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Articles

Coordination of $CB_{11}H_{12}^-$ to Cationic Zirconium(IV) Complexes. Synthesis and Structures of $(C_5H_5)_2Zr(\eta^2\text{-}CH_2Ph)(CB_{11}H_{12})$, $(C_5H_4Me)_2Zr(CH_3)(CB_{11}H_{12})$, and $(C_5Me_5)Zr(CH_3)_2(CB_{11}H_{12})$

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The reaction of $Ag[CB_{11}H_{12}]$ with $Cp_2Zr(CH_2Ph)_2$ yields $Cp_2Zr(\eta^2\text{-}CH_2Ph)(\eta^1\text{-}CB_{11}H_{12})$ (1), in which the carborane coordinates to Zr via a single B–H–Zr bridge involving the B–H bond trans to the carbon of the closo $CB_{11}H_{12}^-$ anion. Data for 1: $a = 9.802(5)$ Å, $b = 13.663(5)$ Å, $c = 10.860(4)$ Å, $\beta = 92.48(4)°$, $V = 1453(2)$ Å^3, $Z = 2$, in space group $P2_1/m$. A similar structure is observed for $Cp'_2Zr(CH_3)(\eta^1\text{-}CB_{11}H_{12})$ (2, Cp′ = C_5H_4Me), which is prepared by reaction of $Cp'_2Zr(CH_3)_2$ with $Ag[CB_{11}H_{12}]$. Data for 2: $a = 13.504(2)$ Å, $b = 19.432(3)$ Å, $c = 7.919(1)$ Å, $V = 2078(1)$ Å^3, $Z = 4$, in space group $Pnn2$. The reaction of $Cp^*Zr(CH_3)_3$ (Cp* = C_5Me_5) with $Ag[CB_{11}H_{12}]$ yields $Cp^*Zr(CH_3)_2(\eta^3\text{-}CB_{11}H_{12})$ (3), in which the carborane coordinates in a unique tridentate fashion via three B–H–Zr bridges involving the B–H bonds on a triangular face opposite the carborane carbon. Data for 3: $a = 12.360(3)$ Å, $b = 19.450(4)$ Å, $c = 9.161(2)$ Å, $\beta = 90.93(4)°$, $V = 2202(1)$ Å^3, $Z = 4$, in space group $P2_1/c$. Complex 1 polymerizes ethylene, and 2 oligomerizes propene under mild conditions, while 3 is unreactive with propene, 2-butyne, or styrene, apparently due to the lower lability of the tridentate carborane ligand. The $CB_{11}H_{12}^-$ ligands of 1–3 are rapidly displaced by CH_3CN or THF.

The reactivity of electrophilic cationic organometallic species such as $Cp_2Zr(R)^+$ and $Cp_2Zr(R)(L)^+$ is strongly influenced by the availability of vacant coordination sites, which in turn is determined by ligand lability, solvent coordination, intramolecular agostic interactions, and cation–anion interactions.[1] One strategy for accessing reactive but still isolable organometallic cations is to utilize a weakly coordinating anion which coordinates or ion-pairs strongly enough to impart solubility in nonpolar, poorly coordinating solvents but is sufficiently labile to be displaced by substrates of interest (e.g. olefins).[2] Hlatky and Turner have demonstrated that anionic carborane clusters are useful weakly coordinating anions for $Cp_2Zr(R)^+$ cations through their preparation of $Cp^*_2Zr(CH_3)(C_2B_9H_{12})$ (Cp* = C_5Me_5).[3] This ion pair contains a $C_2B_9H_{12}^-$ counterion linked to the Zr cation by a B–H–Zr bridge, is soluble in toluene, and is an active ethylene polymerization catalyst. Reed has popularized the closo carborane anion $CB_{11}H_{12}^-$,[4,5] which also binds weakly to metal cations via B–H–Zr bridging from the H antipodal to C.[6,7] On the basis of structural, spectroscopic, and reactivity studies, Reed has dubbed $CB_{11}H_{12}^-$ the "least coordinating" anion. While $CB_{11}H_{12}^-$ is somewhat less synthetically accessible than $C_2B_9H_{12}^-$, it has a major advantage in the context of early metal alkyl chemistry in that it lacks acidic hydrogens. In this paper we describe the synthesis and characterization of a series of cationic Zr(IV) alkyl complexes containing the $CB_{11}H_{12}^-$ counterion and discuss in some detail the Zr–carborane interactions.[8] The Exxon group has reported the generation and olefin polymerization activity of $(C_5R_5)_2Zr(R)(CB_{11}H_{12})$ and related species in a patent,[9] and other weakly coordinating anions have been used in base-free $Cp_2M(R)^+$ systems.[10]

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(1) Jordan, R. F. *Adv. Organomet. Chem.* **1991,** *32,* 325 and references therein.

(2) For reviews see: (a) Strauss, S. H. *Chem. Rev.* **1993,** *93,* 927. (b) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1181. (c) Beck, W.; Sünkel, K. *Chem. Rev.* **1988,** *88,* 1405. (d) Lawrance, G. A. *Adv. Inorg. Chem.* **1989,** *34,* 145. (e) Lawrance, G. A. *Chem. Rev.* **1986,** *86,* 17. (f) Rosenthal, M. R. *J. Chem. Educ.* **1973,** *50,* 331.

(3) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989,** *111,* 2728.

(4) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1967,** *89,* 1274. (b) Knoth, W. H. *Inorg. Chem.* **1971,** *10,* 598. (c) Plesek, J.; Jelínek, T.; Drdaková, E.; Hermánek, S.; Stíbr, B *Collect. Czech. Chem. Commun.* **1984,** *49,* 1559.

(5) Sivaev, I. B.; Kayumov, A.; Yakushev, A. B.; Solntsev, A.; Kuznetsov, N. T. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1987,** *15,* 837.

(6) (a) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985,** *107,* 5955. (b) Shelly, K.; Reed, C. *J. Am. Chem. Soc.* **1986,** *108,* 3117. (c) Gupta, G.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987,** *26,* 3022. (d) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989,** *111,* 6643.

(7) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987,** *26,* 2739.

(8) We recently noted the preparation of a metastable $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$ complex: Borkowsky, S. L.; Baenziger, N. C.; Jordan, R. F. *Organometallics* **1993,** *12,* 486.

(9) Turner, H. W.; Hlatky, G. G. European Patent Appl. 88300698.3, 1988.

(10) For examples see the following. (a) $MeB(C_6F_5)_3^-$: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991,** *113,* 3623. (b) $B(C_6H_4F)_4^-$: Horton, A. D.; Orpen, A. G. *Organometallics* **1991,** *10,* 3910. (c) $HB(C_6F_5)_3^-$: Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1375. (d) $B(C_6F_5)_4^-$: Turner, H. W. European Patent Appl. 88300699.1, 1988. (e) $B(3,5\text{-}(CF_3)_2Ph)_4^-$: Bochmann, M.; Jaggar, A. J. *J. Organomet. Chem.* **1992,** *424,* C5.

