−**d**. While a number of the ^{1}H NMR resonances characteristic of **5a** were also observed in the ^{1}H NMR spectra of **5b**−**d** (Table 5), isolation of pure samples of **5b**−**d** was not possible, even after several recrystallizations.

Surprisingly, the insertion of propene into the Zr−diene bond of **4a** proved to be reversible. The reaction may be followed by monitoring the ^{1}H NMR resonance of the Zr−CH_a environment of **5a** (δ −0.58) with respect to the analogous position in the starting material **4a** ($H_{anti} = H_{d'}$, δ 0.06). Both resonances were calibrated against an internal standard (the residual protons in the C_6D_6 solvent at δ 7.15) to ascertain the extent of any decomposition (Scheme 3).

At 25 °C, despite the presence of an atmosphere of propene gas, the signals for **5a** were accompanied by a small resonance assigned to the starting material, **4a**. Warming the NMR sample to 60 °C resulted in a change in the **4a**:**5a** ratio from 1:17 to 1:2, with little decomposition or side reactions. Allowing the 1:2 mixture of **4a** and **5a** to stand for 24 h at room temperature under a propene atmosphere resulted in the regeneration of **5a**. The process is illustrated in Figure 2. A similar series of ^{1}H NMR experiments, performed under nitrogen upon complete removal of propene, further demonstrated the reversible nature of the reaction, with the appearance of distinct propene resonances, although in this instance a large amount of side products arising from the thermal decomposition of **4a** were also observed.

Scheme 3



The reaction of propene with compound **4a** is strictly regiospecific, affording exclusively the 1,2-insertion product. Compounds of type **4** are chiral, and careful baseline analysis in the region of the H_a proton environment at ca. δ −0.7 revealed that the propene insertion is highly stereospecific, giving rise to major and minor isomers, **5a-A** and **5a-B**, in a ratio of about 9:1. These isomers arise from the addition of propene to the Zr−CH_2 bond with *si* and *re* stereochemistry, respectively (Scheme 4).

The structure of the isomers may be determined from consideration of the coupling constants to H_a. To minimize steric interaction with the cyclopentadienyl ligand, the methyl group of the inserted propene moiety will be equatorial in a chair (**5a-A**) or boat (**5a-B**) conformation of the metallacycle. In the former (**5a-A**, major isomer), the geminal ($^2J_{gem}$) and vicinal ($^3J_{vic}$) coupling constants to H_a ($^2J(H_a-H_b)$ and $^3J(H_a-H_c)$) are sufficiently similar (15.0 and 12.2 Hz, respectively), so that

(14) Hessen, B.; van der Heijden, H. *J. Am. Chem. Soc.* **1996**, *118*, 11670.

