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Titanium and Zirconium $Et_2C_2B_4H_4$−Metal−Phosphine Complexes: Synthesis, Characterization, and Ethylene Polymerization Activity[1]

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Abstract: The synthesis, structures, and reactivity of a series of 14-electron complexes including $L_2Cl_2Ti(Et_2C_2B_4H_4)$ (**1**−**3**, L_2 = 2 PMe_3, $Me_2P(CH_2)_2PMe_2$, or $Me_2P(CH_2)_3PMe_2$], $[Me_2P(CH_2)_3PMe_2]_2Me_2Ti(Et_2C_2B_4H_4)$ (**22**), and related compounds are reported together with the preparation and spectroscopic characterization of the analogous zirconium species $L_2Cl_2Zr(Et_2C_2B_4H_4)$ (L_2 = 2PMe_3 or $Me_2P(CH_2)_3PMe_2$ (**24** and **25**). Compounds **1**−**3**, **22**, and **25** are catalyst precursors for the polymerization of ethylene at 1 atm pressure in the presence of methylaluminoxane, thus extending Ziegler−Natta chemistry for the first time to complexes of the $[R_2C_2B_4H_4]^{2-}$ small carborane ligands. Although the choice of phosphine ligand has a dramatic effect on catalyst activity, NMR data reveal aluminum−phosphine binding under conditions approximating the catalytic mixtures for the PMe_3 and $Me_2P(CH_2)_2PMe_2$ (dmpe) systems, whereas the state of $Me_2P(CH_2)_3PMe_2$ (dmpp) coordination is not clear. Multiple catalyst species are probably active in these reaction mixtures, giving rise to polyethylene products of broad polydispersity; melting points and ^{13}C NMR data provide evidence for significant chain branching. (dmpp)$Me_2Ti(Et_2C_2B_4H_4)$ produces a highly active ethylene polymerization catalyst with much narrower molecular weight distributions than the other systems described here. The complexes $(PMe_3)_2Cl_2Ti(Et_2C_2B_4H_4)$ (**1**), (dmpp)$Cl_2Ti(Et_2C_2B_4H_4)$ (**3**), and (dmpp)$Me_2Ti(Et_2C_2B_4H_4)$ (**22**) have been structurally characterized by X-ray crystallography.

Introduction

Boron-containing ligands that can replace η^5-cyclopentadienyl units in transition metal sandwich and half-sandwich complexes have attracted increasing attention in recent years.[4−9] Such systems often exhibit substantially different steric and electronic properties in comparison to their cyclopentadienyl analogues, which is significant in that most of the diverse and important reactions mediated by metallocene complexes are highly sensitive to the nature of the ligands.[10] When complexed to transition metal centers, organoboron groups such as borataarenes[5] and borollides,[6] and carborane ligands such as $C_2B_9H_{11}^{2-}$ (dicarbollide),[7] $[R_2C_2B_4H_4^{2-}]$ (R = alkyl, aryl, $SiMe_3$),[1a,4a,d,8,9] and their substituted derivatives, often lead to higher stability and altered reactivity compared to their metallocene counterparts, in some cases generating quite unusual or even unique chemistry.

Several groups, including those of Jordan, Ashe, Bazan, and Bercaw,[5−7] have reported the synthesis and olefin polymerization activity of catalysts that contain heterocyclic or dicarbollide ligands in place of the cyclopentadienyl group. In our laboratory, recent investigations[1a,8,9] of Ta(V) and Nb(V) complexes of the small carborane ligands $R_2C_2B_4H_4^{2-}$ (R = Et, Me, or $SiMe_3$) have focused on insertions of unsaturated substrates such as alkenes, alkynes, and nitriles, revealing a rich and versatile chemistry in which the carborane ligand functions as a spectator, as a direct participant in reactions, or both.[8,9] Given the intense interest over five decades in the catalysis of olefin polymerization by soluble bent metallocenes,[11] we have been exploring a possible role for small carborane metal complexes in this area that would exploit the inherent advantages afforded by these

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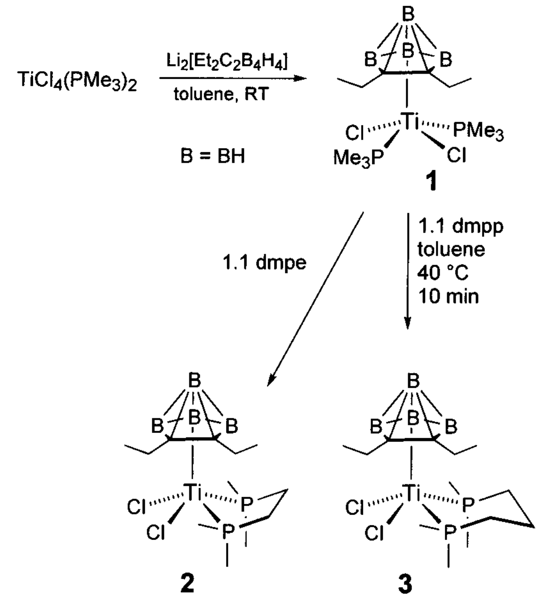
Scheme 1



compounds. Here we report[12] the synthesis and chemistry of novel 14-electron phosphinotitanium and phosphinozirconium *closo*-carboranes and the catalytic activity of selected species toward ethylene polymerization in the presence of methylaluminoxane (MAO) activator.

Results and Discussion

Synthesis of *closo*-Titanacarboranes. As shown in Scheme 1, the reaction of the $[Et_2C_2B_4H_4]^{2-}$ dianion with $TiCl_4(PMe_3)_2$[13] in toluene affords **1** as a red solid in 46% yield, characterized by ^1H, ^{13}C, ^{11}B, and ^{31}P NMR spectroscopy and elemental analysis. X-ray analysis of crystals obtained from pentane/toluene revealed the expected square pyramidal structure with a trans disposition of phosphine ligands (Figure 1). The Ti−Cl and Ti−P distances are unexceptional when compared to those of relevant structures.[14]

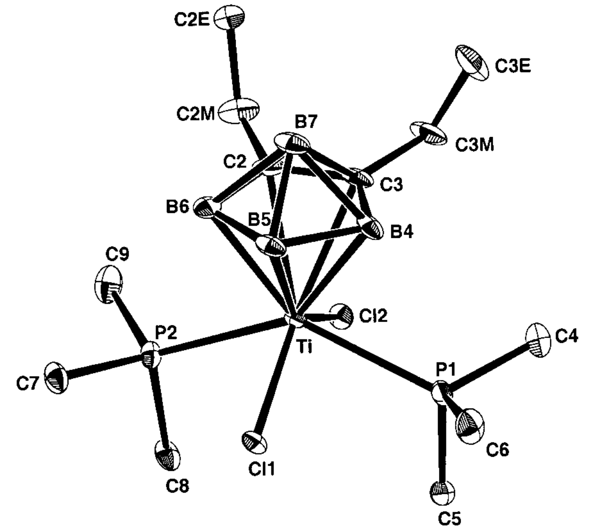


Figure 1. ORTEP plot of $(PMe_3)_2Cl_2Ti(Et_2C_2B_4H_4)$, **1**. Thermal ellipsoids are shown at the 30% probability level. Important bond distances (Å) and angles (deg): Ti−Cl1, 2.328(2); Ti−Cl2, 2.407(5); Ti−P1, 2.591(2); Ti−P2, 2.604(2); Cl1−Ti−Cl2, 124.17(6); P1−Ti−P2, 136.87(6); Cl1−Ti−P1, 78.88(5); P1−Ti−Cl2, 81.96(5); Cl2−Ti−P2, 80.83(5); P2−Ti−Cl1, 78.77(5).