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Table I. Summary of Crystallographic Data for 1–3

	1	2	3
empirical formula	$C_{18}H_{29}B_{11}Zr{\cdot}C_7H_8$	$C_{14}H_{29}B_{11}Zr$	$C_{13}H_{33}B_{11}Zr$
fw	547.71	407.53	399.55
cryst size (mm)	0.20 × 0.35 × 0.55	0.52 × 0.63 × 0.66	0.47 × 0.51 × 0.61
cryst color	yellow	dark red	red
T (K)	295	295	295
space group	$P2_1/m$	$Pnn2$	$P2_1/c$
a (Å)	9.802(5)	13.504(2)	12.360(3)
b (Å)	13.663(5)	19.432(3)	19.450(4)
c (Å)	10.860(4)	7.919(1)	9.161(2)
β (deg)	92.48(4)		90.93(4)
V (Å^3)	1453(2)	2078(1)	2202(1)
Z	2	4	4
D_c (g/cm^3)	1.25	1.31	1.21
no. of reflns; θ range (deg)	25; $16 < 2\theta < 24$	23; $20 < 2\theta < 34$	25; $24 < 2\theta < 29$
λ(Mo Kα radiation) (Å)	0.7107	0.7107	0.7107
scan ratio (ω/θ)	1	1	1
ω scan range (deg)	$0.7 + 0.35 \tan(\theta)$	$0.8 + 0.35 \tan(\theta)$	$0.8 + 0.35 \tan(\theta)$
scan speed (deg/min)	1.5–6.67	1.5–5.0	1.5–5.0
θ range (deg)	$2 < \theta < 25$	$2 < \theta < 30$	$2 < \theta < 30$
data collected			
h	−10, 10	−18, 18	−2, 17
k	0, 14	−27, 18	−27, 27
l	0, 11	−11, 0	−12, 12
no. of tot. reflns	2567	9743	11 673
no. of unique reflns	2100	3202	6363
no. of reflns used, $I > 2\sigma_I$	1137	2344	4613
R_{int}	0.045	0.031	0.022
decay factor cor range	1.00–1.07	0.49–1.66	1.00–1.11
abs coeff (cm^{-1})	3.86	5.18	4.87
empirical abs cor range	not done	1.002–1.042	1.001–1.051
structure soln method	direct methods		direct methods
refinement[a]	all non-H atoms refined anisotropically		
	H atoms fixed isotropic	H atoms refined isotropically	
tot. no. of params	180	270	265
R	0.067	0.025	0.031
R_w	0.083	0.031	0.046
weighting coefficients: P, Q[b]	0.05, 0.0	0.02, 0.0	0.03, 0.0
SDOUW[c]	1.237	0.981	1.162
max shift/esd	0.06	0.33	0.28
max density, final diff density map (e/Å^3)	0.49	0.53	0.49

[a] For 1, C–H = 0.95 Å and B–H = 1.08 Å, $B_{\text{iso}} = 1.1B_{\text{iso}}(\text{C})$ or $1.1B_{\text{iso}}(\text{B})$. [b] $w = (\sigma_F^2 + (PF)^2 + Q)^{-1}$. [c] Standard deviation of unit weight.

Results and Discussion

Synthesis, Structure, and Reactivity of $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CB_{11}H_{12})$ (1). In previous work we have established that reaction of d^0 metal alkyls with one-electron oxidants results in clean oxidative cleavage of metal–alkyl bonds, providing a useful entry to cationic species.[11] The benzene-soluble Ag^+ reagent $Ag[CB_{11}H_{12}]$ proved most useful in the present work.[6] The reaction of $Ag[CB_{11}H_{12}]$ with $Cp_2Zr(CH_2Ph)_2$ in benzene or toluene yields $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CB_{11}H_{12})$ (1, quantitative by ^{1}H NMR, 48% isolated) and bibenzyl (eq 1). Complex 1 crystallizes as a monotoluene solvate which loses the toluene under vacuum.

$$(C_5H_4R')_2ZrR_2 + Ag[CB_{11}H_{12}] \rightarrow (C_5H_4R')_2Zr(R)(CB_{11}H_{12}) + {}^1/_2R\text{-}R + Ag^0 \quad (1)$$

$$1{:}\ R = \eta^2\text{-}CH_2Ph;\ R' = H$$
$$2{:}\ R = CH_3;\ R' = CH_3$$

The solid-state structure of 1 was determined by X-ray diffraction; crystallographic data are listed in Table I, and metrical and positional parameters listed in Tables II and III. Complex 1 adopts the normal bent metallocene structure in which the benzyl and $CB_{11}H_{12}^-$ ligands lie in the plane between the Cp ligands, as illustrated in Figures 1 and 2. A crystallographically imposed mirror plane renders the two Cp ligands equivalent and the halves of the benzyl and carborane ligands equivalent. The benzyl ligand is distorted by a Ph--Zr donor interaction which results in an acute Zr–CH$_2$–C$_{\text{ipso}}$ angle (84.2(8)°) and a short Zr–C$_{\text{ipso}}$ contact (2.65(1) Å). Very similar η^2-benzyl interactions were observed for $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)^+$ (Zr–C–C$_{\text{ipso}}$ = 84.9(4)°, Zr–C$_{\text{ipso}}$ = 2.648(6) Å)[12] and (ethylenebis(tetrahydroindenyl))Zr(η^2-CH$_2$Ph)(CH$_3$CN)$^+$ (Zr–C–C$_{\text{ipso}}$ = 84.4(5)°, Zr–C$_{\text{ipso}}$ = 2.627(9) Å).[13] The $CB_{11}H_{12}^-$ anion is coordinated to Zr via a bridging B–H–Zr bond

Table II. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CB_{11}H_{12})$ (1)[a]

Zr–C11	2.34(1)	$\overline{\text{Zr–C}}_{\text{ring}}$	2.51(3)
Zr–C12	2.65(1)	$\overline{(\text{C–C})}_{\text{ring}}$	1.37(1)
Zr–C_0	2.22	$\overline{\text{C–B}}$	1.67(2)
Zr–HB7	2.30	$\overline{\text{B–B}}$	1.76(3)
Zr–B7	3.33(2)		
C11–Zr–C_0	103.6	Zr–HB7–B7	159
C11–Zr–B7	126.4(6)	Zr–C11–C12	84.2(8)
C_0–Zr–B7	98.6	CB2–B7–Zr	166.0(6)

[a] C_0 = centroid of Cp ring.