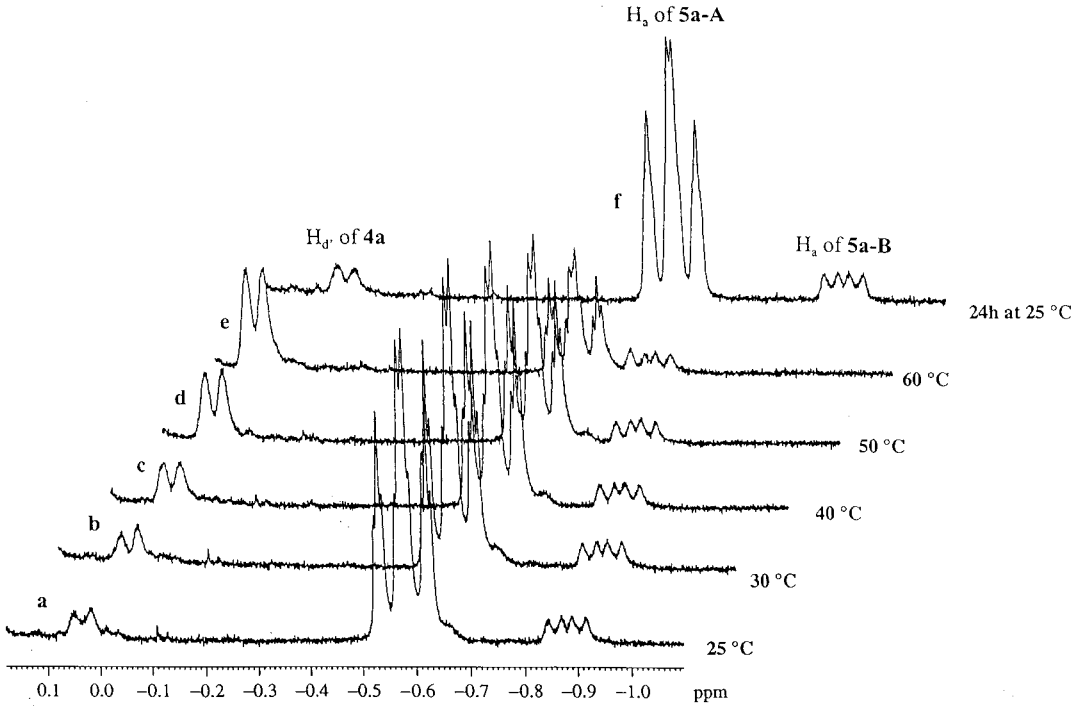
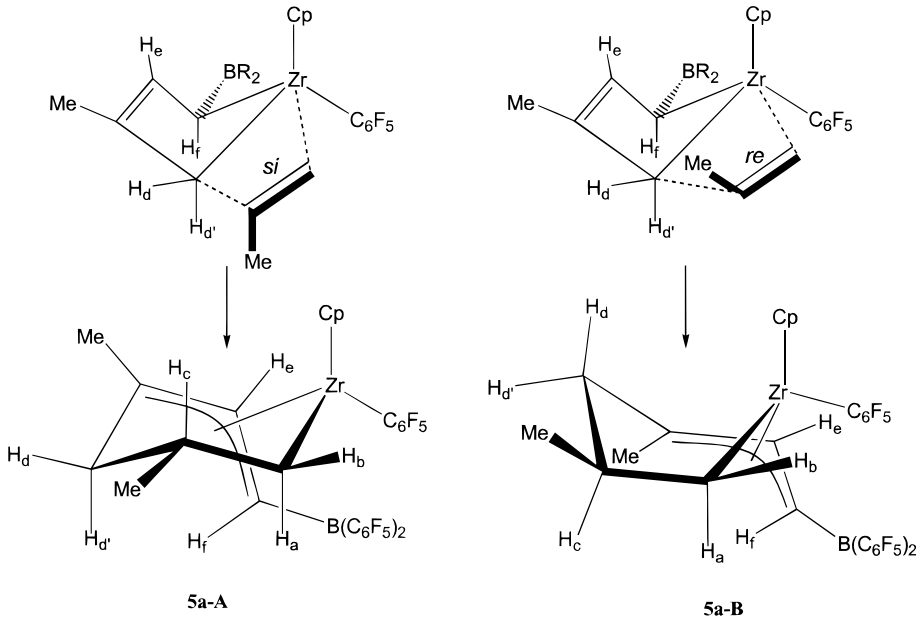


Figure 2. Stacked plot of the ^{1}H NMR spectra of **5a** in the H$_a$ region of the spectrum, in C_6D_6 under 1 bar of propene. Heating from 25 to 60 °C leads to an increase of the H$_{anti}$ signal of **4a** due to propene extrusion from **5a-A**, while the intensity of the **5a-B** signal remains unaffected (**a**−**e**). The original spectrum is restored on standing at 25 °C (**f**). Under these conditions, conversion of **4a** to **5a** remains incomplete.

Scheme 4



the resonance is observed as a pseudo-triplet, with further fine structure due to long-range coupling to the Me protons. In the case of **5a-B**, a decrease in the H$_a$−C−C−H$_c$ dihedral angle results in a decrease in $^3J_{vic}$, and a doublet of doublets is observed ($^2J_{gem}$ and $^3J_{vic}$ = 13.7 and 7.8 Hz, respectively). 2D ^{1}H−^{1}H NOESY and 1D ^{1}H NOE NMR spectroscopic data corroborated the chair conformation of **5a-A**, with notable interactions between the H$_a$, H$_f$, and H$_{d/d'}$ proton environments and no interaction between H$_f$ and H$_b$.