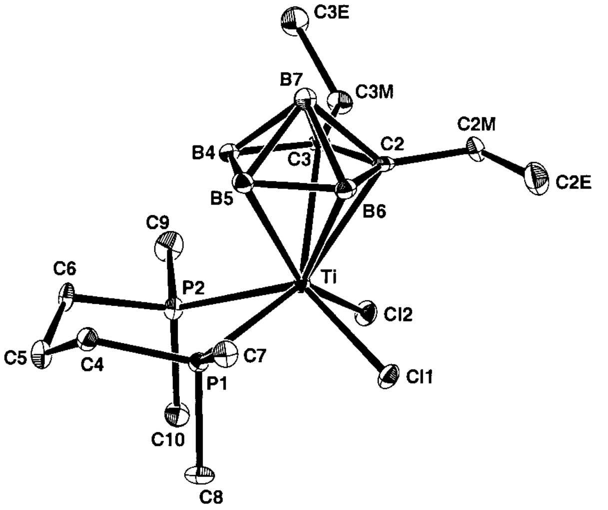


Figure 2. ORTEP plot of $(dmpp)Cl_2Ti(Et_2C_2B_4H_4)$, **3**. Thermal ellipsoids are shown at the 30% probability level. Important bond distances (Å) and angles (deg): Ti−Cl1, 2.319(2); Ti−Cl2, 2.346(2); Ti−P1, 2.606(2); Ti−P2, 2.591(2); Cl1−Ti−Cl2, 91.57(6); P1−Ti−P2, 77.25(5); Cl1−Ti−P1, 77.67(6); P1−Ti−Cl2, 135.48(6); Cl2−Ti−P2, 78.70(5); P2−Ti−Cl1, 131.71(7).

It appears from the NMR spectra that only one isomer of complex **1** is formed in solution; on the basis of steric considerations and analysis of the ^1H NMR $P-CH_3$ resonances (see below), we assume that the compound adopts the trans configuration. The phosphine ligands of **1** are labile, exchanging with an excess of PMe_3-d_9 within minutes at room temperature as monitored by ^1H and ^{31}P NMR. They can also be exchanged for 1,2-bis(dimethylphosphino)ethane (dmpe), forming **2**, and 1,3-bis(dimethylphosphino)propane (dmpp), generating **3**, by gentle heating in the presence of a slight excess of chelating ligand in toluene. Washing with pentane afforded pure **2** and **3** in nearly quantitative yields (Scheme 1). Crystals of **3** were obtained from pentane/toluene, which provided the X-ray structure shown in Figure 2, with the dmpp ligand adopting a cis coordination geometry in the square pyramidal structure. Furthermore, compound **3** is far more stable in the solid state (showing very little decomposition when exposed to air for two weeks) than either **1** or **2** (instant decomposition upon exposure to air).

The NMR spectra of **2** and **3** each show two distinct PMe resonances (syn and anti to the carborane ligand) and one ^{31}P NMR signal, as expected. For **2**, a large displacement (+31.7

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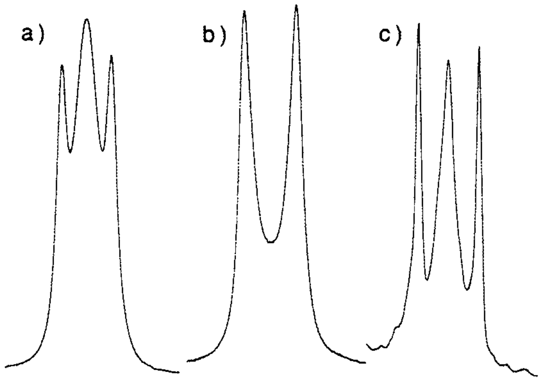


Figure 3. ^{1}H NMR resonances of the P-CH_3 group of $Et_2C_2B_4H_4$—Ti—phosphine complexes: (a) $(PMe_3)_2Cl_2Ti(Et_2C_2B_4H_4)$, (b) (dmpe)$Cl_2Ti(Et_2C_2B_4H_4)$, and (c) (dmpp)$Cl_2Ti(Et_2C_2B_4H_4)$.

ppm) in the resonant frequency of the ^{31}P NMR signal relative to that of **1** is observed, consistent with the expected 35 ppm downfield "chelation shift" of a five-membered-ring diphosphine.[15] However, the ^{31}P resonance of **3** is shifted slightly downfield relative to that of **1** (+2.6 ppm), instead of the expected small upfield shift (−3 ppm) characteristic of six-membered-ring chelating diphosphines.[15] Examination of the ^{1}H NMR resonances of the P—CH_3 groups of compounds **1**, **2**, and **3** (Figure 3) affords insight into the phosphine coordination around the metal center. The line shape of the proton resonance is strongly influenced by the value of ^2J(P,P) coupling in the system,[16] and the magnitude of ^2J(P,P) coupling can be related to the angle between equivalent phosphorus nuclei, supplying information about the coordination environment of the metal. When the phosphorus atoms are trans, the ^2J(P,P) coupling is large and the P—CH_3 resonance appears as a distorted triplet (Figure 3a); however, in a cis configuration the ^2J(P,P) coupling is negligible and the resonance appears as a doublet (Figure 3b). When the angle is between 90° and 180°, the shape of the P—CH_3 resonance is between those of a doublet and a distorted triplet (Figure 3c). Consequently, the phosphorus nuclei of **1** can be assigned the trans geometry, **2** the cis geometry, and **3** the cis configuration with a bite angle greater than 90°.

Phosphorus and Chloride Substitution. The ligand-exchange chemistry of **1** with other mono- and bidentate donors is summarized in Scheme 2 (showing successful substitution reactions) and Chart 1 (listing ligands unsuccessfully employed). Steric factors are clearly important, since the strong donors **7**—**11** fail to displace PMe_3,[17] in contrast to dmpe and dmpp. Interestingly, replacement of the PMe_3 ligands on **1** by **13**, which cannot span the normal angle of two adjacent ligands, caused immediate decomposition of the complex. This suggests that blocking access to the metal center is important in stabilizing the phosphino-titanacarborane system.

Attempted substitution using the bidentate oxides **14**—**18** led to decomposition, perhaps because they displace both PMe_3 ligands but are not able to protect the metal center from further reactions such as aggregation via bridging chlorides or carborane cage fusion.[4a,9] Monodentate phosphine oxide complexes **4** and **5** are accessible via treatment of **1** with an excess of the new donor, but only one PMe_3 ligand is replaced. These complexes are also labile; for example, both the phosphine and phosphine oxide ligands of **5** are easily washed off the metal by use of an excess of PMe_3-d_9. The chloride ligands of **1** may be cleanly displaced by *tert*-butoxide to give **6** accompanied by loss of PMe_3. Nitrogen donors are not effective: pyridine and a hindered diamine (TMEDA, **12**) did not exchange with PMe_3, and substitution with 2,2′-bipyridine gave a mixture of products.

