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and the mixture was allowed to warm to room temperature. THF was evaporated, and the residue was extracted with $CH_2Cl_2$, washed with distilled water, and dried over $MgSO_4$. A filtration through silica gel was performed to eliminate heavy compounds; dichloromethane was evaporated, and the residue was allowed to stand under argon for at least 48 h. During this time, **9** was transformed into **10**. The mixture was chromatographed with toluene. Yield of **10**: 1.6g (40%). $^1$H NMR ($CDCl_3$): $\delta$ 2.14 (s, 3 H, Me), 2.27 (m, 3 H, Me), 6.6–7.8 (m, 16 H, Ph + *H*C–P). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.69 (s, Me), 17.82 (s, Me), 149.97 (dd, $^2J$(C–P) = 6.6 Hz, $^3J$(C–P) = 16.5 Hz, $C_{\beta'}$), 161.31 (dd, $^2J$(C–P) = 12.6 and 5.5 Hz, $C_\beta$). Mass spectrum: *m/z* 404 ($M^+$, 87%), 217 ($Ph_2PS$, 100%). Anal. Calcd for $C_{24}H_{22}P_2S$: C, 71.27; H, 5.48. Found: C, 70.84; H, 5.20.

**3,3′,4,4′-Tetramethyl-2,2′-bis(diphenylphosphino)-1,1′-diphosphaferrocenes (11a and 11b).** To a stirred solution of **10** (1 g, $2.5 \times 10^{-3}$ mol) in THF (20 mL) were added lithium wire (0.05 g, $7.2 \times 10^{-3}$ mol) and naphthalene (0.5 g, $5 \times 10^{-3}$ mol) at room temperature. After 1 h, the mixture was cooled at 0 °C and aluminum chloride (0.08 g, $6 \times 10^{-4}$ mol) was added. After 30 min, the mixture was allowed to warm to room temperature and iron(II) chloride (0.16 g, $1.25 \times 10^{-3}$ mol) added. After an additional 30 min, the THF was evaporated and the residue chromatographed with hexane/toluene 50/50 as the eluent. Two isomers **11a** and **11b** were obtained in an 85/15 ratio. Total yield (**11a** + **11b**): ~0.3 g (40%).

**11a**: $^1$H NMR ($CDCl_3$) $\delta$ 2.00 (s, 6 H, Me), 2.13 (s, 6 H, Me), 3.90 (d, $^2J$(H–P) = 35.6 Hz, 2 H, CH–P); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.50 (d, $^3J$(C–P) = 15 Hz, Me), 16.31 (s, Me), 85.42 (d, $^1J$(C–P) = 63.2 Hz, $C_5H$), 93.85 (dd, $^1J$(C–P) = 80.6 and 15.8 Hz, $C_2P$), 100.20 (dd, $^2J$(C–P) = 20.8 and 5.6 Hz, $C_3$), 101.97 (s, $C_4$); mass spectrum *m/z* 646 ($M^+$, 100%), 461 ($M^+ - PPh_2$, 57%). Anal. Calcd for $C_{36}H_{34}P_4Fe$: C, 66.89; H, 5.30. Found: C, 66.22; H, 5.27.

**11b**: $^1$H NMR ($CDCl_3$) $\delta$ 1.95 (s, 6 H, Me), 2.21 (s, 6 H, Me), 3.74 (m, 2 H, CH–P); $^{13}$C NMR ($CDCl_3$) $\delta$ 12.65 (d, $^3J$(C–P) = 15.5 Hz, Me), 14.28 (s, Me), 83.32 (m, $C_5H$), 100.92 (m, $C_3$), 103.16 (s, $C_4$). The loss of symmetry in **11b** (vs **11a**) explains the appearance of higher-order patterns in the $^1$H and $^{13}$C spectra, thus confirming the structural assignments made on the basis of the preliminary X-ray study of **12a**.

