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# Frustrated $\beta$-Chloride Elimination. Selective Arene Alkylation by α-Chloronorbornene Catalyzed by Electrophilic Metallocenium Ion Pairs

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***Abstract:*** Single-site polymerization catalysts generated in situ via activation of $Cp^*MMe_3$ ($Cp^* = C_5Me_5$; M = Ti, Zr), (CGC)$MMe_2$ (CGC = $C_5Me_4SiMe_2NBu^t$; M = Ti, Zr), and $Cp_2ZrMe_2$ with $Ph_3C^+B(C_6F_5)_4^-$ catalyze alkylation of aromatic molecules (benzene, toluene) with α-chloronorbornene at room temperature, to regioselectively afford the 1:1 addition products *exo*-1-chloro-2-arylnorbornane (aryl = $C_6H_5$ (**1a**), $C_6H_4$-$CH_3$ (**1b**)) in good yields. Analogous deuterium-labeled products *exo*-1-chloro-2-aryl-$d_n$-norbornane-7-$d_1$ (aryl-$d_n$ = $C_6D_5$ (**1a-$d_6$**), $C_6D_4CD_3$ (**1b-$d_8$**)) are obtained via catalytic arylation of α-chloronorbornene in either benzene-$d_6$ or toluene-$d_8$. Isolated ion-pair complexes such as (CGC)ZrMe(toluene)$^+B(C_6F_5)_4^-$ and $Cp^*_2ThMe^+B(C_6F_5)_4^-$ also catalyze the reaction of α-chloronorbornene in toluene-$d_8$ to give **1b-$d_8$** in good yields, respectively. Small quantities of the corresponding bis(1-chloronorbornyl)aromatics **2** are also obtained from preparative-scale reactions. These reactions exhibit turnover frequencies exceeding 120 $h^{-1}$ (for the $Cp^*TiMe_3/Ph_3C^+B(C_6F_5)_4^-$-catalyzed system), and chlorine-free products are not observed. Compounds **1** and **2** were characterized by $^1H$, $^2H$, $^{13}C$, and 2D NMR, GC−MS, and elemental analysis. The aryl group *exo*-stereochemistry in **1a** and **1b** is established using $^1H-^1H$ COSY, $^1H-^{13}C$ HMBC, and $^1H-^1H$ NOESY NMR, and is further corroborated by X-ray analysis of the product 1,4-bis(*exo*-1-chloro-2-norbornyl)benzene (**2a**). Control experiments and reactivity studies on each component step suggest a mechanism involving participitation of the metal electrophiles in the catalytic cycle.

## Introduction

Single-site early-transition-metal catalysts for the coordinative/insertive polymerization of nonpolar olefins have been extensively studied.[1] Such catalysts are of great fundamental scientific and technological importance, and a broad understanding of catalyst−cocatalyst structure−activity−selectivity relationships toward ethylene/α-olefins has recently emerged. However, far less progress has been made toward achieving controlled single-site insertive polymerization of functionalized vinyl monomers (polar monomers such as vinyl chloride, vinyl acetate, acrylates, etc.) or copolymerization of polar and nonpolar monomers.[2,3] Thus, the development and design of catalysts for the insertive polymerization/copolymerization of polar monomers (e.g., vinyl chloride) is a continuing challenge of long-standing interest and has attracted considerable attention in recent years. The discovery and implementation of such catalysts could allow control of product polymer microstructure, polar comonomer incorporation, stereoregularity, and molecular weight characteristics via manipulation and tuning of the catalyst and cocatalyst structure.[4]

Jordan and co-workers recently reported the 1,2-insertion of vinyl chloride at single-site metal−alkyl species (both early- and late-transition-metal catalysts having various ancillary ligand frameworks), generating $\beta$-chloroalkylmetal species.[5] The latter

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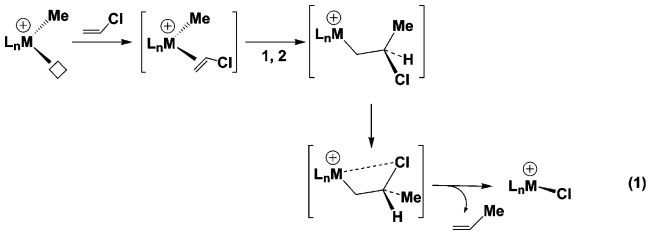
undergo rapid, irreversible $\beta$-Cl elimination to yield catalytically inactive metal−Cl complexes and propylene (eq 1). The