Scheme 2

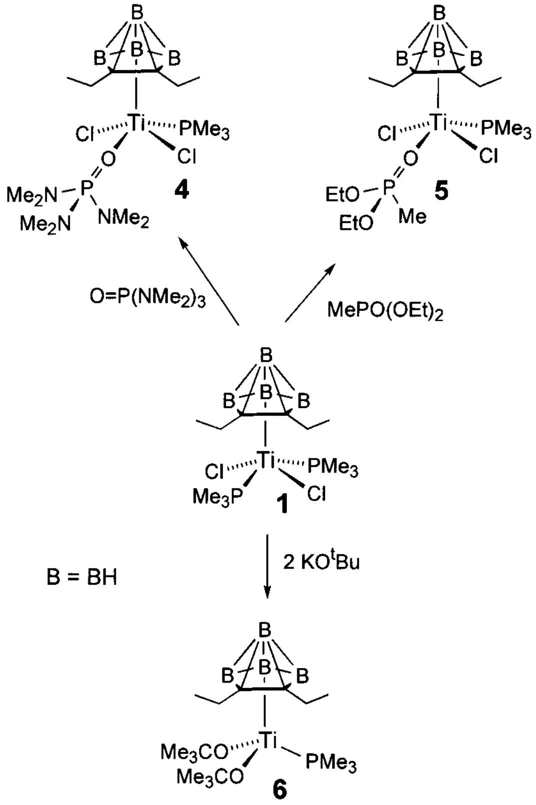
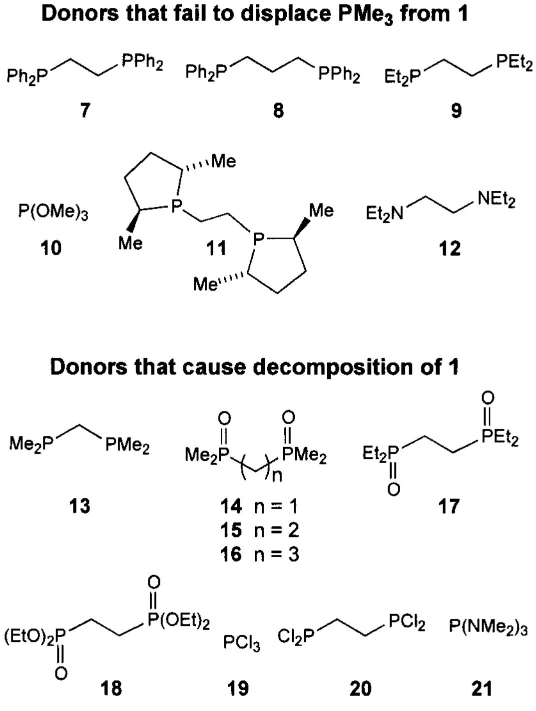


Chart 1



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[17] A small amount of Ti complex decomposition is occasionally observed in the presence of these ligands.

Table 1. Polymerization Catalysis in the Presence of **1**−**3** (0.1 mM) and 1 atm of Ethylene

entry	Ti source	[MAO]/[Ti][a]	temp (°C)	activity[b,e]	mp[c] (°C)	PDI[d]	M_w
1	**1**	2500	25	18.8 ± 0.8	130.1[h]	55.5[f,h]	2.8×10^{5h}
2	**2**	2500	25	78.5 ± 0.6	128.3[h]	7.6[h]	8.5×10^{4h}
3	**2**	1500	25	84 ± 3	129.4	29.4[f]	4.6×10^{5}
4	**2**	1000	25	74 ± 5	127.8	19.7[f]	2.2×10^{5}
5	**2**	500	25	113 ± 15	126.1	10.0	1.2×10^{5}
6	**2**	250	25	90 ± 16	127.1	12.4	1.5×10^{5}
7	**3**	2500	25	202.0 ± 0.5	121.6[h]	11.7[g,h]	3.3×10^{4h}

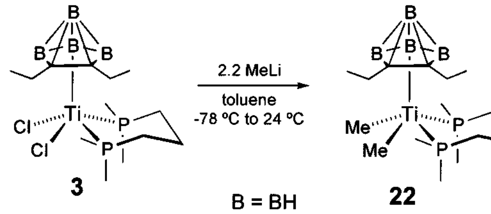
[a] [MAO]/Ti = molar ratio of Al to Ti; MAO used as a 10% stock solution in toluene. [b] Activity = kilograms of polyethylene per mole of precatalyst per hour. [c] Melting point as measured by modulated differential scanning calorimetry (DSC). [d] PDI = polydispersity index = M_w/M_n, measured by gel permeation chromatography. [e] When an error value appears, it represents the standard deviation for three or more independent runs, and the reported number is the average. [f] Strongly bimodal MW distribution is observed; the PDI value takes both peaks into account. [g] Weakly bimodal MW distribution is observed (shoulder on main peak). [h] Average of two runs.

Olefin Polymerization Catalysis. Complexes **1**−**3** function as precatalysts for ethylene polymerization in the presence of excess MAO. Thus, when MAO in ethylene-saturated toluene is treated with the precatalyst, an instantaneous color change from orange to golden brown occurs. Polymerization activities for reactions conducted under 1 atm of ethylene with rapid stirring are reported in Table 1, along with some properties of the polyethylene products. The catalyst derived from **2** is 4−5 times more active than that obtained from **1**, and **3** is about twice as active as **2**.[18] Polyethylene molecular weight distributions are generally broad, with the PMe_3-containing catalyst providing PDI (polydispersity index) values greater than 50. Both polydispersity and catalyst activity vary in a reproducible and nonlinear fashion for **2** as a function of the MAO/Ti ratio (Table 1, entries 2−6). Bimodal molecular weight distributions are observed with **1** and **2**, in the latter case only at intermediate concentrations of MAO. The polyethylene produced with **3** shows a molecular weight distribution that suggests bimodal behavior as well. The melting points of polyethylene produced from **1** and **2** (126−130 °C) are somewhat below the range characteristic of linear, high-molecular-weight material. Compound **3** provides polymer with a substantially lower melting point (121.6 °C), suggesting the presence of branched chains, which was confirmed by ^{13}C NMR analysis (see below).[19] Complexes **4** and **5** catalyze ethylene polymerization with twice the activity of **1** under identical conditions, while **6** is about half as active as **1**. Complexes **1**−**3**, as well as the Ti dimethyl complex **22** and the zirconium complex **25** reported below, are very poor catalysts for the polymerization of propylene in the presence of MAO.

Several experiments were performed to probe the role of phosphine in the catalytic species. Complexes **1**−**3** were mixed with an excess of MAO and monitored by ^{31}P NMR spectroscopy. Toluene-d_8 solutions of **1** and excess MAO show three signals, all of which match those observed for an analogous mixture of PMe_3 with MAO alone (spectra are provided in the Supporting Information). Similarly, the spectrum of a mixture of **2** and MAO exhibits a single dominant peak coincident with that of a mixture of dmpe and MAO in the absence of Ti complex. However, mixtures of **3** and MAO show two dominant broad signals (shifted significantly downfield) and one sharper peak, all clearly distinct from the two peaks exhibited by a mixture of dmpp and excess MAO alone. All of the spectra of precatalysts **1**−**3** with MAO are the same in the presence and in the absence of 1 atm ethylene and for Al:Ti ratios of 60 and 200. It seems likely that phosphine is removed from titanium by excess MAO for **1** and **2** but may remain coordinated to Ti in the catalyst derived from **3**. It should be noted that a single ^{31}P NMR resonance appears for **2** + MAO, as opposed to multiple resonances derived from **1** and **3**, and that the polyethylene produced from **2** has the narrowest molecular weight distribution among the three systems when tested under identical conditions (Table 1). This suggests that the broad polydispersities observed result in part from the presence of multiple catalytic species from **1** and **3**. Certainly, the activity of the catalyst is strongly affected by the choice of phosphine ligands.

We have also observed that some Ti(III) centers are formed when **2** is treated with excess MAO. Thus, a 60:1 mixture of MAO:**2**, examined in frozen toluene solution, shows an EPR triplet arising from Ti(III) coupled to two phosphorus ligands (see Supporting Information), with an integrated intensity corresponding to approximately 8% of the titanium used (determined by comparison to a calibration curve prepared with known amounts of $TiCl_3$). The presence of trimethylaluminum in MAO probably accounts for this reduction to Ti(III), perhaps also contributing to the broad polydispersities observed.