When the NMR sample of **5a** was warmed to 60 °C under 1 bar of propene, the H$_a$ resonances for both stereoisomers shifted slightly, with a notable decrease in intensity of that associated with **5a-A** and a corresponding increase in the intensities of those proton environments associated with the boryldiene complex **4a**, as monitored by the increase in signal intensity for the H$_{anti}$ proton of **4a** at δ 0.09. When the sample was cooled to room temperature, the ratio H$_a$(**5a-A**):H$_a$(**5a-B**) had changed from 9:1 to 5:1 (total experiment time 2.5 h), almost exclusively through elimination of propene from **5a-A**. After a further 24 h under propene, the ratio had returned to 7:1, exclusively through regeneration of the **5a-A** isomer (Figure 2). Over this

time period, only a very small amount of decomposition was observed.

It is thus apparent that an equilibrium exists between **4a** and **5a** under the conditions of the NMR experiment. Both stereoisomers, **5a-A** and **5a-B**, are formed in the initial reaction of **4a** with propene, and warming the NMR sample causes propene extrusion preferentially from **5a-A** via β-alkyl elimination. The ratio **5a-A**:**5a-B** thus changes, but this is due solely to propene elimination from the **A** isomer, and not due to rearrangement to isomer **B**. Related β-alkyl elimination reactions, notably β-methyl eliminations, are rare in d^0 systems but have been observed as chain transfer reactions in some cationic metallocene alkyl complexes and in olefin polymerization systems.[16]

The deinsertion of propene has been proposed to explain the isomerization of the propene insertion products obtained from the reaction of *rac*-[$C_2H_4(Ind)_2$-Zr(η^2-pyridyl)][$MeB(C_6F_5)_3$] with propene.[17] These systems exhibit β-alkyl elimination at 80 °C, whereupon the kinetic products isomerize to give the thermodynamic mixtures. In the system described here such equilibration experiments were prevented by the thermal instability of **4a** above 70 °C.

Conclusion

The thermal stability of zwitterionic zirconium half-sandwich complexes of type **A** (Scheme 1) is strongly dependent on the steric requirements of the cyclopentadienyl ligands. Derivatives with the less bulky Cp ligands described here, $Cp^R = C_5H_5$, Cp′, Cp^{Me}, Ind, are themally labile and readily undergo C−H activation to afford σ^2,π-boryldiene complexes. The crystal structure of the C_5H_5 complex shows that, unlike more bulky congeners, the diene ligand adopts a prone conformation. In contrast to the 1,3-$C_5H_3(SiMe_3)_2$ analogues, these complexes do not undergo a rearrangement to borole complexes **C**. However, a highly regio- and stereoselective propene insertion reaction is observed to give new metallacycles. The insertion is reversible and involves a β-alkyl elimination pathway, preferentially from the stereoisomer with chair conformation.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk line techniques. Solvents were distilled under nitrogen from sodium (toluene, 1,2-dimethoxyethane (dme)), sodium−benzophenone (thf), sodium−potassium alloy (light petroleum; bp 40−60 °C), or CaH_2 (CH_2Cl_2). Deuterated solvents were degassed by several freeze−thaw cycles and stored over activated 4 Å molecular sieves. The compounds $CpZrCl_3$(dme) and (Ind)$ZrCl_3$(dme) (Ind = η^5-C_9H_7) were prepared according to literature procedures.[18,19] Unless stated otherwise, all chemicals were used as purchased without further purification. Isoprene was dried over Na and freshly distilled prior to use. The NMR spectra were recorded on a Bruker DPX300 spectrometer. ^{1}H NMR spectra (300.1 MHz) were referenced to the residual solvent protons of the deuterated solvent used; ^{13}C NMR spectra (75.4 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent; ^{19}F NMR spectra (282.2 MHz) were referenced externally to $CFCl_3$.