**[3,3′,4,4′-Tetramethyl-2,2′-bis(diphenylphosphino)-1,1′-diphosphaferrocene]tetracarbonylmolybdenum (12a and 12b).** Two different experiments were performed: (1) Diphosphaferrocene **11a** (0.28 g, $0.43 \times 10^{-3}$ mol) was heated at 100 °C in 5 mL of toluene with molybdenum hexacarbonyl (0.12 g, $0.46 \times 10^{-3}$ mol) for 90 min. Toluene was removed, and the residue was chromatographed with hexane/toluene 50/50 as the eluent. Yield of **12a**: 0.32 g (85%). (2) Diphosphaferrocene **11b** (0.11 g, $0.17 \times 10^{-3}$ mol) was heated at 60 °C in 5 mL of toluene with norbornadiene–$Mo(CO)_4$ (0.05 g, $0.17 \times 10^{-3}$ mol) for 15 min. Toluene was removed and the residue chromatographed as before. Yield of **12b**: 0.08 g (55%).

**12a**: $^{31}$P NMR ($CH_2Cl_2$) $\delta$(*P*$Ph_2$) +34.7, $\delta$(cyclic P) −54 (both resonances appear as complex multiplets); $^1$H NMR ($CDCl_3$) $\delta$ 1.60 (s, 6 H, Me), 1.88 (s, 6 H, Me), 3.70 (m, 2 H, CH–P); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.99 (s, Me), 14.66 (s, Me), 80.22 (m, $C_5H$), 99.72 (m, $C_3$), 102.88 (m, $C_4$). Anal. Calcd for $C_{40}H_{34}O_4P_4FeMo$: C, 56.21; H, 3.98. Found: C, 56.59; H, 3.93.

**12b**: $^{31}$P NMR (toluene) $\delta$(*P*$Ph_2$) +35.6, $\delta$(cyclic P) −42.7 (both resonances appear as complex multiplets); $^1$H NMR ($CDCl_3$) $\delta$ 2.25 (s, 6 H, Me), 2.31 (s, 6 H, Me), 3.62 (m, 2 H, CH–P).

**Registry No.** **6**, 138784-72-2; **9**, 138784-68-6; **10**, 138784-69-7; **11a**, 138874-90-5; **11b**, 138784-70-0; **12a**, 138875-98-6; **12b**, 138784-71-1; 1-phenyl-3,4-dimethylphosphole sulfide, 30540-37-5; chlorodiphenylphosphine, 1079-66-9.

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# Metallacarboranes as Labile Anions for Ionic Zirconocene Olefin Polymerization Catalysts

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*Summary:* Anions of the type $[(C_2B_9H_{11})_2M]^-$ (M = Fe, Co, Ni) are suitable for use as "noncoordinating" anions with $[Cp_2ZrMe]^+$ cations. Catalysts generated from $Cp_2ZrMe_2$ and $[PhNMe_2H][(C_2B_9H_{11})_2M]$ are active for the polymerization and copolymerization of ethylene and $\alpha$-olefins. Spectroscopic examination of the cobalt complex indicates that the anion is weakly coordinated to the metal at room temperature. At low temperatures, however, the aniline-coordinated adduct $[Cp_2ZrMe(NMe_2Ph)][(C_2B_9H_{11})_2M]$ is present. These catalysts are active in toluene or hexane for the polymerization of ethylene and the copolymerization of ethylene and 1-butene.

Homogeneous Ziegler–Natta polymerization catalysts based on bis(cyclopentadienyl)metal complexes of the type $Cp'_2MX_2$, discovered in the early 1950s,[1] have long been used as model systems for mechanistic studies. Whether the active catalytic species is cocatalyzed by trialkylaluminum reagents or by methylaluminoxane,[2] the nature of this species has for many years been the subject of controversy. It is now generally established through many approaches, including electrochemical,[3] theoretical,[4] trapping,[5] XPS,[6] surface studies[7] and research on neutral isoelectronic compounds,[8] that the active complex is the formally three-coordinate cation $[Cp'_2MR]^+$.[9] A clear determination of the structures of these catalysts, however, has been precluded by the instability of the catalyst[1a] or the indeterminate nature of methylaluminoxane.