Synthesis of and Polymerization Catalysis by Ti-Alkyl and Zr *closo*-Carboranes. The observation of loss of phosphine, Ti(III) generation, and probable participation of multiple catalytic centers led us to pursue alkyltitanium compounds that could be activated without MAO. A wide variety of reagents and conditions were employed in an effort to alkylate the Ti−Cl groups of **1** and **2**, resulting in rapid decomposition in all cases. However, **3** is smoothly converted to the dimethyl complex **22** on treatment with MeLi, as shown in eq 1.[20]



(1)

X-ray crystallographic analysis (Figure 4) reveals that **22** adopts the monomeric cis-chelating form in the solid state. The Ti−CH_3 signal in the ^1H NMR spectrum is a simple triplet at 0.66 ppm with a single $^3J_{P,H}$ coupling constant of 5.4 Hz. The ^1H NMR resonance of the P−CH_3 groups is very similar to that of compound **3**, suggesting that the solution-phase structures of **22** and **3** are the same.

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(18) For comparison, ethylene polymerizations with Cp_2ZrCl_2 and Cp_2TiCl_2 were found to proceed approximately 50 and 14 times faster, respectively, than those with **2**, under identical conditions. Comparable rates for zirconocene dichloride are reported in the following: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625.

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(20) Two forms of complex **22** are accessible, which are distinguished by a small difference in the ^1H NMR chemical shifts of their PMe_2 resonances. One form appears to be the kinetic alkylation product, as it undergoes spontaneous conversion to the more stable form within hours at room temperature in solution or the solid state. Storage in frozen benzene solution preserves the less stable isomer; occasionally, the preparation of **22** affords only the thermodynamically stable form without the metastable isomer being observed. Only the stable form has been employed as a polymerization catalyst.

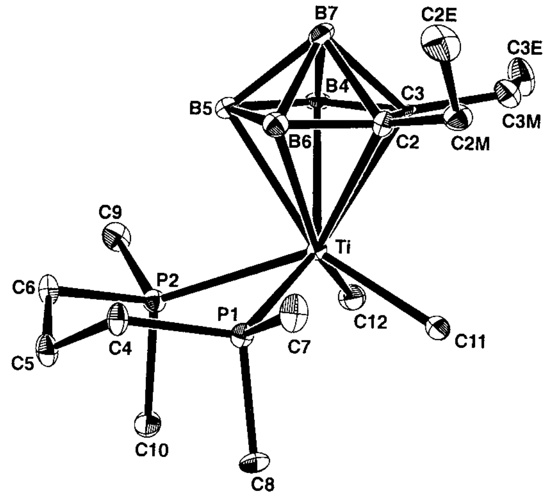


Figure 4. ORTEP plot of (dmpp)$Me_2Ti(Et_2C_2B_4H_4)$, **22**. Thermal ellipsoids are shown at the 30% probability level. Important bond distances (Å) and angles (deg): Ti−C11, 2.182(5); Ti−C12, 2.155(5); Ti−P1, 2.589(1); Ti−P2, 2.593(1); C11−Ti−C12, 89.7(2); P1−Ti−P2, 77.81(4); C11−Ti−P1, 78.9(1); P1−Ti−C12, 132.6(1); C12−Ti−P2, 77.8(1); P2−Ti−C11, 133.8(1).

To allow investigation of the catalytic properties of **22**, the ^{13}C-enriched analogue **22-$^{13}C_2$** was prepared with $^{13}CH_3Li$.[21] The ^{13}C-labeled analogue shows the expected large $^1J_{C,H}$ coupling constant (120 Hz) and a small value of $^2J_{P,C}$ (11.0 Hz), observed in the ^{13}C NMR spectrum; the ^{31}P NMR signal is a broadened singlet. The interaction of **22-$^{13}C_2$** with $[Ph_3C][B(C_6F_5)_4]$[22] was followed by ^1H and ^{13}C NMR spectroscopy, but unfortunately the spectra were very complex and inconclusive. NMR confirmed the formation of Ph_3C-$^{13}CH_3$, indicating that abstraction of the Me group from **22-$^{13}C_2$** had occurred; however, the exact nature of the resulting titanium species could not be elucidated.[23,24]

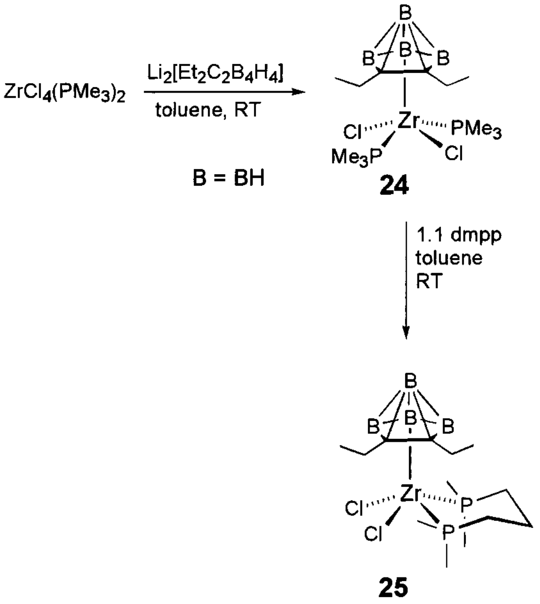
Treatment of **22** with $[Ph_3C][B(C_6F_5)_4]$ in the presence of ethylene failed to produce polyethylene. However, strong activity was observed when **22** was combined with smaller amounts of MAO than are used to activate **1**−**3**. When MAO in ethylene-saturated toluene was treated with a toluene solution of **22**, an instantaneous color change from yellow to golden brown occurred, and rapid polymerization commenced. The reactions were quenched after 5 min to obtain measurements of catalyst activity, minimizing mass transport problems caused by the rapid formation of a thick suspension of polymer. Even with such precautions, the activity values obtained (summarized in Table 2) displayed more scatter than observed for the other catalysts due to the short reaction time and unavoidable small inconsistencies in polymerization initiation. Significantly greater activity is observed for **22** than for **3**, and the former system is active in the presence of 100 equiv of MAO, whereas the latter requires a minimum of 250 equiv of MAO. As with **3**, catalyst activity appears to reach a maximum value at 500 equiv of MAO, although fewer increments were tested. Most importantly, the polydispersities are substantially lower with **22**, suggesting the cleaner formation of a dominant catalytic species. The melting points of the polymers produced are low (124−126 °C), again suggesting chain branching, which was confirmed by ^{13}C NMR spectroscopy.

Table 2. Polymerization Catalysis in the Presence of Ti or Zr Precatalyst (0.1 mM) and 1 atm of Ethylene

entry	M source	[MAO]/[M]	temp (°C)	activity[b,e]	mp[c,e] (°C)	PDI[d,e]	M_w[e]
1	**22**	2500[a]	25	1480 ± 190	124.6	2.58	2.6×10^4
2	**22**	500[a]	25	1890 ± 150	124.3	2.29	5.1×10^4
3	**22**	100[a]	25	1080 ± 50	126.8	2.34	1.5×10^5
4	**25**	2500[f]	25	104 ± 2	134.3	23.7[g]	4.3×10^5

[a] [MAO]/Ti = molar ratio of Al to Ti; MAO used as a 10% stock solution in toluene. [b] Activity = kilograms polyethylene per mole of precatalyst per hour. [c] Melting point as measured by modulated DSC. [d] PDI = polydispersity index = M_w/M_n, measured by gel permeation chromatography. [e] Average of two simultaneous runs. [f] [MAO]/Zr = molar ratio of Al to Zr; MAO used as a solid. [g] Strongly bimodal MW distribution is observed; the PDI value takes both peaks into account.

Scheme 3



As shown in Scheme 3, the zirconium congeners of **1** and **3** (**24** and **25**, respectively) are accessible. However, **24** is thermally unstable and decomposes in solution or in vacuo with loss of PMe_3, and addition of dmpe fails to give an isolable zirconium analogue of **2**. Complex **25**, obtained by immediate trapping of **24** with dmpp, is a thermally stable, air-sensitive, off-white crystalline solid, again demonstrating the stabilizing effects of dmpp. The ^1H and ^{31}P NMR spectra of **24** and **25** are very similar to those of **1** and **3**.