propylene generated in situ subsequently reacts with regenerated metal−alkyl species to afford *atactic* oligopropylene, with no PVC formed. Similarly, vinyl fluoride ($CH_2$═CHF) reacts with early-transition-metal complexes and undergoes insertion followed by $\beta$-F elimination, yielding the corresponding metal−fluoride complexes and olefins.[6,7] Wolczanski and co-workers recently showed that ($^t$Bu$_3$SiO)$_3$TaH$_2$ also undergoes reaction with $CH_2$═CHX (X = F, Cl, Br) via 1,2-insertion and rapid $\beta$-halide elimination.[8] An elegant way to detect/quantify the significance of such insertion/$\beta$-Cl elimination pathways was demonstrated by Boone and co-workers using deuterium-labeled vinyl chloride.[9] In copolymerization studies of vinyl chloride with ethylene (VC:ethylene = 1:9 molar ratio) using the Fe−alkyl species of the (pyridinebisimine)$FeCl_2$/MAO (methylalumoxane) catalyst system, the low molecular weight ethylene oligomers obtained contained the deuterium label located exclusively at the olefin terminus with no Cl functionality present.

Thus, to date, the unsuccessful attempts to effect vinyl chloride polymerization using single-site catalysts are due to rapid, catalyst-deactivating $\beta$-Cl elimination following the first vinyl chloride insertion at the metal−alkyl species.[5] It is likely that $\beta$-Cl elimination is driven thermodynamically by the very large bond dissociation enthalpies of metal−Cl bonds relative to metal−alkyl bonds.[10] However, consideration of the likely *syn*-periplanar transition state required for $\beta$-Cl elimination at single-site centers suggests that the insertion of rigid haloolefins such as α-chloronorbornene at metal−alkyl ion pairs should stereochemically disfavor the metal−chlorine conformation necessary for subsequent $\beta$-Cl elimination.[11,12] This picture is supported by Spartan-level calculations[13] comparing the approaches to the $\beta$-Cl elimination transition states (TSs) of

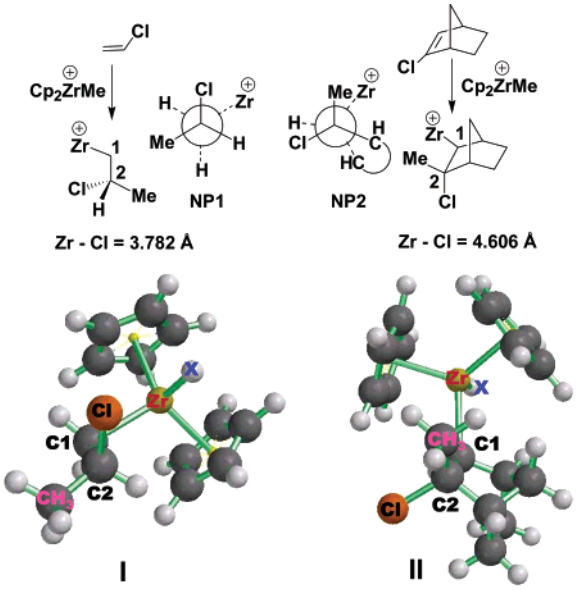



***Figure 1.*** Energy-minimized Spartan-level molecular geometries of the 1,2-insertion products of vinyl chloride (**I**) and α-chloronorbornene (**II**) into the $Zr^+$−Me bond of the $Cp_2ZrMe^+$ cation. X represents the vacant coordination site of the zirconocenium cation. **NP1** and **NP2** represent the Newman projections of the corresponding energy-minimized Spartan structures **I** and **II**, respectively.

inserted vinyl chloride vs α-chloronorbornene at the model $Cp_2ZrMe^+$ cation (Figure 1).

The computed Zr−Cl bond distance in optimized structure **I** is 3.782 Å, whereas in structure **II**, the corresponding distance is 4.606 Å. In the Newman projection of the transition state, the vinyl chloride insertion product allows the metal cation and Cl moiety to attain a favorable mutual *syn*-periplanar orientation due to the free rotation about the unconstrained C−C bond. In contrast, the bicyclic system is locked into a conformation where the metal cation and the $\beta$-Cl moiety are necessarily *anti*-periplanar (**II**); hence, it would appear markedly unsuited for rapid $\beta$-Cl elimination. These considerations raise the intriguing question of just what reactivity such a bicyclic vinyl chloride might display with respect to single-site olefin polymerization catalysts.

In this paper, we report our findings on the insertion chemistry of α-chloronorbornene with respect to a representative series of group 4 and 5f$^0$ single-site olefin polymerization catalysts (shown in Chart 1) differing in metal and ancillary ligation and activated with either a strong Lewis acid ($B(C_6F_5)_3$) or methide-abstracting ($Ph_3C^+B(C_6F_5)_4^-$) cocatalysts in either benzene or toluene solution. It will be seen that the result is a unique group 4 metal-centered catalytic C−C bond forming arylation process.