Preparation of $CpZrCl_3$·dme (1a), Cp′$ZrCl_3$·dme (1b), $Cp^{Me}ZrCl_3$·dme (1c), and (Ind)$ZrCl_3$·dme (1d). These complexes were prepared by following the procedure by Lund and Livinghouse for the synthesis of $CpZrCl_3$(dme).[18] A typical preparative route is given below for the synthesis of **1c**. A suspension of freshly sublimed $ZrCl_4$ (22.0 g, 94 mmol) in CH_2Cl_2 (200 mL) was treated with SMe_2 (12.0 g, 194 mmol) at 0 °C. After the mixture was warmed to room temperature, $C_5H_4Me(SiMe_3)$ (14.5 g, 95 mmol) was added dropwise and the reaction mixture stirred for 16 h. The pale green suspension was treated with dme (100 mL) until all the solid had dissolved. The solvent was then removed in vacuo, and the resulting white-green solid washed with dme (3 × 30 mL) and dried to afford **1c** as an off-white powder (28.2 g, 82%).

Cp′$ZrCl_3$·dme (1b). ^{1}H NMR (C_6D_6, 24 °C): δ 0.49 (s, 9H, $SiMe_3$), 3.28 (s, br, 10H, dme), 6.52 (t, 2H, J = 2.5 Hz, Cp), 6.73 (t, 2H, J = 2.5 Hz, Cp). ^{13}C NMR (C_6D_6, 24 °C): δ 0.41 ($SiMe_3$), 64.3 (OMe), 72.5 (OCH_2), 122.0 (Cp), 126.1 (Cp). Anal. Found (calcd) for $C_{12}H_{23}O_2Cl_3SiZr$: C, 33.8 (33.9); H, 5.3 (5.5).

$Cp^{Me}ZrCl_3$·dme (1c). ^{1}H NMR (C_6D_6, 24 °C): δ 2.42 (s, 3H, Me), 3.36 (s, br, 10H, dme), 6.26 (m, 4H, Cp). ^{13}C NMR (C_6D_6, 24 °C): δ 16.6 (Me), 64.6 (OMe), 73.4 (OCH_2), 118.2 (Cp), 120.5 (Cp). Anal. Found (calcd) for $C_{10}H_{17}O_2Cl_3Zr$: C, 32.2 (32.7); H, 4.6 (4.7).

Preparation of $CpZr(\eta^3$-$C_3H_5)(\eta^4$-C_4H_5Me-2) (2a). This compound was prepared by modification of a literature procedure.[5] To a Schlenk tube charged with a freshly prepared sodium amalgam (1% Na, 1.0 g, 43 mmol) and isoprene (1.45 g, 21 mmol) in thf (60 mL) at −78 °C was added a warm thf solution (250 mL) of $CpZrCl_3$·dme (7.5 g, 21 mmol), with the immediate formation of a pale yellow slurry. The reaction mixture was warmed to room temperature and stirred for 12 h to afford a dark purple solution over pale gray solids. The solution was filtered and cooled to −78 °C, and a solution of $MgCl(C_3H_5)$ in thf (2.0 M, 11.0 mL, 22 mmol) was added dropwise. An immediate color change to dark brown was observed. The reaction mixture was warmed to room temperature and stirred for a further 3 h. The solvent was removed in vacuo to yield a sticky brown solid, which was extracted into light petroleum (3 × 50 mL). The resulting dark red solution was concentrated to ca. 50 mL and cooled to −30 °C to afford **2a** as a red crystalline solid (3.4 g, 13 mmol, 61%). Anal. Found (calcd) for $C_{13}H_{18}Zr$: C, 57.8 (58.8); H, 6.8 (6.8).

By the procedure for **2a**, compounds **2b**−**d** were prepared similarly.

Cp′$Zr(\eta$-$C_3H_5)(\eta^4$-C_4H_5Me-2) (2b): red crystalline solid (6.3 g, 75%). Anal. Found (calcd) for $C_{16}H_{26}SiZr$: C, 56.9 (56.9); H, 7.9 (7.8).

$Cp^{Me}Zr(\eta$-$C_3H_5)(\eta^4$-C_4H_5Me-2) (2c): maroon oil (3.2 g, 76%). Anal. Found (calcd) for $C_{14}H_{20}Zr$: C, 57.3 (60.2); H, 7.1 (7.2).

(Ind)$Zr(\eta$-$C_3H_5)(\eta^4$-C_4H_5Me-2) (2d); maroon microcrystalline solid (1.20 g, 25%). Anal. Found (calcd) for $C_{17}H_{20}Zr$: C, 64.5 (64.7); H, 6.3 (6.4).

(15) (a) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428. (b) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 914. (c) Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656.