Complex **25** is a precatalyst for the polymerization of ethylene, when activated by MAO from which the solvent and volatile components (principally trimethylaluminum) have been removed by evacuation (Table 2, entry 4). In contrast, the Ti

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(21) Reynolds, K. A.; O'Hagen, D.; Gani, D.; Robinson, J. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3195−3207.

(22) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571.

(23) Treatment of **22-$^{13}C_2$** with $[Ph_3C][B(C_6F_5)_4]$ resulted in the formation of Ph_3C-$^{13}CH_3$ (confirmed by independent synthesis) and a single broad ^{13}C-enriched peak approximately 10 ppm downfield from the Ti-$^{13}CH_3$ resonance of the starting material, presumably arising from the titanacarborane methyl cation in the salt tentatively formulated as $[(Et_2C_2B_4H_4)Ti(dmpp)CH_3^+][B(C_6F_5)_4^-]$, **23**. The ^{31}P NMR spectrum of **23** shows broad peaks near, but not coincident with, those observed for **3** + MAO. There is no evidence that dmpp dissociates from the metal in **23**, except for its evident lack of $^{13}C-^{31}P$ coupling; however, the broad nature of these peaks and the small $^2J_{P,C}$ coupling constant observed for **22-$^{13}C_2$** renders this observation inconclusive.

(24) Three other well-known activating agents of alkylmetal precursors to Ziegler−Natta catalysts failed to give discrete products by NMR and induced no polymerization activity: $[H(OEt_2)_2][(3,5-(CF_3)_2C_6H_3)_4B]$ (Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922), $[PhMe_2NH]BPh_4$ (Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780−782), and excess $B(C_6F_5)_3$ (Pellecchia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 277−281. Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565−3567).

systems are not activated by this form of MAO, but only by the 10% toluene stock solution. Note that the Zr complex gives polyethylene with a melting point characteristic of linear, high-density material, substantially higher than that generated by any of the titanium catalysts. Whether this difference is due to the nature of the catalyst or to the presence of $AlMe_3$ in the titanium reactions is not known.

Conclusions. The dinegative *nido*-$R_2C_2B_4H_4^{2-}$ unit can formally replace two cyclopentadienide ligands, thereby opening additional coordination sites at the metal center and facilitating catalyst modification via introduction of ancillary donor ligands, such as phosphine in the present case. In the context of early transition metal Ziegler−Natta catalysis, in which highly electrophilic metal centers are required,[11] such coordinative unsaturation helps to compensate for the relatively strong electron-donating properties of the carborane framework.[25] Another attractive feature of metal complexes of the *nido*-$[Et_2C_2B_4H_4]^{2-}$ ligand is the tailorability of the C_2B_4 cage via substitution at the boron and/or carbon atoms,[1a,8,9,26] a task not easily accomplished on aromatic hydrocarbon ligands bound to metals. This work demonstrates the first examples of early transition metal Ziegler−Natta catalysis promoted by the presence of phosphine ligands;[27] indeed, catalytic activity is enhanced by 2 orders of magnitude in the dmpp-dimethyl complex **22** vs the parent system **1**. Furthermore, these catalysts produce high-molecular-weight polyethylene of substantially lower melting point than is normal for metallocene systems. The stabilities and catalytic activities of the titanium and zirconium systems described here are dramatically affected by the nature of the phosphine, with dmpp proving to be far more effective than either dmpe or trimethylphosphine. It therefore seems likely that dmpp remains coordinated to the group 4 metal during catalysis. New systems, including "constrained-geometry" carborane−phosphine catalysts, are being developed and will be described in due course.

Experimental Section

General. ^1H (300 MHz), ^{11}B (96.4 MHz), ^{13}C (75.5 MHz), and ^{31}P (202.4 MHz, 121.7 MHz) NMR spectra were acquired on Varian Unity/Inova 300/51, Varian Unity/Inova 500/51, and GE GN-300 instruments. In all cases, ^{13}C spectra were recorded with proton decoupling; peak splitting arises from (C,P) coupling. Except where noted, ^{13}C signals of cage carbon nuclei were not oberved (not uncommon for skeletal carbons in carboranes). Visible−ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. The unit resolution mass spectrum of **3** was obtained on a Finnegan MAT 4600 spectrometer using perfluorotributylamine (FC43) as calibration standard and chemical ionization using CH_4; both positive- and negative-ion spectra were recorded. Strong parent ion envelopes were observed. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory in Woodside, NY. In each case, NMR spectra established compound purity and identity, supplemented for **3** by mass spectrometry showing the expected isotopic envelope. X-ray crystallography provided unambiguous structural assignments in three cases (**1**, **3**, **22**). Infrared spectra were recorded as thin films on a Nicolet Impact-400 spectrometer. Phosphines were obtained from Strem, Lancaster, and Aldrich chemical companies, and used as received. A 10% MAO solution in toluene was purchased from Albemarle Corp. Hydrocarbon and ethereal solvents were distilled under a dry argon atmosphere from sodium/benzophenone ketyl. Halogenated solvents were degassed and distilled from P_2O_5. The carborane $Et_2C_2B_4H_6$ was prepared on a multigram scale by the reaction of B_5H_9 and 3-hexyne in diethyl ether solution, in a modification[28] of the literature method.[29] Unless otherwise noted, all manipulations were performed under a dry nitrogen atmosphere, maintained by standard glovebox and Schlenk techniques.

$TiCl_4(PMe_3)_2$. In a modification of the method of Chatt and Hayter,[13] a solution of $TiCl_4$ (4.44 g, 0.023 mol) in 250 mL of dry pentane was cooled to −78 °C and treated with PMe_3 (1 M solution in toluene, 51.5 mL, 0.051 mol) in dropwise fashion with stirring. The resulting red suspension was stirred for 4 h while warming to room temperature. The solid was collected by vacuum filtration in a glovebox, washed thoroughly with dry pentane, and dried in vacuo. Yield: 7.44 g (93%). ^1H NMR (C_6D_6, δ): 1.04 (s). ^{31}P NMR (C_6D_6, δ): −7.59 (s).

$(PMe_3)_2Cl_2Ti(Et_2C_2B_4H_4)$ (1). A solution of $Et_2C_2B_4H_6$ (0.50 g, 3.80 mmol) in 75 mL of dry ether was cooled to 0 °C and treated with 1.7 M *tert*-butyllithium in pentane (4.48 mL, 7.60 mmol) in dropwise fashion with stirring. The cooling bath was removed and the yellow solution allowed to stir for 1 h. The solvent was then removed in vacuo and the resulting solid redissolved in dry toluene. The toluene solution was added to a solution of $TiCl_4(PMe_3)_2$ (1.56 g, 4.56 mmol) in 300 mL of dry toluene using a dropping funnel, causing a color change to dark brown. The reaction was allowed to stir for 4 h, followed by removal of the toluene in vacuo. The residue was then stirred in 75 mL of dry pentane for 1.5 h. The mixture was filtered through Celite in a glovebox and concentrated at −40 °C to give **1** (0.704 g, 46%) as a red, crystalline solid. ^1H NMR (C_6D_6, δ): 1.15 (t, 18H, $J = 4.2$ Hz, PCH_3), 1.27 (t, 6H, $J = 7.8$ Hz, ethyl CH_3), 3.02 (q, 2H, $J = 7.5$ Hz, ethyl CH_2), 3.03 (q, 2H, $J = 7.5$ Hz, ethyl CH_2). ^{31}P NMR (C_6D_6, δ): −3.46 (s). ^{13}C NMR (C_6D_6, δ): 14.79 (t, $J = 24$ Hz, PCH_3), 15.11 (s, ethyl CH_3), 25.34 (s, ethyl CH_2). ^{11}B NMR ($CDCl_3$, δ): 52.0 (d, 1B), 29.6 (d, 2B), −3.30 (d, 1B). IR (NaCl, cm^{-1}): 2972 (s), 2934 (m), 2908 (m), 2875 (w), 2555 (m), 2509 (m). UV−vis [CH_2Cl_2, λ_{max} nm (ϵ)]: 280, 236 (5354). Anal. Calcd for $TiC_{12}H_{32}B_4Cl_2P_2$: C, 36.00; H, 8.06. Found: C, 35.60; H, 8.71.