## Experimental Section

**General Procedures.** All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold

(6) (a) Reaction of $(C_5Me_5)_2ScMe$ with vinyl fluoride yields $(C_5Me_5)_2ScF$ and propylene via insertion and subsequent $\beta$-F elimination; see: Burger, B. Thesis, California Institute of Technology, 1987. (b) Reaction of vinyl fluoride with $Cp_2ZrHCl$ proceeds via insertion/$\beta$-F elimination, yielding $Cp_2ZrFCl$ and ethylene; see: Watson, L. A.; Yandulov, D. V.; Caulton, K. G. *J. Am. Chem. Soc.* **2001**, *123*, 603−611.

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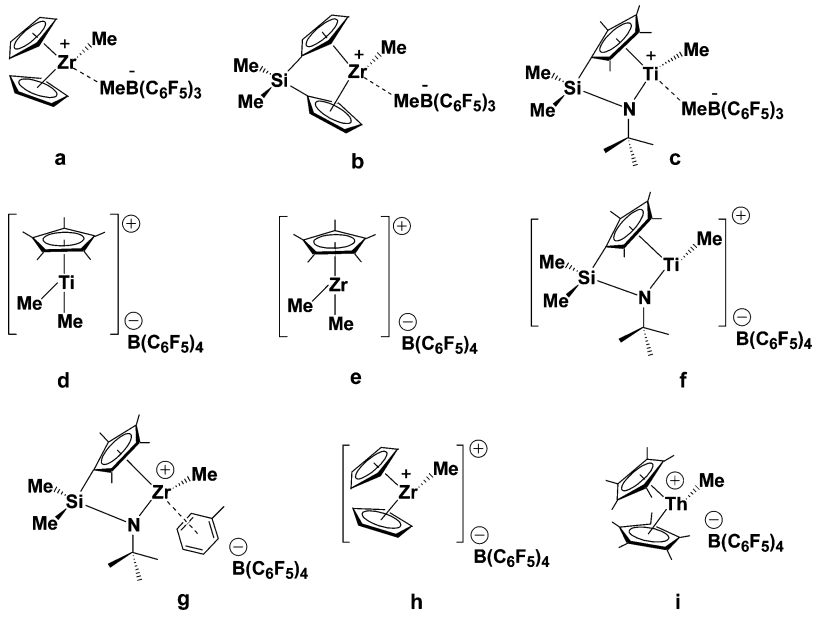
(13) Spartan/MM2-level molecular modeling studies were carried out using the Spartan '02 windows program (Wavefunction, Inc., Irvine, CA, 2001).

***Chart 1*** [a]




[a] Brackets indicate that the exact structure of the ion pair has not yet been established.

Schlenk line, interfaced to a high-vacuum manifold ($10^{-6}$ Torr), or in a nitrogen-filled Vacuum Atmospheres or Mbraun glovebox with a high-capacity recirculator (<2 ppm $O_2$). Argon (Matheson, prepurified) was purified by passage through a MnO oxygen-removal column and a Davison 4A molecular sieve column. All hydrocarbon solvents were dried and degassed over Na/K alloy and transferred in vacuo immediately prior to use. Deuterated solvents (benzene-$d_6$ and toluene-$d_8$) were purchased from Cambridge Isotope Laboratories (all >99 atom % D), dried over Na/K alloy, frozen−pumped−thawed−degassed, and stored in Teflon valve-sealed storage tubes. Commercially available materials were purchased from Aldrich and used without further purification unless otherwise noted. $B(C_6F_5)_3$ was a gift from Dow Chemical and was purified by recrystallization from pentane, followed by vacuum sublimation. $Ph_3C^+B(C_6F_5)_4^-$ was obtained from Asahi Glass Co. or synthesized and purified by a literature procedure.[14] MAO (obtained as a toluene solution from Aldrich) was dried under high vacuum before use for 48 h to remove excess volatile aluminum alkyls. α-Chloronorbornene was prepared and purified by published methods.[15] The organometallic complexes Cp*$MMe_3$ (M = Ti,[16] Zr[17]), (CGC)-$MMe_2$ (M = Ti, Zr),[18] $Cp_2ZrMe_2$,[19] (CGC)ZrMe(toluene)$^+B(C_6F_5)_4^-$,[20] and $Cp^*_2ThMe^+B(C_6F_5)_4^-$ [20] were prepared and purified according to literature procedures. The contact ion pairs $Cp_2ZrMe^+MeB(C_6F_5)_3^-$,[21] $Me_2SiCp_2ZrMe^+MeB(C_6F_5)_3^-$,[22] and (CGC)$TiMe^+MeB(C_6F_5)_3^-$ [23] were synthesized by literature procedures, isolated as solids by recrystallization, and dried under vacuum.