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(11) (a) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *9*, 2574. (b) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041.

(12) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(13) Jordan, R. F.; LaPointe, R. E.; Baenziger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

Table III. Positional Parameters for $Cp_2Zr(\mu^2\text{-}CH_2Ph)(CB_{11}H_{12})$ (1)[a,b]

atom	*x*	*y*	*z*	*B* (Å^2)
Zr	0.6631(1)	0.250	0.1248(1)	3.21(3)
C1	0.621(1)	0.0710(8)	0.176(1)	5.7(3)
C2	0.684(1)	0.0743(8)	0.068(1)	6.3(3)
C3	0.597(1)	0.1147(8)	−0.020(1)	6.3(3)
C4	0.480(1)	0.1402(9)	0.037(1)	6.6(3)
C5	0.495(1)	0.1162(8)	0.160(1)	5.9(3)
C11	0.697(2)	0.250	0.339(1)	5.1(4)
C12	0.845(1)	0.250	0.312(1)	4.7(4)
C13	0.917(1)	0.1635(9)	0.291(1)	6.5(3)
C14	1.055(1)	0.165(1)	0.260(1)	7.8(4)
C15	1.118(2)	0.250	0.248(2)	8.4(6)
B1	1.162(2)	0.250	−0.195(2)	8.4(7)
CB2	1.077(1)	0.250	−0.330(1)	5.9(4)
B3	1.058(1)	0.185(1)	−0.090(1)	6.3(4)
B4	1.074(1)	0.148(1)	−0.245(1)	6.6(4)
B5	0.929(1)	0.189(1)	−0.331(1)	5.3(3)
B6	0.913(1)	0.146(1)	−0.176(1)	6.5(4)
B7	0.905(2)	0.250	−0.081(1)	3.8(4)
B8	0.828(2)	0.250	−0.232(2)	5.1(5)
C_0	0.5751	0.1032	0.0844	0*

[a] Asterisk indicates that atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] C_0 is the Cp ring centroid.

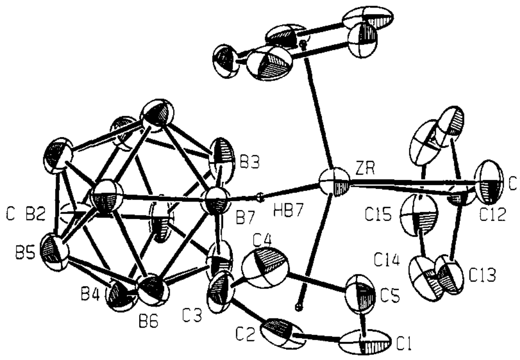

Figure 1. ORTEP view of $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CB_{11}H_{12})$ (1).

involving the B–H bond opposite the cage carbon. This is consistent with the structures of $Ag[CB_{11}H_{12}]$, $CpFe(CO)_2(CB_{11}H_{12})$, $(TPP)Fe(CB_{11}H_{12})$ (TPP = tetraphenylporphyrin), and other complexes characterized by Reed and Scheidt,[6] and with general observations that electrophilic attack on $CB_{12}H_{12}^-$ is favored at this position.[14] The μ-H atom was located but not refined, so a detailed discussion of the Zr–H–B bridge is not warranted. However, it is clear that the Zr–H–B angle (ca. 159°) is more linear than those in $Ag[CB_{11}H_{12}]$ (113.6, 121.0°) and $CpFe(CO)_2(CB_{11}H_{12})$ (141.1°), perhaps as a result of the rather crowded structure of this (formally) 9-coordinate species. The B–H–Fe angle in $(TPP)Fe(CB_{11}H_{12})$ is 151°. The IR spectrum of 1 (KBr) exhibits two ν_{B-H} stretching bands (2559, 2287 cm^{-1}), consistent with the loss of symmetry associated with coordination of $CB_{11}H_{12}^-$ to Zr.[6]

NMR studies establish that 1 maintains the solid-state structure in hydrocarbon solution. The ^{1}H NMR spectrum of 1 in toluene-d_8 contains a resonance at δ 6.30 for the ortho hydrogens of the phenyl ring which is shifted considerably upfield from the corresponding resonance of $Cp_2Zr(CH_2Ph)_2$ (δ 6.88), which contains undistorted benzyl ligands. The ^{13}C NMR Zr–CH_2 resonance also appears at high field, and the J_{CH} is unusually large (δ 50.6, *J* = 140 Hz; vs δ 60.0, *J* = 119 Hz for $Cp_2Zr(CH_2Ph)_2$). These data confirm that the η^2-benzyl structure is maintained in solution.[12,13,15] The ^{1}H NMR spectrum of 1 also contains resonances for the terminal C–H (δ 2.56, s, 1H), the terminal B–H (δ 3.1–0.8, br m, ca. 10H), and the bridging B–H–Zr (δ −3.15, br q, J_{BH} = 108 Hz) hydrogens of the $CB_{11}H_{12}^-$ ligand. The ^{11}B NMR spectrum includes three doublets at δ −8.1 (1*B*, J_{BH} = 100 Hz), −14.1 (5B, J_{BH} = ca. 154 Hz), and −15.6 (5B, J_{BH} = ca. 160 Hz), consistent with interaction of the anion with Zr via the unique B–H bond. The J_{BH} value for the μ-B–H closely matches that observed in the ^{1}H NMR spectrum and is significantly reduced from the values for the terminal B–H's, indicating some B–H bond weakening upon bridging to Zr. The chemical shift difference of the two upfield ^{11}B resonances (Δδ = 1.5) is much smaller than that observed for free $CB_{11}B_{12}^-$ (e.g. Δδ = 3.1 for $Cs[CB_{11}H_{12}]$ in acetone-d_6[16] and Δδ = 0 for $Ag[CB_{11}H_{12}]$ in benzene), which is also consistent with coordination of the anion in solution.

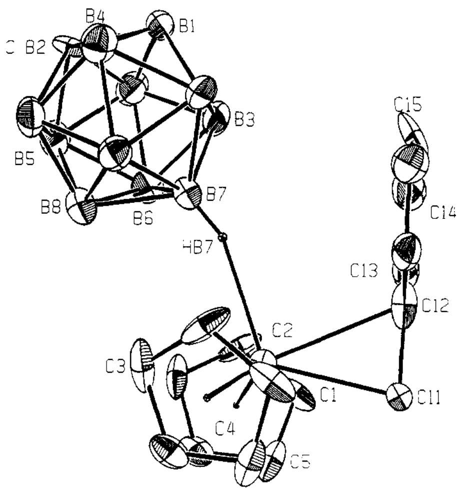

Figure 2. Alternate view of 1.