$[Me_2P(CH_2)_2PMe_2]Cl_2Ti(Et_2C_2B_4H_4)$ (2). A 50-mL Schlenk flask was charged in a glovebox with toluene (5 mL), **1** (156 mg, 0.389 mmol), and dmpe (70 mg, 0.467 mmol). The flask was removed to a vacuum line and the mixture heated at 40 °C for 10 min. The toluene was removed in vacuo and the residue washed three times with dry pentane. The solid was dried to give **2** (140 mg, 90%) as an orange powder. ^1H NMR (C_6D_6, δ): 0.73 (d, 2H, $J = 8.4$ Hz, PCH_3), 0.89 (m, 2H, PCH_2), 1.51 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 1.60 (d, 6H, $J = 11.4$ Hz, PCH_3), 1.96 (m, 2H, PCH_2), 2.80 (sextet, 2H, $J = 7.5$ Hz, ethyl CH_2), 3.23 (sextet, 2H, $J = 7.5$ Hz, ethyl CH_2). ^{31}P NMR (C_6D_6, δ): 28.10 (s). ^{13}C NMR (C_6D, δ): 15.17 (s, ethyl CH_3), 17.61 (t, $J = 7.6$ Hz, PCH_3), 18.77 (d, $J = 35.3$ Hz, PCH_3), 24.81 (t, $J = 17.1$ Hz, PCH_2), 27.34 (s, ethyl CH_2). ^{11}B NMR ($CDCl_3$, δ): 33.9 (d, 1B), 27.1 (d, 2B), −5.4 (d, 1B). IR (NaCl, cm^{-1}): 2964 (s), 2928 (s), 2916 (m), 2871 (w), 2852 (w), 2554 (s), 2512 (m). UV−vis [CH_2Cl_2, λ_{max} nm (ϵ)]: 416, 348, 252 (9303). Anal. Calcd for $TiC_{12}H_{30}B_4Cl_2P_2$: C, 36.18; H, 7.56. Found: C, 36.65; H, 8.11.

$[Me_2P(CH_2)_3PMe_2]Cl_2Ti(Et_2C_2B_4H_4)$ (3). The above procedure for the preparation of **2** was applied, giving **3** (45 mg, 88%) as an orange powder. ^1H NMR (C_6D_6, δ): 0.68 (t, 6H, $J = 4.2$ Hz, PCH_3). 0.94 (m, 2H, PCH_2), 1.32 (m, 2H, PCH_2CH_2), 1.46 (t, 6H, $J = 7.5$ Hz, ethyl

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[25] For example, we have found complexes of the type (carborane)-$CpTaX_2$ (X = halide, alkyl), which are isoelectronic to the effective precatalyst Cp_2ZrX_2, to be inactive toward olefin insertion or polymerization in the presence of MAO. Ziegler−Natta polymerization activity with group 5 Cp*(diene)MX_2 complexes has been reported: Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633−2640. For a demonstration of the electron-donating capabilities of the $[C_2B_3]^{2-}$ system, see: Curtis, M. A.; Finn, M. G.; Grimes, R. N. *J. Organomet. Chem.* **1998**, *350*, 469−472.

[26] (a) Stockman, K. E.; Garrett, D. L.; Grimes, R. N. *Organometallics* **1995**, *14*, 4661−4667. (b) Curtis, M. A.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1996**, *35*, 6703−6707. (c) Curtis, M. A.; Müller, T.; Beez, V.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *Inorg. Chem.* **1997**, *36*, 3602−3608.

[27] The addition of PMe_3 to a Brintzinger-type cationic zirconium alkyl system has been observed to suppress olefin polymerization catalysis even at 60 °C: Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **1993**, *445*, 111−114. Note that phosphine-containing alkylidene hydride complexes of tantalum are active polymerization catalysts: Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942−4950. Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331−2333.

[28] Stockman, K. E., Ph.D. Dissertation, University of Virginia, 1995.

[29] Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211.

CH_3), 1.63 (t, 6H, J = 5.1 Hz, PCH_3), 1.96 (t, 2H, J = 13.5 Hz, PCH_2), 2.90 (sextet, 2H, J = 7.5 Hz, ethyl CH_2), 3.23 (sextet, 2H, J = 7.5 Hz, ethyl CH_2). ^{31}P NMR (C_6D_6, δ): −1.01 (s). ^{13}C NMR (C_6D_6, δ): 14.19 (t, J = 8.0 Hz, PCH_3), 15.26 (s, ethyl CH_3), 18.59 (s, PCH_2CH_2), 20.60 (t, J = 18.2 Hz, PCH_3), 26.93 (s, ethyl CH_2), 28.73 (t, J = 9.5 Hz, PCH_2). IR (NaCl, cm^{-1}): 2973 (w), 2931 (w), 2911 (w), 2561 (w), 2292 (m), 1554 (s), 1255 (s), 1218 (s), 1113 (w), 1070 (w), 1003 (s), 974 (s). UV−vis [CH_2Cl_2, λ_{max} nm (ϵ)]: 288 (2935), 343 (1832). Anal. Calcd for $TiC_{13}H_{32}B_4Cl_2P_2$: C, 37.86; H, 7.82. Found: C, 37.61; H, 8.11. MS: parent ion envelope at *m*/*z* 413.

[OP(NMe$_2$)$_3$]PMe$_3$Cl$_2$Ti(Et$_2$C$_2$B$_4$H$_4$) (4). A solution of **1** (20 mg, 0.049 mmol) in 5 mL of pentane was treated with HMPA (9.8 mg 0.055 mmol) in dropwise fashion with stirring, causing immediate precipitation of an orange solid. The reaction mixture was stirred for 10 min and the volume reduced to 2 mL. The remaining liquid was removed by syringe, and the residual solid was washed three times with dry pentane and dried in vacuo, giving **4** as an orange powder, which is unstable and decomposes within hours upon standing. ^{1}H NMR (C_6D_6, δ): 1.53 (t, 15H, J = 7.2 Hz, ethyl CH_3 and P(CH_3)$_3$), 2.22 (d, 18H, J = 9.9 Hz, N(CH_3)$_2$), 2.63 (m, 2H, ethyl CH_2), 3.03 (m, 2H, ethyl CH_2). ^{31}P NMR (C_6D_6, δ): 9.85 (s, P(CH_3)$_3$), 29.06 (s). ^{13}C NMR (C_6D_6, δ): 15.14 (s, ethyl CH_3), 17.36 (d, J = 24.2 Hz, P(CH_3)$_3$), 25.78 (s, ethyl CH_2), 36.83 (d, J = 4.0 Hz, N(CH_3)$_2$).