(16) (a) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277. (b) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (c) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (d) Mise, T.; Kageyama, A.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1991**, 1525. (e) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (f) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392. (g) Horton, A. D. *Organometallics* **1996**, *15*, 2675. (h) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145 and references therein.

(17) Dagorne, S.; Rodewald, S.; Jordan, R. F. *Organometallics* **1997**, *16*, 5541.

(18) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426.

(19) Shaw, S. L.; Morris, R. J.; Huffman, J. C. *J. Organomet. Chem.* **1995**, *489*, C4.

Preparation of $Cp^RZr(\eta\text{-}C_3H_5)\{\eta^4\text{-}CH_2CMeCHCH_2B(C_6F_5)_3\}$ (Cp^R = Cp (3a), Cp′ (3b), Cp^{Me} (3c), Ind (3d)). A typical preparative route is given below for the synthesis of **3a**. To an NMR tube charged with **2a** (20 mg, 75 μmol) in toluene-d_8 (0.3 mL) and cooled to −78 °C was carefully added a toluene-d_8 solution (0.3 mL) of $B(C_6F_5)_3$ (38 mg, 75 μmol). An immediate color change from red to clear orange was observed. Compound **3a** was identified as the sole reaction product by low-temperature ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy.

Compounds **3b**−**d** were prepared similarly; in all cases, at no point were the reaction vessels allowed to be above −50 °C. All attempts to isolate **3a**−**d** resulted in propene evolution and the formation of **4a**−**d**.

Preparation of $CpZr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ (4a). To a Schlenk tube charged with a toluene solution (30 mL) of **2a** (0.9 g, 3.40 mmol) cooled to −78 °C was added a toluene solution (50 mL) of $B(C_6F_5)_3$ (1.7 g, 3.33 mmol). An immediate color change of red to yellow-brown was observed. The reaction mixture was placed under reduced pressure, warmed to room temperature, and stirred until all the volatiles had been removed (ca. 2 h). The resulting red-brown solid was extracted into light petroleum (3 × 50 mL). The dark red solution obtained was concentrated to ca. 50 mL and cooled to −30 °C to afford **4a** as a red crystalline solid (1.7 g, 2.31 mmol, 68%). Anal. Found (calcd) for $C_{28}H_{12}BF_{15}Zr$: C, 45.8 (45.7); H, 1.9 (1.6).

By following the procedure for **4a**, compounds **4b**−**d** were prepared similarly. **$Cp'Zr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ (4b)**: maroon crystalline solid (2.4 g, 35%). Anal. Found (calcd) for $C_{31}H_{20}BF_{15}SiZr$: C, 46.5 (46.1); H, 2.7 (2.5).

$Cp^{Me}Zr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ (4c): dark red crystalline solid (2.5 g, 3.33 mmol, 58%). Anal. Found (calcd) for $C_{29}H_{14}BF_{15}Zr$: C, 47.1 (46.5); H, 2.3 (1.9).

$(Ind)Zr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ (4d): dull maroon solid (0.75 g, 0.96 mmol, 60%). Anal. Found (calcd) for $C_{29}H_{14}BF_{15}Zr$: C, 47.0 (46.5); H, 2.3 (1.9).

Preparation of $CpZr(C_6F_5)\{\eta^1\text{:}\eta^3\text{-}CH_2CH(Me)CH_2C(Me)CHCHB(C_6F_5)_2\}$ (5a). A Schlenk tube charged with a dark red toluene solution (50 mL) of compound **4a** (0.30 g, 0.41 mmol) was cooled to −30 °C, placed under vacuum for ca. 10 min, and back-filled with propene gas. The mixtures was warmed to room temperature, sealed with 1 atm of propene (ca. 80 mL, 3.33 mmol) above the toluene solution, and stirred for 48 h to afford a pale yellow solution with dark brown oily deposits. The solvent was removed in vacuo, and the resulting orange powder was extracted into light petroleum (3 × 20 mL). The solvent was removed in vacuo to afford a sticky pale yellow powder, characterized as a mixture of compounds by ^{1}H NMR spectroscopy. Repeated recrystallization from light petroleum at −30 °C afforded **5a** as a pale yellow powder (0.12 g, 0.15 mmol, 38%). The compound retained small quantities of propene oligomers (cf. Supporting Information, Figure S-1), which prevented accurate elemental analyses. The compound was identified by NMR spectroscopy. ^{19}F NMR (282.2 MHz, C_6D_6, 24 °C): δ −123.1 (s, br, $F_{o(1)}$), −129.0 (d, J = 21 Hz, 2F, $F_{o(3)}$), −133.3 (m, 2F, $F_{o(2)}$); *p*-F, −123.1 (t, J = 21 Hz, 1F), −152.9 (t, J = 21 Hz, 1F), −153.3 (t, J = 21 Hz, 1F); *m*-F, −160.4 (2F), −161.2 (2F), −161.6 (2F).