The reaction of 1 with CH_3CN results in displacement of the $CB_{11}H_{12}^-$ ligand and formation of the known CH_3CN complex $Cp_2Zr(CH_2Ph)(CH_3CN)^+$ and free $CB_{11}H_{12}^-$.[12] The ^{11}B NMR spectrum of a solution of $[Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)][CB_{11}H_{12}]$ in CD_3CN contains three doublets (δ −6.29 (1H), −12.60 (5H), −15.4 (5H)) with a normal J_{BH} value (135 Hz) for the unique boron atom. This spectrum is very similar to that of $Cs[CB_{11}H_{12}]$ in acetone-d_6, i.e. to that for free $CB_{11}H_{12}^-$. Solutions of complex 1 in toluene polymerize ethylene above 0 °C (ca. 1 atm). Low-temperature ^{1}H NMR monitoring of this reaction reveals no change in the spectrum of 1 below ca. 0 °C. Above this temperature several new resonances are observed, one of which (δ 5.40 (Cp)) may be due to a new $Cp_2Zr(CH_2CH_2R)(CB_{11}H_{12})$ alkyl species; no evidence for a stable ethylene adduct is observed. Significant polyethylene forms before the resonances for 1 disappear, consistent with slow initial insertion.[12]

Synthesis, Structure, and Reactivity of $Cp'_2Zr(CH_3)(CB_{11}H_{12})$ (2). The reaction of $Cp'_2Zr(CH_3)_2$ (Cp′ = C_5H_4Me) with $Ag[CB_{11}H_{12}]$ in toluene or benzene yields $Cp'_2Zr(CH_3)(CB_{11}H_{12})$ (2, 95% NMR, 37% isolated) and

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(14) (a) Halogens: Jelínek, T.; Plesek, J.; Heřmánek, S.; Stíbr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819. (b) H$^+$: Jelínek, T.; Plesek, J.; Mares, F.; Heřmánek, S.; Stíbr, B. *Polyhedron* **1987**, *6*, 1981.

(15) Leading references: (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Scholz, J.; Schlegel, M.; Thiele, K. H. *Chem. Ber.* **1987**, *120*, 1369. (c) Scholz, J.; Rehbaum, F.; Thiele, K.-H.; Goddard, R.; Betz, P.; Krüger, C. *J. Organomet. Chem.* **1993**, *443*, 93.

(16) See Experimental Section and: Wiersema, R.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 785.

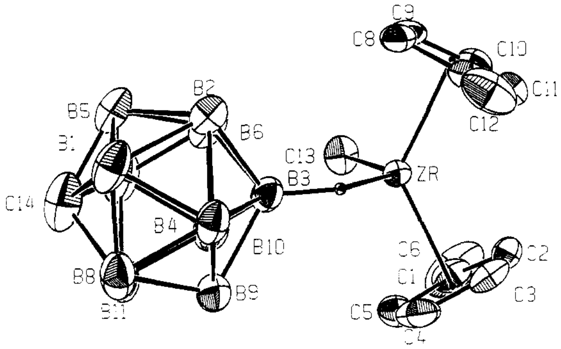

Figure 3. ORTEP view of $Cp'_2Zr(CH_3)(CB_{11}H_{12})$ (**2**).

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $Cp'_2Zr(CH_3)(CB_{11}H_{12})$ (2)[a]

Zr–C13	2.270(3)	$\overline{\mathrm{Zr{-}C}}_{\mathrm{ring1}}$	2.50(4)
Zr–B3	2.881(3)	$\overline{\mathrm{Zr{-}C}}_{\mathrm{ring2}}$	2.51(3)
Zr–C_0	2.209	$\overline{\mathrm{C{-}C}}_{\mathrm{ring1}}$	1.38(3)
Zr–C_{00}	2.208	$\overline{\mathrm{C{-}C}}_{\mathrm{ring2}}$	1.39(2)
Zr–HB3	2.06(3)	$\overline{\mathrm{B{-}B}}$	1.77(2)
B3–HB3	1.19(5)	$\overline{\mathrm{C{-}B}}$	1.71(3)
C1–C6	1.500(6)	$\overline{\mathrm{B{-}H}}$	1.11(5)
C7–C12	1.504(5)		
C13–Zr–B3	105.6(1)	B3–Zr–C_{00}	106.1
C13–Zr–C_0	104.9	C_0–Zr–C_{00}	128.1
C13–Zr–C_{00}	103.7	Zr–HB3–B3	123(2)
B3–Zr–C_0	107.1	Zr–B3–C14	144.5(2)

[a] C_0 = centriod of C1–C5 Cp′ ring; C_{00} = centroid of C7–C11 Cp′ ring.

ethane, as indicated in eq 1. Manipulation of **2** was hindered by thermal decomposition which appears to yield several products and was not studied in detail. Complex **2** is also formed by reaction of $Cp'_2Zr(CH_3)_2$ with $[Cp'_2Fe][CB_{11}H_{12}]$, although this reaction is not as clean as the $Ag[CB_{11}H_{12}]$ reaction.

The molecular structure of **2** as determined by a single-crystal X-ray diffraction study is shown in Figure 3. Metrical and positional parameters are listed in Tables IV and V. The structure of **2** consists of an unexceptional bent metallocene $Cp'_2Zr(CH_3)^+$ fragment to which the $CB_{11}H_{12}^-$ anion is coordinated via a single B–H–Zr bridge. As for **1**, the B–H bond opposite the CH of the cage bridges to Zr. The bridging H atom was located and isotropically refined. The Zr–μ-H–B angle (123°) is considerably smaller and the Zr–B distance shorter than the values estimated for **1**, indicating a stronger Zr–carborane interaction.[17] The Zr–H–B angle is more in line with what has been observed for other M–H–B systems.[6] The CH_3–Zr–HB angle (105.4°) is somewhat larger than generally observed for d^0 Cp_2MX_2 complexes (94–97°),[18] perhaps as a result of the bulky $CB_{11}H_{12}^-$, although this structure is clearly less crowded than **1**.

NMR studies of **2** indicate that the $CB_{12}H_{12}^-$ ligand is highly labile. The ^1H NMR spectrum of a toluene-d_8 solution of **2** at 25 °C contains only two multiplets for the C_5H_4Me hydrogens, and the ^{13}C NMR spectrum contains only two Cp′ CH resonances. These data indicate that the sides of the Cp′ ligands are equivalent and establish that rapid site exchange of the Zr–CH_3 and Zr–carborane ligands is occurring. An upfield ^1H NMR Zr–H–B resonance is not observed in this case; presumably it is broadened by exchange. The $\{^1H\}^{11}B$ NMR spectrum is similar to that for **1**. Addition of THF to **2** yields the known THF adduct $Cp'_2Zr(CH_3)(THF)^+$.[19] Complex **2** catalyzes the oligomerization of propene to primarily 2-methyl-1-pentene and 2,4-dimethyl-1-heptene (toluene-d_8, 23 °C, <1 atm), via an insertion/β-H elimination process.