[OP(OEt)$_2$MeP](PMe$_3$)Cl$_2$Ti(Et$_2$C$_2$B$_4$H$_4$) (5). The above procedure for the preparation of **4** was employed using diethylmethylphosphonate. The reaction mixture was cooled to −78 °C to induce precipitation; standard workup then provided **5** as an oily red solid. ^{1}H NMR (C_6D_6, δ): 0.92 (t, 6H, J = 6.9 Hz, $POCH_2CH_3$), 1.12 (d, 3H, J = 18 Hz, PCH_3), 1.53 (d, 9H, J = 5.1 Hz, P(CH_3)$_3$), 1.56 (t, 6H, J = 7.5 Hz, ethyl CH_3), 2.46 (sextet, 2H, J = 7.2 Hz, ethyl CH_2), 2.87 (sextet, 2H, J = 7.2 Hz, ethyl CH_2), 3.84 (m, 4H, POCH_2). ^{31}P NMR (C_6D_6, δ): 11.76 (s, P(CH_3)$_3$), 35.29 (d). ^{13}C NMR (C_6D_6, δ): 10.52 (s, OCH_2CH_3), 14.83 (s, ethyl CH_3), 15.89 (d, J = 6.9 Hz, P(CH_3)$_3$), 17.32 (d, J = 26.2 Hz, PCH_3), 25.55 (s, ethyl CH_2), 63.85 (s, OCH_2). Anal. Calcd for $TiC_{14}H_{36}B_4Cl_2P_2$: C, 35.30; H, 7.62. Found: C, 34.16; H, 7.71.

(OCMe$_3$)$_2$(PMe$_3$)Ti(Et$_2$C$_2$B$_4$H$_4$) (6). A solution of **1** (20 mg, 0.049 mmol) in 1 mL of dry benzene was treated with potassium *tert*-butoxide (11.2 mg, 0.0998 mmol). The reaction mixture was allowed to stir for 30 min, followed by removal of solvent in vacuo to give a mixture of **7** and KCl as a yellow solid. ^{1}H NMR (C_6D_6, δ): 0.97 (d, 9H, J = 5.4 Hz, P(CH_3)$_3$), 1.25 (s, 18H, C(CH_3)$_3$), 1.49 (t, 6H, J = 4.8 Hz, ethyl CH_3), 2.74 (septet, 2H, J = 4.5 Hz, ethyl CH_2), 2.97 (septet, 2H, J = 4.5 Hz, ethyl CH_2). ^{31}P NMR (C_6D_6, δ): −10.41 (s).

[Me$_2$P(CH$_2$)$_3$PMe$_2$]$_2$Me$_2$Ti(Et$_2$C$_2$B$_4$H$_4$) (22). A solution of **3** (46 mg, 0.111 mmol) in 12 mL of toluene was cooled to −78 °C and treated with a 0.56 M solution of methyllithium (429 μL, 0.240 mmol) in dropwise fashion with stirring. The mixture was then allowed to come to room temperature over 4 h and the toluene removed in vacuo. The crude solid was then redissolved in a small amount of toluene and filtered in a glovebox to remove the lithium salts. Toluene was removed in vacuo and the resulting solid dissolved in CH_2Cl_2. Pentane was added until the solution was turbid, and the mixture was stored at −20 °C for 18 h. The solids were filtered off, and evaporation of the solvent provided **22** (19 mg, 47%) as a yellow solid. ^{1}H NMR (C_6D_6, δ): 0.66 (t, 6H, J = 5.7 Hz, Ti−CH_3), 0.68 (t, 6H, J = 3.9 Hz, PCH_3), 0.87 (m, 2H, PCH_2), 1.34 (t, 6H, J = 3.9 Hz, PCH_3), 1.44 (m, 2H, PCH_2CH_2), 1.60 (t, 6H, J = 7.5 Hz, ethyl CH_3), 1.76 (t, 2H, J = 14.8 Hz, PCH_2), 3.02 (m, 4H, ethyl CH_2). ^{31}P NMR (C_6D_6, δ): −9.25 (s). ^{13}C NMR (C_6D_6, δ): 12.45 (t, J = 4.8 Hz, PCH_3), 16.26 (s, ethyl CH_3), 18.94 (s, PCH_2CH_2), 19.29 (t, J = 16.7 Hz, PCH_3), 26.27 (s, ethyl CH_2), 29.86 (t, J = 11.1 Hz, PCH_2), 58.55 (t, J = 8.1 Hz, Ti-CH_3). ^{11}B NMR (C_6D_6, δ): −10.5 (d, 1B), 24.6 (d, 2B), 29.7 (d, 1B). Anal. Calcd for $TiC_{15}H_{38}B_4P_2$: C, 48.49; H, 10.31. Found: C, 47.58; H, 10.39.

[Me$_2$P(CH$_2$)$_3$PMe$_2$]$_2$^{13}C-Me$_2$Ti(Et$_2$C$_2$B$_4$H$_4$) (22-^{13}C$_2$). The above procedure was employed with $^{13}CH_3Li$,[21] giving **22-^{13}C$_2$** in similar yield. ^{1}H NMR (CD_2Cl_2, δ): 1.44 (t, 3H, J = 5.7 Hz, TiCH_3), 1.84 (t, 3H, J = 5.7 Hz, TiCH_3), 2.62 (t, 6H, J = 7.5 Hz, ethyl CH_3), 2.65 (t, 6H, J = 3.3 Hz, PCH_3), 2.88 (t, 6H, J = 3.9 Hz, PCH_3,), 3.02 (m, 2H, PCH_2), 3.33 (t, 2H, J = 14.6 Hz, PCH_2), 3.52 (m, 2H, PCH_2CH_2), 4.14 (q, 4H, J = 7.5 Hz, ethyl CH_2). ^{31}P NMR (CD_2Cl_2, δ): −8.54 (s). ^{13}C NMR (CD_2Cl_2, δ): 13.25 (t, J = 5.0 Hz, PCH_3), 15.97 (s, ethyl CH_3), 19.34 (s, PCH_2CH_2), 19.39 (t, J = 16.9 Hz, PCH_3), 30.52 (t, J = 12.2 Hz, PCH_2), 58.62 (t, J = 11.1 Hz, TiCH_3).

22-^{13}C$_2$ + [Ph$_3$C][(B(C$_6$F$_5$)$_4$]. Treatment of a CD_2Cl_2 solution of **22-^{13}C$_2$** (6 mg, 0.016 mmol) with [Ph_3C][(B(C_6F_5)$_4$] (18 mg, 0.0194 mmol) in a Teflon-sealed NMR tube (J. Young) provided an orange solution which was examined by NMR within 5 min of mixing. The resulting ^{1}H NMR and ^{13}C NMR spectra were complex but were dominated by the following resonances. ^{1}H NMR (CD_2Cl_2, δ): −0.01 (s, Ti$^+$-^{13}CH_3), 0.41 (s, Ti$^+$-^{13}CH_3), 1.95 (s, (C_6H_5)$_3$C-^{13}CH_3), 2.38 (s, (C_6H_5)$_3$C-^{13}CH_3). ^{13}C NMR (CD_2Cl_2, δ): 30.58 (s, [(C_6H_5)$_3$C-^{13}CH_3]), 65.58 (bs, Ti$^+$-^{13}CH_3). For purposes of assignment, an authentic sample of (C_6H_5)$_3$C-^{13}CH_3 was prepared by the method of Eisch et al.,[30] using $^{13}CH_3I$, and recrystallized from ethanol. ^{1}H NMR (CD_2Cl_2, δ): 1.97 (s), 2.40 (s), 7.11 (m), 7.24 (m). ^{13}C NMR (CD_2Cl_2, δ): 30.61 (s), 126.29 (s), 128.19 (s), 129.05 (s).