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**Table I. $^{13}C$ NMR Chemical Shifts of Zirconocene Complexes (in Toluene-$d_8$)**

| compd | $^{13}C$ NMR chem shifts, ppm (vs TMS) | | | | |
|---|---|---|---|---|---|
| | Zr–$CH_3$ | $(C_2B_9H_{11})_2Co$ | $C_5H_5$ | $Ph_2N(CH_3)_2$ | $(C_6H_5)_2NMe_2$ |
| $Cp_2ZrMe_2$ | 30.3 | | 110.3 | | |
| $PhNMe_2$ | | | | 40.2 | 112.9, 116.9, 129.3, 150.9 |
| **1a** (at 264 K) | 30.0 | 52.8 | 112.1 | 40.1[a] | 112.8, 116.9, 129.3, 150.8[a] |
| **2a** (at 233 K) | 45.6 | 52.2 | 115.4 | 48.8 | 119.5, 148.1[b] |

[a] Free DMA from reaction. [b] Other DMA signals overlap.

For these reasons, aluminum alkyl free ionic compounds of the type $[Cp'_2MR][A]$ (Cp′ = substituted or unsubstituted cyclopentadienide, A = "noncoordinating" anion) have received increasing attention in recent years as olefin polymerization catalysts.[10] The preparation of effective and versatile catalysts has been hampered by a paucity of suitable counterions for the strongly Lewis acidic metallocene cation. The use of $PF_6^-$ or $BPh_4^-$ with "naked" $Cp'_2MR^+$ cations can result in anion degradation,[11] poor anion lability,[12] or instability at elevated temperatures in chlorinated solvents.[13] Base-coordinated adducts such as $[Cp'_2MMe(THF)][BPh_4]$ polymerize ethylene relatively slowly and require solvents of higher dielectric constant due to the insufficient lability of the Lewis base.[14] Recently, base-free catalysts, prepared by protonolysis of $Cp^*_2ZrMe_2$ ($Cp^* = C_5Me_5$) by $C_2B_9H_{13}$ or $[HNR_3][BPh_4]$, have been prepared and characterized,[15] but less substituted metallocenes undergo secondary reactions with these compounds to give catalytically inactive materials.[16] We have found that polyhedral borane complexes of even greater size and lower chemical reactivity, such as metallacarboranes, lead to more versatile ionic metallocene catalysts which are active in low-dielectric solvents such as toluene.[17] Recent reports in the literature[18,19] concerning the use of metallacarboranes as anions compatible with electrophilic metallocene cations have prompted us to present our results on the preparation, NMR characterization, and polymerization behavior of metallacarborane-based zirconocene catalysts.

## Experimental Section

All reactions were carried out under a nitrogen atmosphere. Toluene was distilled from sodium benzophenone ketyl. $Cp_2ZrMe_2$ was prepared by a literature procedure.[20] $[(C_2B_9H_{11})_2M]^-$ anions (M = Co, Fe, Ni) were prepared by a literature procedure[21] and precipitated from aqueous solutions as the *N,N*-dimethylanilinium (DMAH) salts by addition of [DMAH][Cl]. The salts were recrystallized from $CH_2Cl_2$–hexane and then from hot toluene.

All NMR results were obtained with a Bruker MSL 400 spectrometer ($\nu_0(^{13}C) = 100.62$ MHz, $\nu_0(^{11}B) = 128.39$ MHz). All $^{11}B$ chemical shifts were measured with $BF_3{\cdot}OEt_2$ at 0 ppm as an internal coaxial reference. The $^{13}C$ NMR spectra were referenced to lock solvents with standard values. $^{11}B$–$^{11}B$ COSY spectra were zero-filled to 512 × 256, Fourier-transformed with $\sin^2$ apodization, and symmetrized, the accumulation time being several hours.