Table V. Positional Parameters for $Cp'_2Zr(CH_3)(CB_{11}H_{12})$ (2)[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Zr	0.40901(1)	0.21530(1)	0.523	2.766(3)
C1	0.4919(3)	0.3013(2)	0.3218(5)	5.03(7)
C2	0.5599(2)	0.2802(2)	0.4401(6)	4.38(7)
C3	0.5801(2)	0.2105(2)	0.4186(6)	4.81(8)
C4	0.5240(3)	0.1871(2)	0.2879(5)	5.22(7)
C5	0.4693(3)	0.2405(2)	0.2286(5)	6.28(9)
C6	0.4589(4)	0.3739(2)	0.291(1)	10.9(2)
C7	0.4707(2)	0.1674(2)	0.8024(4)	3.87(6)
C8	0.3671(3)	0.1669(2)	0.8100(5)	4.38(6)
C9	0.3341(2)	0.2360(2)	0.8062(5)	4.89(7)
C10	0.4164(2)	0.2778(2)	0.7944(6)	4.26(7)
C11	0.4989(2)	0.2364(2)	0.7955(5)	4.12(6)
C12	0.5371(3)	0.1054(2)	0.8116(6)	6.43(9)
C13	0.2812(2)	0.2872(1)	0.4637(6)	4.76(8)
B1	0.2341(3)	−0.0454(2)	0.4213(7)	5.0(1)
B2	0.2737(3)	0.0205(2)	0.5601(5)	4.24(9)
B3	0.3408(2)	0.0797(2)	0.4328(5)	3.61(7)
B4	0.3517(2)	−0.0088(2)	0.3940(6)	4.03(8)
B5	0.1515(2)	0.0204(2)	0.4774(7)	4.8(1)
B6	0.2168(2)	0.0987(2)	0.4916(8)	5.1(1)
B8	0.2765(3)	−0.0263(2)	0.2207(7)	5.01(9)
B9	0.3444(3)	0.0499(2)	0.2209(6)	4.50(8)
B10	0.2608(3)	0.1168(2)	0.2804(7)	4.83(9)
B11	0.2206(3)	0.0491(2)	0.1474(7)	5.7(1)
B12	0.1431(3)	0.0798(2)	0.3133(9)	5.5(1)
C14	0.1564(3)	−0.0071(2)	0.2780(9)	6.8(1)
C_0	0.5250	0.2439	0.3393	4*
C_{00}	0.4174	0.2168	0.8017	4*

[a] See footnote *a*, Table III.

Attempts to extend the synthesis of **2** to other zirconocene–methyl systems met with only minimal success due in part to the thermal instability of the products. We were able, however, to isolate the parent system $Cp_2Zr(CH_3)(CB_{11}H_{12})$, which has been characterized spectroscopically and exhibits properties similar to those of **2**. $Cp_2Zr(CH_3)(CB_{11}H_{12})$ reacts with CH_3CN to give the known $Cp_2Zr(CH_3(CH_3CN)_2^+$;[11b] this complex is also formed directly via reaction of $[Cp'_2Fe][CB_{11}H_{12}]$ with $Cp_2Zr(CH_3)_2$ in CH_3CN. $Cp_2Zr(CH_3)(CB_{11}H_{12})$ also oligomerizes propene (to predominantly 2-methyl-1-pentene, <1 atm, 23 °C, benzene-d_6).

Reaction of Cp'_2ZrCl_2 and $Ag[CB_{11}H_{12}]$. One question of long-standing interest is whether the Ag^+ cleavage of Zr–R bonds in eq 1 and related reactions involves alkyl group abstraction to yield intermediate [AgR] species (which decompose to R_2) or proceeds via electron transfer yielding the R radical and Ag^0 directly.[1,11,12,20] The former seems unlikely, given the low nucleophilicity of $CB_{11}H_{12}^-$ and the expected poor leaving-group ability of CH_3^-. Reed has commented previously on the unfavorability of X$^-$

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[17] See Discussion in: Bau, R.; Teller, R. G.; Kirtly, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

[18] (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B.* **1974**, *B30*, 2290. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood, Ltd.: Chichester, U.K., 1986; Chapter 4.

[19] Wang, Y.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406.

[20] (a) Burk, M. R.; Tumas, W.; Ward, M. D.; Wheeler, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 6133. (b) See also: Seligson, A. L; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 7085.

"abstraction" or transfer reactions in the absence of nucleophilic solvents, ligands, or anions.[6d,7] To probe this question, we briefly investigated the reaction of Cp'_2ZrCl_2 with $Ag[CB_{11}H_{12}]$, in which electron-transfer pathways should be much less accessible. In fact, when this reaction is monitored by ^1H NMR, very small but reproducible shifts in the resonances of the reactants are observed, suggesting some adduct formation (eq 2). However, there is no evidence for the formation of AgCl and $Cp'_2ZrCl(CB_{11}H_{12})$,[21] even after heating to 50 °C. These results strongly suggest that electron transfer from a Zr–R bond to Ag^+ (probably after initial adduct formation) is the key step in these oxidative cleavage reactions.

$$Cp_2Zr\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + Ag[CB_{11}H_{12}] \rightleftharpoons Cp_2Zr\begin{smallmatrix}Cl\\Cl{-}Ag[CB_{11}H_{12}]\end{smallmatrix} \quad (2)$$

Synthesis, Structure, and Reactivity of $Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3). Ten-electron, d^0 cations of general form $CpMR_2^+$ are of interest because of the high electrophilicity/reactivity which is expected to result from the high coordinative unsaturation. Cations of this type are possible active species in $CpMX_3$-based syndiospecific styrene polymerization catalysts.[22] We previously described a series of $Cp^*Zr(CH_3)_2L_n^+$ complexes (L = THF, phosphine), which due the presence of stabilizing ligands L are relatively unreactive.[23] The lability of the $CB_{11}H_{12}^-$ ligands of 1 and 2 suggested that $Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3) might be more reactive, and we therefore explored the synthesis of this complex.