Attempted Syntheses of $Cp^RZr(C_6F_5)\{\eta^1\text{:}\eta^3\text{-}CH_2CH(Me)CH_2C(Me)CH{-}CHB(C_6F_5)_2\}$ (Cp^R = Cp′ (5b), Cp^{Me} (5c), Ind (5d)). A preparative route identical with that outlined above for compound **5a** was employed in the attempted syntheses of compounds **5b**−**d**. Similar color changes were observed throughout. Pure samples of the desired products were not isolated. The sticky powders obtained were characterized as a mixture of compounds, containing the complexes **5b**−**d** by ^{1}H NMR spectroscopy.

NMR Tube Reaction of $CpZr(C_6F_5)\{\eta^4\text{-}CH_2C(Me)CHCHB(C_6F_5)_2\}$ with Propene. A 5 mm NMR tube fitted with a PTFE valve and charged with **4a** (70 mg, 95 μmol) in C_6D_6 (0.5 mL) was cooled to −78 °C, evacuated, and back-filled with propene (2.8 mL, 116 μmol). The sample was warmed to room temperature before the PTFE valve was closed.

X-ray Crystallography. A crystal of **4a**·OEt_2 was coated in an inert perfluoropolyether oil and mounted in a nitrogen stream at 100(2) K on a Nonius Kappa CCD area-detector diffractometer. Data collection was performed using Mo Kα radiation (λ = 0.710 73 Å) with the CCD detector placed 30 mm from the sample via a mixture of 1° ϕ and ω scans at different θ and κ settings using the program COLLECT.[20] The raw data were processed to produce conventional data using the program DENZO-SMN.[21] The data sets were corrected for absorption using the program SORTAV.[22] The structure was solved by heavy-atom methods using SHELXS-97[23] and refined by full-matrix least-squares refinement (on F^2) using SHELXL-97.[24] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized positions.

Crystal Data: $C_{32}H_{22}BF_{15}OZr$, fw 809.53; crystal size 0.29 × 0.29 × 0.07 mm; monoclinic, space group $P2_1/n$, a = 12.6710(2) Å, b = 11.9740(1) Å, c = 20.8219(3) Å; β = 99.0930(8)°; V = 3119.45(7) Å^3; Z = 4, D_{calcd} = 1.724 g cm^{-3}; μ = 0.470 mm^{-1}; 11 528 reflections collected, of which 6001 were unique (R_{int} = 0.0115) and 5549 with $I > 2\sigma(I)$ were observed; maximum and minimum transmission 0.9679 and 0.8758, respectively; final R1 ($I > 2\sigma(I)$) = 0.0307, wR2 (all data) = 0.0840;[25] goodness of fit S = 1.038 for 471 parameters.

Acknowledgment. This work was supported by the Engineering and Physical Sciences Research Council. We gratefully acknowledge fellowships by the Spanish Ministry for Education and Culture (to G.J.P.) and by BP-Amoco Chemicals Ltd. (to M.J.S.).

Supporting Information Available: Additional NMR information and tables giving details of the X-ray structure analysis of **4a**·OEt_2. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990859T

(20) Collect, Data Collection Software; Nonius BV, Delft, The Netherlands, 1999.

(21) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1996; Vol. 276, pp 307−326.

(22) Blessing, R. H. *Acta Crystollogr., Sect. A* **1995**, *51*, 33.

(23) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(24) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany. 1997.

(25) $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where a = 0.0512, b = 2.0350, and $P = [2F_c^2 + \max(F_o^2, 0)]/3$.