Polymerizations were carried out in a thermostated 1-L stainless-steel autoclave with heating/cooling provided through a steam–water mixture circulating through a stainless-steel jacket surrounding the autoclave body. Residual air and moisture was removed from the interior of the sealed reactor by heating to 125 °C under a dynamic purge of dry nitrogen for 30 min to 1 h. Dry, deoxygenated solvent followed by a toluene solution of the catalyst were added to the autoclave by a double-ended needle. If used, 1-butene was transferred from a cylinder through molecular sieves into a metering vessel and then added to the autoclave under nitrogen pressure. The reactor contents were stirred and heated to the polymerization temperature before the introduction of ethylene.

Molecular weights were determined at 145 °C in 1,2,4-trichlorobenzene using a Waters 150-C gel phase chromatograph and referenced to polystyrene standards.

**Bis(cyclopentadienyl)methyl(bis(undecahydro-7,8-dicarbaundecaborato)cobalt)zirconium (1a).** $Cp_2ZrMe_2$ (100 mg, 0.40 mmol) and $[DMAH][(C_2B_9H_{11})_2Co]$ (180 mg, 0.40 mmol) were stirred at room temperature in toluene (40 mL). After 1 h, the volume of the mixture was reduced in vacuo to 10 mL and pentane (50 mL) added carefully. The yellowish precipitate formed was filtered off, washed with pentane, and dried in vacuo to give 187 mg of **1a** (83% based on theoretical formulation). Products formed from these reactions contained variable and nonstoichiometric amounts of *N,N*-dimethylaniline. While accurate elemental analysis of the product was not possible, **1a** was characterized by $^1H$ and $^{13}C$ NMR spectroscopy. $^1H$ NMR (toluene-$d_8$, room temperature): $\delta$ 0.38 (s, Zr–$CH_3$), 2.80 (br s, $[(C_2B_9H_{11})_2Co]$), 5.60 (s, $C_5H_5$). $^{13}C$ NMR (toluene-$d_8$, room temperature): $\delta$ 30.8 (Zr–$CH_3$), 52.9 ($[(C_2B_9H_{11})_2Co]$), 112.3 ($C_5H_5$).

## Results and Discussion

**NMR Characterization.** Metallacarborane compounds of the type $[(C_2B_9H_{11})_2M]^-$ (M = Co, Fe, Ni)[20] are much larger than $[C_2B_9H_{12}]^-$, lack the secondary acidic hydrogens of the *nido*-carborane anions, and can be used as extremely labile counterions for a wide range of cationic $[Cp'_2ZrMe]^+$ complexes.[17,19] The reaction of $Cp_2ZrMe_2$ with $[DMAH][(C_2B_9H_{11})_2M]$ in toluene results in the formation of the moderately soluble monomethyl complexes $Cp_2ZrMe((C_2B_9H_{11})_2M)$ (**1a–c**; eq 1).

$$Cp_2ZrMe_2 + [DMAH][(C_2B_9H_{11})_2M] \rightarrow Cp_2ZrMe((C_2B_9H_{11})_2M) + DMA + CH_4 \quad (1)$$

**1a**: M = Co
**1b**: M = Fe
**1c**: M = Ni

Examination of the reaction mixture of $Cp_2ZrMe_2$ and $[DMAH][(C_2B_9H_{11})_2Co]$ by $^{13}C$ NMR spectroscopy indicates that an exchange between the cation–anion pair and the free amine is taking place. The $^{13}C$ NMR spectrum in toluene-$d_8$ of the reaction product of 1 equiv of $Cp_2ZrMe_2$ and 1 equiv of $[DMAH][(C_2B_9H_{11})_2Co]$ at room temperature shows that the adduct $Cp_2ZrMe((C_2B_9H_{11})_2Co)$ (**1a**) and free DMA are present (Table I). As the temperature of the mixture was lowered, the signals