The reaction of $Cp^*Zr(CH_3)_3$ with $Ag[CB_{11}H_{12}]$ yields $Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3, quantitative by ^1H NMR, 40% isolated) and ethane (eq 3). Complex 3 is isolated as a yellow crystalline solid and is considerably more thermally stable than 1 and 2. It is stable below 70 °C in toluene for hours but reacts above 80 °C to yield as yet uncharacterized products.

$$Cp^*Zr(CH_3)_3 + Ag[CB_{11}H_{12}] \rightarrow \underset{\mathbf{3}}{Cp^*Zr(CH_3)_2(CB_{11}H_{12})} + {}^1\!/_2CH_3CH_3 + Ag^0 \quad (3)$$

The molecular structure of 3, as determined by X-ray diffraction, is shown in Figure 4. Metrical and positional parameters are listed in Tables VI and VII. The hydrogen atoms were located and refined isotropically. The $CB_{11}H_{12}^-$ anion is coordinated to the $Cp^*Zr(CH_3)_2^+$ fragment in a tridentate fashion via three B–H–Zr bridges involving the B–H bonds on a triangular face opposite the carborane carbon. This is a new coordination mode for $CB_{11}H_{12}^-$ and can be ascribed to the high electrophilicity and uncrowded structure of the $Cp^*Zr(CH_3)_2^+$ cation. This structure is reminiscent of the tridentate coordination (via three B–H–Mn bridges) of $B_3H_8^-$ and the $B_8H_{13}^-$ fragment to "$Mn(CO)_3$" in $Mn(CO)_3(B_3H_8)$ and $Mn(CO)_3(B_8H_{13})$.[24] More recently, similar interactions of electrophilic metal centers with triangular faces of boron hydride cluster species were observed in $[Cp^*_2Th(CH_3)][(C_2B_9H_{11})_2Fe)]$[25] and invoked to explain the fluxional behavior of lanthanide carborane species.[26] The Zr–Cp* and Zr–CH_3 distances are comparable to those in $Cp^*Zr(CH_3)_2(THF)_2^+$.[23]

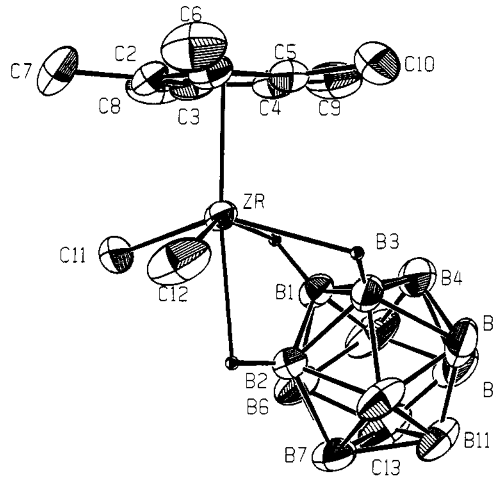

Figure 4. ORTEP view of $Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3).

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3)[a]

Zr–C11	2.245(2)	B1–HB1	1.18(2)
Zr–C12	2.236(2)	B2–HB2	1.09(2)
Zr–C_0	2.200	B3–HB3	0.97(2)
Zr–B_0	2.536	$\overline{\mathrm{Zr{-}C_{ring}}}$	2.505(6)
Zr–B1	2.720(2)	$\overline{\mathrm{(C{-}C)_{ring}}}$	1.41(1)
Zr–B2	2.751(2)	$\overline{\mathrm{C_{ring}{-}C_{Me}}}$	1.51(1)
Zr–B3	2.717(3)	$\overline{\mathrm{B{-}B}}$	1.75(2)
Zr–HB1	2.24(2)	$\overline{\mathrm{C{-}B}}$	1.71(2)
Zr–HB2	2.40(2)	$\overline{\mathrm{B{-}H}}$	1.04(3)
Zr–HB3	2.32(2)	$\overline{\mathrm{C_{Me}{-}H}}$	0.97(7)
C11–Zr–C12	99.6(1)	C_0–Zr–HB1	100.7
C11–Zr–C_0	107.6	C_0–Zr–HB2	174.9
C12–Zr–C_0	107.9	C_0–Zr–HB3	104.6
C11–Zr–HB1	79.7(6)	C11–Zr–B_0	101.2
C11–Zr–HB2	77.2(5)	C12–Zr–B_0	105.0
C11–Zr–HB3	142.6(6)	C_0–Zr–B_0	104(2)
C12–Zr–HB1	150.0(6)	Zr–HB1–B1	101(1)
C12–Zr–HB2	72.8(5)	Zr–HB2–B2	97(1)
C12–Zr–HB3	87.9(6)	Zr–HB3–B3	104(2)

[a] C_0 and B_0 = centroids of the Cp ring and the B1–B2–B3 face.

NMR spectral data do not provide detailed information about the solution structure of 3, although it is likely that the η3-coordination mode is retained. The ^1H NMR spectrum contains the expected Cp*, Zr–CH_3, and carborane C–H resonances and broad terminal B–H resonances; resonances assignable to the μ-H hydrogens are not observed. The $\{^1H\}^{11}B$ NMR spectrum contains two signals (integrating for 1B and 10B) and is similar to but shifted from that of $Ag[CB_{11}H_{12}]$. The ^1H and ^{11}B NMR spectra remain essentially unchanged down to 208 K.[27] It is likely that the $Cp^*Zr(CH_3)_2^+$ fragment undergoes rapid migration around the five equivalent triangular faces opposite the carbon of the $CB_{11}H_{12}^-$ cluster.

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[21] For $Cp_2Zr(X)L_n^+$ complexes see: Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383.

[22] For leading references and discussions of possible active species in these catalyst systems see: (a) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356. (b) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1991**, *192*, 223. (c) Chien, J. C. W.; Salajka, Z.; Dong, S. *Macromolecules* **1992**, *25*, 3199. (d) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rap. Commun.* **1992**, *13*, 265. (e) Campbell, R. E. European Patent Appl. 90310495.8, 1990.

[23] Crowther, D. J.; Jordan, R. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 2574.

[24] (a) Gaines, D. F.; Hildebrandt, S. J. *Inorg. Chem.* **1978**, *17*, 794. (b) Calabrese, J. C.; Fischer, M. B.; Gaines, D. F.; Lott, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 6318.

[25] See ref 11 in: Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

[26] Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009.

[27] ^1H-coupled spectra were obtained, but it was not possible to reliably determine J_{BH} values due to overlapping resonances.