(PMe$_3$)$_2$Cl$_2$Zr(Et$_2$C$_2$B$_4$H$_4$) (24) and [Me$_2$P(CH$_2$)$_3$PMe$_2$]Cl$_2$Zr(Et$_2$C$_2$B$_4$H$_4$) (25). To a slurry of $ZrCl_4$ (233 mg, 1.00 mmol) in 20 mL of dry pentane was added neat PMe_3(220 μL, 2.16 mmol) with stirring. The resulting orange suspension was stirred for 1 h, followed by removal of solvent in vacuo. In a second flask, a solution of $Et_2C_2B_4H_6$ (131 mg, 1.00 mmol) in 20 mL of dry ether was treated with 1.75 M *n*-butyllithium in hexanes (1.14 mL, 2.00 mmol) in a dropwise fashion and allowed to stir for 2 h. The solvent was then removed in vacuo and the resulting glassy solid redissolved in 20 mL of dry toluene. The Li_2[$Et_2C_2B_4H_4$] solution was added to the partially dissolved $ZrCl_4$(PMe_3)$_2$ in 50 mL of dry toluene using a dropping funnel over 1 h, causing a color change to brown. The reaction was allowed to stir for 3 h. Complex **24** was not isolated at this point due to thermal instability; **25** was instead generated directly by addition of a 25% (w/w) solution of 1,3-bis(dimethylphosphino)propane in hexanes (743 mg, 1.13 mmol), followed by stirring overnight at room temperature. The reaction mixture was filtered to afford a yellow solution, and the solvent was evaporated. The resulting residue was extracted with two 15-mL portions of pentane to remove undesired bis(carborane) [($Et_2C_2B_4H_4$)$_2$-ZrL_2] species, and the remaining crude product was dissolved in 5 mL of CH_2Cl_2 and layered with 30 mL of pentane. Over a period of several weeks at −20 °C, large off-white crystals of **25** formed (186 mg, 41%). The following are data for **24**. ^{1}H NMR ($CDCl_3$, δ): 1.21 (t, 6H, J = 7.4 Hz, ethyl CH_3), 1.44 (t, 18H, J = 3.5 Hz, PCH_3), 2.86 (m, 4H, ethyl CH_2). The following data are for **25**. ^{1}H NMR (CD_2Cl_2, δ): 1.28 (d, 6H, J = 6.3 Hz, PCH_3), 1.29 (t, 6H, J = 7.5 Hz, ethyl CH_3), 1.55 (m, 2H, PCH_2CH_2), 1.76 (d, 6H, J = 8.7 Hz, PCH_3), 1.94 (m, 2H, PCH_2), 2.39 (t, 2H, J = 13.0 Hz, PCH_2), 2.67 (sextet, 2H, J = 7.5 Hz, ethyl CH_2), 2.84 (sextet, 2H, J = 7.5 Hz, ethyl CH_2). ^{31}P NMR (CD_2Cl_2, δ): −14.85 (s). ^{13}C NMR (CD_2Cl_2, δ): 12.00 (distorted t, J = 8.0 Hz, PCH_3), 15.37 (s, ethyl CH_3), 17.78 (distorted t, J = 15.0 Hz, PCH_3), 18.95 (s, PCH_2CH_2), 26.12 (s, ethyl CH_2), 28.71 (distorted t, J = 11.0 Hz, PCH_2), 130.77 (s, br, carborane C). ^{11}B NMR (CD_2Cl_2, δ): 29.04 (d, 1B), 25.47 (d, 2B), −10.05 (d, 1B) Anal. Calcd for $ZrC_{13}H_{32}B_4Cl_2P_2$: C, 34.26; H, 7.08. Found: C, 33.43; H, 7.01.

General Polymerization Procedures. (a) For Ti Complexes. A 250-mL Schlenk flask was evacuated and refilled three times with ethylene. The flask was then charged with the appropriate amount of a 10% MAO solution in toluene, and sufficient toluene was added to make a total volume of 99 mL. The desired amount of precatalyst in 1 mL of toluene was then injected into the rapidly stirred flask to initiate the reaction under 1 atm of monomer. After a measured time interval, the reaction was quenched by addition of 100 mL of 20% aqueous HCl in methanol. The polyethylene was collected by vacuum filtration, washed with methanol, and dried under vacuum at 80 °C for 18 h.

(b) For Zr Complex 25. MAO (10% in toluene) was evaporated (40 °C, 0.1 mmHg) to give a white solid. The required amount of this material was weighed into a Schlenk flask and dissolved in 90 mL of toluene, and the solution was saturated with ethylene. A solution of **25** in 10 mL of toluene was then injected with a large-bore needle directly into the stirred MAO/ethylene solution under ethylene atmosphere to initiate polymerization; runs were quenched after 8 min and processed as above.

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^{13}C NMR Analysis of Polyethylene. ^{13}C NMR analysis of the polyethylene samples was done at 128 °C using a GE GN-300 instrument. Spectra were recorded in a 10-mm tube using a delay time of 1 s. The sample was prepared by dissolving 150 mg of polymer in 3 mL of 1,2,4-trichlorobenzene at 140 °C. DMSO-d_6 (0.5 mL) was added to serve as a lock solvent. Spectra were referenced to the main-chain CH_2 groups of polyethylene at 30.0 ppm. The nomenclature of the peak assignments is that of Usami and Takayama,[31b] and values for peak assignments are taken from ref 31.

(a) Polyethylene from 1 Using 2500 Equiv of MAO. ^{13}C NMR (($(CD_3)_2SO$, δ): 30.0 (s, main chain CH_2).

(b) Polyethylene from 2 Using 2500 Equiv of MAO. ^{13}C NMR (($(CD_3)_2SO$, δ): 30.0 (s, main chain CH_2).

(c) Polyethylene from 3 Using 2500 Equiv of MAO. ^{13}C NMR (($(CD_3)_2SO$, δ): 14.20 (s, $1B_{7+}$), 22.89 (s, $2B_{\text{longer+}}$), 27.49 (s, βB_{6+}), 29.57 (s, $4B_{6+}$), 30.0 (s, main chain CH_2), 30.37 (s, γB_{6+}), 32.17 (s, $3B_{\text{longer+}}$).

(d) Polyethylene from 22 Using 2500 Equiv of MAO. ^{13}C NMR (($(CD_3)_2SO$, δ): 27.44 (s, βB_{6+}), 30.00 (s, main chain CH_2), 30.37 (s, γB_{6+}).

Gel Permeation Chromatography. GPC was performed at Union Carbide Corp. on a Waters 150C+ instrument. Conditions: mobile phase, 1,2,4-trichlorobenzene; temperature, 145 °C; columns, 1-Polymer Labs PL Gel Guard (7.5 × 50 mm), 1-Polymer Labs PL Gel 50A (7.5 × 30 mm), 3-Shodex AT-806MS (8 × 250 mm); injection volume, 300 μL; sample preparation, 0.1% (wt/vol) in trichlorobenzene, solubilized at approximately 165−170 °C for 60 min with gentle stirring for the last 5 min. Several samples were analyzed at Symyx Technologies using similar equipment, but for consistency only the values from the Union Carbide facility are reported here.

Differential Scanning Calorimetry. DSC was performed on a TA Instruments automated differential scanning calorimeter, with the following method: (1) a 5−10-mg sample is heated from −20 to 200 °C at 10 °C/min under nitrogen; (2) the sample is held at 200 °C for 1 min and then cooled at 10 °C/min; (3) the sample is held at 0 °C for 1 min and then heated again at 10 °C/min to 200 °C. The reported values are those obtained in the second heating scan, which were highly reproducible in subsequent scans.

NMR Spectroscopy of Precatalysts + MAO. In a nitrogen-filled drybox, 5 mg of each complex was dissolved in 0.5 mL of dry toluene-d_8 and then treated with the appropriate amount of dry MAO (60 or 200 equiv dissolved in 0.5 mL of toluene-d_8). ^{31}P NMR spectra were recorded immediately.

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Supporting Information Available: Details of X-ray crystal structure determinations, ^{31}P NMR spectra of **1−3** in the presence and absence of MAO, and EPR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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