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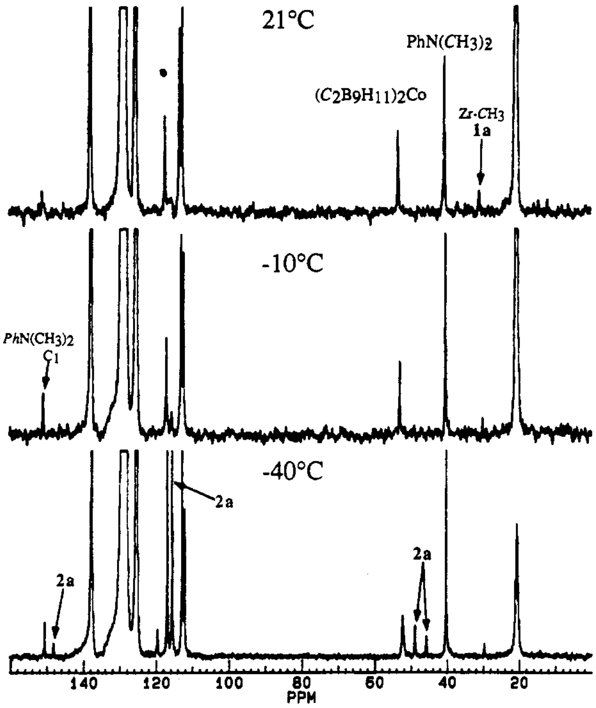

**Figure 1.** Variable-temperature $^{13}$C NMR spectra of **1a** with an additional 2 equiv of DMA (spectra in toluene-$d_8$).

of **1a** decreased and new signals appeared. An equilibrium exists between the neutral anion-coordinated complex **1a** and the amine-coordinated species **2a**, where the anion remains closely associated with the metallocene (eq 2).

$$\underset{\mathbf{1a}}{Cp_2ZrMe(A)} + DMA \rightleftarrows \underset{\mathbf{2a}}{[Cp_2ZrMe(DMA)][A]} \quad (2)$$

$$A = (C_2B_9H_{11})_2Co$$

Coordination of DMA to the metal center to produce **2a** resulted in a significant downfield shift of the zirconium methyl and DMA methyl signals (Table I). The shift of the DMA methyl signal was analogous to the shift observed upon quaternization or protonation of an amine; for instance, the methyl carbon signal of DMAH$^+$ appeared at 49.2 ppm. Overlap of some of the signals of the DMA ring carbon atoms in **2a** occurred, so that not all of these signals could be identified at all temperatures. Also, the cyclopentadienyl carbon signals of **1a** and **2a** were resolved. The equilibrium of eq 2 was illustrated clearly by the variable-temperature $^{13}$C NMR spectra of the 1:1 mixture of $Cp_2ZrMe_2$ and [DMAH][$(C_2B_9H_{11})_2Co$] to which was added an additional 2 equiv of DMA (Figure 1). Below about −10 °C a significant amount of **2a** was seen. At a temperature of about −80 °C the signals assigned to **1a** had disappeared, leaving only those of **2a**. The temperature dependence of the equilibrium indicates that **1a** and **2a** are enthalpically similar and that the low-temperature preponderance of **2a** is entropically driven. The rate of exchange between **1a** and **2a** is relatively slow even at room temperature, as evidenced by the lack of significant broadening or shifting of the Zr–$CH_3$ or DMA signals. The signal of the carbons of [$(C_2B_9H_{11})_2Co$]$^-$ appears broadened at −40 °C. This may be due to fluxionality of this anion in **2a**, whereas the anion in **1a** may be more rigidly coordinated; however, this was not conclusive.