Table VII. Positional Parameters for $Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3)[a]

atom	x	y	z	B (Å^2)
Zr	0.69352(1)	0.06838(1)	0.30090(2)	3.104(3)
C1	0.7510(2)	0.1872(1)	0.2266(2)	4.30(4)
C2	0.6427(2)	0.1784(1)	0.1766(3)	4.85(5)
C3	0.6432(2)	0.1269(1)	0.0662(3)	4.86(4)
C4	0.7502(2)	0.1044(1)	0.0514(2)	4.45(4)
C5	0.8154(2)	0.1413(1)	0.1495(2)	4.14(4)
C6	0.7927(3)	0.2432(1)	0.3261(4)	7.15(8)
C7	0.5498(3)	0.2213(2)	0.2247(5)	9.4(1)
C8	0.5494(3)	0.1052(2)	−0.0296(4)	9.62(8)
C9	0.7886(4)	0.0557(2)	−0.0653(3)	7.75(9)
C10	0.9380(2)	0.1379(2)	0.1591(4)	6.89(7)
C11	0.5148(2)	0.0484(2)	0.3083(3)	5.83(6)
C12	0.7182(3)	0.1169(2)	0.5201(3)	7.43(8)
B1	0.7323(2)	−0.0653(1)	0.2321(3)	4.28(5)
B2	0.7290(2)	−0.0592(1)	0.4221(3)	3.85(4)
B3	0.8441(2)	−0.0327(1)	0.3300(4)	4.83(5)
B4	0.8633(3)	−0.0896(2)	0.1820(4)	8.39(8)
B5	0.7582(4)	−0.1511(2)	0.1862(4)	8.6(1)
B6	0.6744(3)	−0.1318(2)	0.3358(4)	5.88(6)
B7	0.7532(3)	−0.1409(1)	0.4978(4)	5.63(6)
B8	0.8591(3)	−0.0787(2)	0.4949(4)	5.78(6)
B9	0.9421(3)	−0.0983(2)	0.3469(6)	8.1(1)
B10	0.8849(4)	−0.1697(2)	0.2593(5)	8.44(9)
B11	0.8839(3)	−0.1636(2)	0.4457(4)	6.27(7)
C13	0.7754(3)	−0.1932(2)	0.3505(4)	8.17(9)
C_0	0.7204	0.1476	0.1340	4*

[a] See footnote *a*, Table III.

Complex **3** is much less reactive than **1** or **2**. It does not react at an appreciable rate with propene (23 °C), 2-butyne (23 °C), or styrene (75 °C). This is presumably due to the inability of these hydrocarbon substrates to displace the η^3-carborane ligand. Complex **3** does react with THF to yield the known $Cp^*Zr(CH_3)_2(THF)_3^+$ and free $CB_{11}H_{12}^-$.

Summary

The reaction of $Ag[CB_{11}H_{12}]$ with Zr(IV) alkyls provides a route to soluble ion pairs in which $CB_{11}H_{12}^-$ bonds to the metal cation via one or three B–H–Zr bridges. The $Cp_2Zr(R)(\eta^1\text{-}CB_{11}H_{12})$ species **1** and **2** are highly reactive due to the lability of the monodentate carborane ligand and catalyze the polymerization of ethylene and the oligomerization of propene. In contrast, $Cp^*Zr(CH_3)_2(\eta^3\text{-}CB_{11}H_{12})$ is relatively unreactive with unsaturated hydrocarbons under comparable conditions, probably because the tridentate carborane ligand is not as easily displaced. Thus the "least coordinating" anion has met its match in "$Cp^*Zr(CH_3)_2^+$". In our future work we hope to learn more about the advantages and disadvantages of $CB_{11}H_{12}^-$ versus other weakly coordinating anions in early metal systems.[1,3,10]

Experimental Section

General procedures used in our laboratories have been described in detail in previous publications.[28] ^{11}B NMR spectra are referenced to $BF_3\cdot OEt_2$. $Cp_2Zr(CH_3)_2$,[29] $Cp'_2Zr(CH_3)_2$,[30] $Cp_2Zr(CH_2Ph)_2$,[31] and $Cp^*Zr(CH_3)_3$[32] were prepared by literature methods. $Cs[CB_{11}H_{12}]$ was prepared by Reed's modification of the literature procedure ($\{^1H\}^{11}B$ NMR (acetone-d_6) δ −6.1 (1B), −12.55 (5B), −15.63 (5B)).[6a] $Ag[CB_{11}H_{12}]$ was prepared via metathesis of the Cs^+ salt according to Reed's procedure[6a] (^1H NMR (C_6D_6) δ 2.62 (CH); $\{^1H\}^{13}C$ NMR (C_6D_6) δ 55.5 (CH); $\{^1H\}^{11}B$ NMR (C_6D_6) δ −11.27 (1B), −14.95 (10B)).

$[Cp'_2Fe][CB_{11}H_{12}]$. A mixture of Cp'_2Fe (1.55 g, 7.25 mmol) in 85% H_2SO_4 (20 mL) was stirred at 25 °C for 40 min. The reaction mixture was poured into 600 mL of H_2O/ice, and the resultant mixture was filtered to yield a clear blue filtrate. The filtrate was added to an aqueous solution (400 mL) of $Cs[CB_{11}H_{12}]$ (2.0 g, 7.25 mmol). A light blue solid formed immediately and was collected by filtration and dried under high vacuum for 12 h (1.60 g, 16.5%). This compound is only sparingly soluble in benzene or toluene but very soluble in acetone. $\{^1H\}^{11}B$ NMR (75/25 benzene-d_6/acetone-d_6): δ −16.5 (1B), −21.5 (5B), −22.3 (5B). Anal. Calcd for $C_{13}H_{26}B_{11}Fe$: C, 43.72; H, 7.34. Found: C, 43.37; H, 7.65.

$Cp_2Zr(CH_2Ph)(CH_{11}H_{12})$ (1). A slurry of $Cp_2Zr(CH_2Ph)_2$ (0.256 g, 0.634 mmol) and $Ag[CB_{11}H_{12}]$ (0.164 g, 0.653 mmol) in toluene (25 mL) was prepared at −78 °C. The reaction mixture was warmed to 23 °C, and a black precipitate formed. The reaction mixture was stirred for 3.5 h and centrifuged to remove most of the Ag^0, and the supernate was filtered to remove the remaining Ag^0. The filtrate was evaporated to dryness under vacuum, benzene (25 mL) was added, and the solution was stirred for 12 h. The solvent volume was reduced to 15 mL, producing a crystalline solid, which was collected by filtration and dried for 15 h under high vacuum, yielding 0.140 g (48%) of bright yellow $Cp_2Zr(CH_2Ph)(CB_{11}H_{12})$. Crystals of **1** were obtained by slow evaporation of a toluene solution. They were coated with solvent-saturated Apiezon H grease to minimize solvent loss and mounted in 0.5-mm capillaries under N_2. ^1H NMR (toluene-d_8): δ 7.24 (t, J = 7.6 Hz, 2H, *m*-H), 6.30 (d, J = 7.5 Hz, 2H, *o*-H), 5.42 (s, 10H, Cp), 3.1–0.8 (br m, ca. 10H, $HCB_{11}H_{10}$), 2.56 (br s, 1H, carborane CH), 2.21 (s, 2H, $ZrCH_2$), −3.15 (br q, J_{BH} = 108 Hz, 1H, μ-H); *p*-H obscured by solvent. ^{11}B NMR (toluene-d_8): δ −8.1 (d, J_{BH} = 100 Hz, 1B), −14.1 (d, J_{BH} = ca. 154 Hz, 5B), −15.6 (d, J_{BH} = 160 Hz, 5B). ^{13}C NMR (benzene-d_6); δ 132.0 (d of d, $^1J_{CH}$ = 162 Hz, $^3J_{CH}$ = 8.2 Hz, *o*- or *m*-C), 125.6 (d of t, $^1J_{CH}$ = 155 Hz, $^3J_{CH}$ = 6.3 Hz, *p*-C), 111.6 (d, J_{CH} = 176 Hz, Cp), 53.2 (d, J_{CH} = 168 Hz, carborane CH), 50.6 (t, J_{CH} = 140 Hz, $ZrCH_2$); remaining aryl resonance obscured by solvent. Anal. Calcd for $C_{18}H_{29}B_{11}Zr$: C, 47.46; H, 6.41; Zr, 20.02. Found: C, 47.16; H, 6.39; Zr, 19.94.