The cation–anion interaction in complex **1a**, which is a critical factor in determining the stability of the catalyst, was further investigated by $^{11}$B NMR spectroscopy. The $^{11}$B NMR chemical shifts of the ionic compound [DMAH][$(C_2B_9H_{11})_2Co$] and the catalytically active species **1a** at room temperature in various solvents are summarized in Table II. The chemical shifts were somewhat dependent on solvent, but no conclusions could be drawn. In order to understand the $^{11}$B NMR data for **1a**, the anion of [DMAH][$(C_2B_9H_{11})_2Co$] was first studied as a model compound. The $^{11}$B chemical shifts observed for [$(C_2B_9H_{11})_2Co$]$^-$ were quite similar to those observed for ($\eta^5$-$C_5H_5$)Co($C_2B_9H_{11}$).[22] Assignments of the signals in the $^{11}$B spectrum and the 2D $^{11}$B–$^{11}$B COSY studies have been made. The 1D proton-coupled $^{11}$B spectrum of [DMAH][$(C_2B_9H_{11})_2Co$] in acetone-$d_6$ consists of three doublets of intensity 2 at δ −4.96, −5.68, and −16.86 ppm and three doublets of intensity 1 at δ 6.98, 1.76, and −22.30 ppm. The doublets of intensity 2 are the equivalent B–H types, boron atoms B(2,4), and B(9,11); the numbering scheme for the carborane cage is shown in Figure 2. The doublets of intensity 1 are the unique boron atoms B(1), B(3), and B(10). Analysis of the 2D $^{11}$B–$^{11}$B COSY spectrum gives the following correlations: B(1) ↔ B(2,4) strong, B(1) ↔ B(3) weak, B(1) ↔ B(5,6) weak, B(2,4) ↔ B(3) weak, B(2,4) ↔ B(5,6) strong, B(5,6) ↔ B(9,11) strong B(5,6) ↔ B(10) intermediate, B(9,11) ↔ B(10) strong. Analysis of these correlations and intensities readily shows that the $^{11}$B NMR spectra are consistent with the undecaborane structure except that a cross peak for B(2,4) ↔ B(9,11) is missing. It is not known why this cross peak should not appear.

**Table II. $^{11}$B NMR Chemical Shifts of [DMAH][$(C_2B_9H_{11})_2Co$] and 1a**

| compd (solvent) | $^{11}$B NMR chem shift, ppm B(10) | B(1) | B(9,11) | B(5,6) | B(2,4) | B(3) |
|---|---|---|---|---|---|---|
| [DMAH]-[$(C_2B_9H_{11})_2Co$] (acetone-$d_6$) | 7.0 | 1.8 | −5.0 | −5.7 | −16.9 | −22.3 |
| **1a** ($CD_2Cl_2$) | 5.2 | 1.4 | −5.9 | −6.8 | −17.4 | −22.8 |
| [DMAH]-[$(C_2B_9H_{11})_2Co$] ($CD_2Cl_2$) | 4.9 | 1.6 | −5.8 | −6.8 | −17.2 | −22.6 |
| **1a** (toluene-$d_8$) | 4.7 | 2.2 | −5.8 | −6.8 | −15.7 | −21.8 |
| [DMAH]-[$(C_2B_9H_{11})_2Co$] (toluene-$d_8$) | 4.8 | 2.6 | −5.8 | −5.9 | −16.7 | −22.3 |

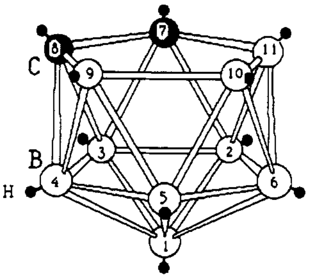

**Figure 2.** Numbering scheme for the carborane cage.

An examination of **1a** in toluene-$d_8$ by variable-temperature $^{11}$B NMR spectroscopy reveals that the structure adopted by this complex is temperature-dependent. The exchange shown in eq 2 occurs relatively slowly on the NMR time scale, and **1a** was the predominant species observed at temperatures above about −10 °C. Thus, the signals observed in the $^{11}$B NMR spectrum of the mixture of eq 1 in toluene-$d_8$ at temperatures from −10 to +60 °C are those only of **1a**. Below about −10 °C the $^{11}$B signals were too broad to observe due to reduced $T_1$. As the temperature was lowered from 60 °C, the signals of B(10)