$Cp'_2Zr(CH_3)(CB_{11}H_{12})$ (2). Solid $Ag[CB_{11}H_{12}]$ (0.85 g, 0.34 mmol) was added to a solution of $Cp'_2Zr(CH_3)_2$ (0.97 g, 0.35 mmol) in 20 mL of toluene. The reaction mixture was stirred for 12 h at 23 °C and filtered through Celite. The yellow filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (20 mL) and cooling to −35 °C resulted in the precipitation of a yellow solid, which was collected by filtration and dried under vacuum; yield 0.51 g, 37%. Attempts to purify this compound further were unsuccessful due to thermal decomposition. Crystals for the X-ray diffraction study were obtained by slow cooling of the original toluene filtrate and mounted in capillaries under N_2. ^1H NMR (toluene-d_8): δ 5.54 (m, 4H, C_5H_4Me), 5.25 (m, 4H, C_5H_4Me), 2.50 (s, 1H, carborane CH), 1.65 (s, 6H, C_5H_4Me), 0.39 (s, 3H, $ZrCH_3$). $\{^1H\}^{13}C$ NMR (toluene-d_8): δ 126.4 (Cp′ ipso), 113.9 (Cp′), 110.7 (Cp′), 53.7 (carborane C), 38.3 ($ZrCH_3$), 15.2 (Cp′ CH_3). $\{^1H\}$ ^{11}B NMR (toluene-d_8): −8.4 (1B), −13.8 (5B), −15.0 (5B).

$Cp_2Zr(CH_3)(CB_{11}H_{12})$. A solution of $AgCB_{11}H_{12}$ (0.15 g, 0.60 mmol) in 5 mL of toluene was added to a solution of Cp_2ZrMe_2 (0.15 g, 0.59 mmol) in toluene (7 mL), resulting in the immediate formation of a black precipitate. After 10 min, the reaction mixture was filtered through Celite to yield an orange-yellow filtrate. Evaporation of the filtrate under high vacuum yielded an orange solid (0.21 g, 92%). Attempts to further purify this product were thwarted by the thermal decomposition. ^1H NMR (benzene-d_6): δ 5.40 (s, 10H, Cp), 2.60 (s, 1H, $CHB_{11}H_{11}$), 0.45 (s, 3H, ZrMe). $\{^1H\}^{11}B$ NMR (toluene-d_8): δ −9.4 (ca. 1B), −13.9 (10B).

Reaction of Cp'_2ZrCl_2 with $Ag[CB_{11}H_{12}]$. A solution of Cp'_2ZrCl_2 (12 mg, 0.037 mmol) and $Ag[CB_{11}H_{12}]$ (9.4 mg, 0.037

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(28) Leading reference: Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098.

(29) Samuel, E.; Rausch, M. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

(30) Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291.

(31) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406 and references therein.

(32) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

mmol) in toluene-d_8 was prepared and monitored by ^{1}H NMR. Slight but reproducible shifts in the resonances for both reactants were observed, indicating adduct formation. There was no further change after 24 h at 23 °C nor after heating to 50 °C for 18 h. $Cp'_2ZrCl_2 + Ag[CB_{11}H_{12}]$: ^{1}H NMR (benzene-$d_6$) δ 5.78 (t, J = 3 Hz, 4H), 5.69 (t, J = 3 Hz, 4H), 2.67 (s, 1H, carborane CH), 2.07 (s, 6H); ^{13}C NMR δ 129.3, 117.6, 112.6, 55.2 (carborane CH), 15.5. Cp'_2ZrCl_2: ^{1}H NMR (benzene-d_6) δ 5.77 (t, J = 3 Hz, 4H), 5.65 (t, J = 3 Hz, 4H), 2.10 (s, 6H); ^{13}C NMR (benzene-d_6) δ 129.9, 117.4, 112.0, 15.5.

$Cp^*Zr(CH_3)_2(CB_{11}H_{12})$ (3). A solution of $Cp^*Zr(CH_3)_3$ (0.95 g, 3.5 mmol) and $Ag[CB_{11}H_{12}]$ (0.97 g, 3.9 mmol) in hexane (50 mL) was prepared at −78 °C and warmed to 23 °C with stirring. After 2 h, the reaction mixture was filtered, leaving a black solid and a yellow filtrate. The filtrate was evaporated to dryness under vacuum and the resulting yellow solid washed with hexane and dried under vacuum; yield 0.56 g, 40%. The product may be recrystallized from toluene/hexane. X-ray crystals were grown by cooling a toluene/hexane solution to −35 °C and mounted in capillaries under N_2. ^{1}H NMR (toluene-d_8): δ 2.49 (2, 1H, carborane CH), 1.64 (s, 15H, Cp*), 0.32 (s, 6H, $ZrCH_3$). {^{1}H}^{13}C NMR (toluene-d_8): δ 124.0 (C_5Me$_5$), 59.0 (carborane C), 47.2 ($ZrCH_3$), 11.9 (C_5*Me*$_5$). {^{1}H}^{11}B NMR (toluene): δ −11.3 (1B), −12.8 (10B). Anal. Calcd for $C_{13}H_{33}B_{11}Zr$: C, 39.08; H, 8.32; Zr, 22.83. Found: C, 39.05; H, 8.37; Zr, 23.19.

X-ray Crystallography. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer system, and the crystallographic calculations were performed by using the SDP package for that system.[33] Details are summarized in the tables.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and H atom positions for **1**–**3**, positional parameters (including disordered solvent molecule) for **1**, and H atom bond distances and angles for **2** and **3** (27 pages). Ordering information is given on any current masthead page.

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[33] Frenz, B. A. The Enraf-Nonius CAD4 SDP System. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.