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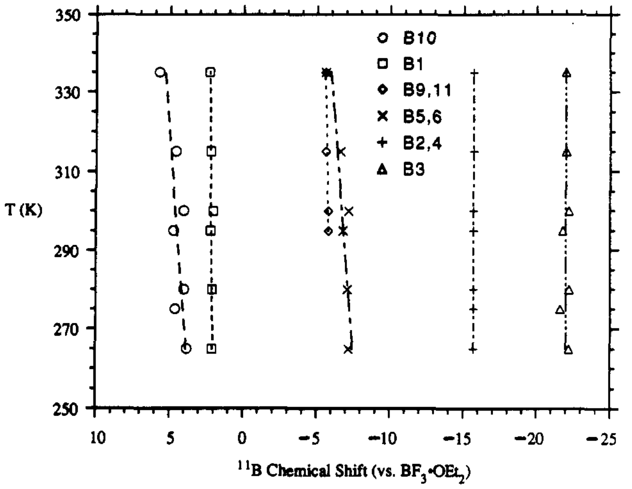

**Figure 3.** Temperature dependence of $^{11}$B NMR chemical shifts of **1a** in toluene-$d_8$.

and B(5,6) moved upfield (Figure 3). The $^{11}$B–$^{1}$H scalar couplings of all sites remained the same. These facts suggest that the binding interaction between the zirconium atom and the carborane cage occurs through the hydrides B(10)-*H*, B(5)-*H*, and B(6)-*H*, which are located on one triangular face of the icosahedron. Marks et al. have reported that the X-ray crystal structure of a related complex, $(Cp^*{}_2ThMe)_2((C_2B_9H_{11})_2Fe)$, also shows the $Cp^*{}_2ThMe^+$ cations coordinating through the same B–H groups as in **1a**.[18] By comparison, the positions of the signals in the $^{11}$B NMR spectrum of **1a** in $CD_2Cl_2$ and $[DMAH][(C_2B_9H_{11})_2Co]$ in $CD_2Cl_2$ or toluene-$d_8$ were temperature-invariant. The signals of the hydrides B(10)-*H*, B(5)-*H*, and B(6)-*H* were not observed separately in the $^1$H NMR spectrum. In the 2D $^{11}$B–$^{11}$B COSY NMR spectrum, the same correlations were observed for B(10), B(5), and B(6) of **1a** in toluene-$d_8$ as for $[DMAH][(C_2B_9H_{11})_2Co]$ in toluene-$d_8$ (Figure 4). The lack of perturbation of the $^1$H and $^{11}$B spectra suggests that the interaction between the zirconocene cation and the cobaltacarborane anion is quite weak.

**Polymerization Studies.** In the absence of a stabilizing solvento molecule such as THF, $[Cp_2MR]^+$ cations which use $[BPh_4]^-$ as the counterion can be degraded to catalytically inactive species by B–C bond cleavage,[16] though the use of peralkylcyclopentadienyl ligands leads to the formation of catalytically active $Cp^*{}_2Zr^{(+)}$-$(C_6H_4)$-$B^{(-)}Ph_3$ complexes.[14e,15] The catalytic activity of solvated metallocene cations $[Cp'_2MMe(THF)]^+$ is frequently low due to the competition between the THF molecule and the incoming monomer.[10]

Whereas THF- or THT-coordinated zirconocene monomethyl cations require high-polarity solvents ($CH_2Cl_2$, PhCl, PhOMe) to function as polymerization catalysts,[14] compounds **1a–c** react rapidly with ethylene to form linear polyethylene in a toluene diluent.[23] Compound **1a** in toluene polymerizes ethylene (90 psi, 60 °C) to linear polyethylene with activities as high as 400 g·(mmol of **1a**)$^{-1}$ h$^{-1}$ atm$^{-1}$.[24] Surprisingly, **1a** is active even in hexane (90 psi of ethylene, 40 °C) but with much lower activity (40 g of PE·(mmol of **1a**)$^{-1}$·h$^{-1}$·atm$^{-1}$). It should be noted that another metallocene cation using a metallacarborane as a counterion, $(Cp^*{}_2ThMe)_2((C_2B_9H_{11})_2Fe)$,[17] has no activity at all for ethylene polymerization. One possible reason is that the smaller ionic radius of $Zr^{4+}$ (0.79 Å) vs that of $Th^{4+}$ (1.01 Å) may allow a higher degree of ion separation despite the absence of steric constraints exerted by peralkylated cyclopentadienyl rings.

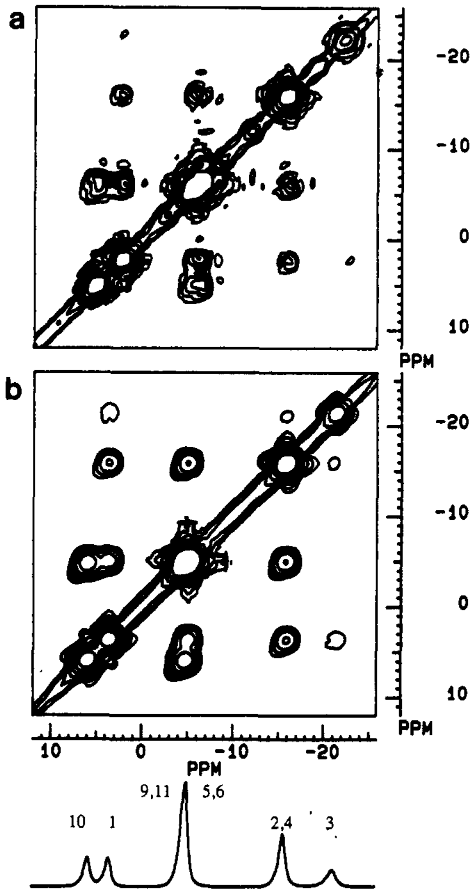

**Figure 4.** 2D $^{11}$B–$^{11}$B COSY spectra of (a) **1a** and (b) $[DMAH][(C_2B_9H_{11})_2Co]$ in toluene–$d_8$.

Ethylene and 1-butene have also been copolymerized by **1a** to produce an ethylene–butene copolymer with activities of about 900 g of copolymer·(mmol of **1a**)$^{-1}$·h$^{-1}$ (50 °C, toluene diluent, 200 mL of 1-butene, 120 psi of ethylene) with a weight-average molecular weight of 11 000 and a molecular weight distribution of 2.9. The polymer contains from 10 to 20 ethyl branches per 1000 carbon atoms (as determined by $^{13}$C NMR).[25]

**Acknowledgment.** We thank S. M. Wapp and D. J. Upton for expert technical assistance and C. J. Ruff for the $^{13}$C NMR analyses on the polymers.

**Registry No.** **1a**, 138834-48-7; **1b**, 138834-46-5; **1c**, 138834-47-6; **2a**, 138834-49-8; $Cp_2ZrMe_2$, 12636-72-5; $[DMAH][(C_2B_9H_{11})_2Co]$, 118536-44-0; ethylene, 74-85-1; 1-butene, 106-98-9.

**Supplementary Material Available:** Descriptions of the NMR experiments, 1D $^{11}$B and $^{11}$B–$^{11}$B 2D COSY spectra for $[PhNHMe_2][(C_2B_9H_{11})_2Co]$, 1D $^{11}$B spectra and $^1$H spectra for **1a**, and variable-temperature $^{13}$C spectra for a $Cp_2ZrMe_2$–$[PhNHMe_2][(C_2B_9H_{11})_2Co]$–$PhNMe_2$ mixture (7 pages). Ordering information is given on any current masthead page.

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[23] There have also been recent reports that base-free complexes of the type $[Cp'_2ZrMe][B(C_6F_5)_3Me]$, prepared from $Cp'_2ZrMe_2$ and $B(C_6F_5)_3$, are active for olefin polymerization in nonpolar diluents: (a) Ewen, J. A. Eur. Pat. Appl. 0427697, 1991. (b) Yang, X; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

[24] The molecular weights of the polyethylenes produced range from 35 000 to 94 000, and the molecular weight distributions range from 3.3 to 11.6. We have not found any correlations to explain these diverse results. All polyethylenes from **1a** melt at 132–136 °C.

[25] Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 353.