**Physical and Analytical Measurements.** NMR spectra were recorded on either a Varian Mercury-400 (FT; 400 MHz, $^1$H; 100 MHz, $^{13}$C) or UNITY Inova-500 (FT; 500 MHz, $^1$H; 125 MHz, $^{13}$C) spectrometer in Teflon-valved NMR (J. Young) tubes at 23 °C unless otherwise indicated. $^1$H and $^{13}$C chemical shifts ($\delta$) are reported vs the $SiMe_4$ resonance and were determined by reference to the residual solvent peaks. $^{19}$F NMR chemical shifts are reported vs the $CFCl_3$ peak ($\delta = 0$). Coupling constants are given in hertz. The assignment of the signals for spectroscopically pure compounds was made from $^1$H−$^1$H COSY, gated {$^1$H}$^{13}$C, DEPT $^{13}$C, $^1$H−$^{13}$C HMQC, $^1$H−$^{13}$C HMBC, and $^1$H−$^1$H NOESY spectroscopy. GC−MS experiments were conducted using a Hewlett-Packard 5973N instrument operating at 70 eV. Elemental analyses were performed by Midwest Microlab.

**Additional Purification of α-Chloronorbornene.** A portion of α-chloronorbornene (20.0 g) was vacuum-transferred into a storage flask containing $CaH_2$ (predried under vacuum overnight) and was stirred at room temperature for 2 days. It was then vacuum-transferred into a storage tube containing Davison 4A molecular sieves (activated under vacuum at 150 °C overnight). After stirring at room temperature for 1 day, followed by freeze−pump−thaw−degassing (three times) on the high-vacuum line, the α-chloronorbornene was vacuum-transferred and stored in a Teflon valve-sealed storage tube as a colorless liquid. $^1$H NMR (toluene-$d_8$): $\delta$ 5.58 (d, $J$ = 2.4, 1H, =C*H*), 2.63 (s, 1H, allylic C*H*), 2.53 (s, 1H, allylic C*H*), 1.35−1.40 (m, 3H), 1.10−1.14 (m, 1H), 0.90−0.95 (m, 1H), 0.77−0.80 (m, 1H). A portion of α-chloronorbornene (0.20 g, 0.87 mmol) in toluene-$d_8$ (0.6 mL) was exposed to $Cp_2ZrMe_2$ (5.0 mg, 0.02 mmol). Evolution of $CH_4$ was not detected by $^1$H NMR. Similarly, when $La[CH(SiMe_3)_2]_3$ was contacted with an excess of α-chloronorbornene in toluene-$d_8$, generation of $CH_2(SiMe_3)_2$ was not detected by $^1$H NMR, indicating the absence of any trace amounts of moisture or other protic reagents in the α-chloronorbornene.

**Reaction of α-Chloronorbornene with Isolated/Purified $L_2MMe^+$-$MeB(C_6F_5)_3^-$ Contact Ion Pairs ($L_2$ = $Cp_2$, M = CGC, M = Ti).** A J. Young NMR tube was charged with $Cp_2ZrMe^+MeB(C_6F_5)_3^-$ (8.9 mg, 0.012 mmol) and toluene-$d_8$ (0.60 mL), and 1.0 equiv of α-chloronorbornene (1.5 $\mu$L) was added in the glovebox. The tube was sealed and vigorously agitated, and the reaction was monitored periodically by $^1$H and $^{19}$F NMR spectroscopy. No reaction was observed at room temperature over the course of at least 12 h. $^{19}$F NMR

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showed only the presence of the coordinated $MeB(C_6F_5)_3^-$ group ($\delta_F$ −133.8, −159.0, −164.3). The mixture was next heated at 60 °C for 6 h, and a $^1$H NMR spectrum evidenced no detectable reaction. The use of polar solvents such as methylene chloride-$d_2$ and chlorobenzene-$d_5$ was also attempted, and no detectable reaction was observed. Similarly, combining either $Me_2SiCp_2ZrMe^+MeB(C_6F_5)_3^-$ or $(CGC)TiMe^+MeB(C_6F_5)_3^-$ in toluene-$d_8$ with either 1.0 or 10.0 equiv of α-chlorononorbornene at room temperature/60 °C showed no detectable reaction.

**Quantification of Generated $Ph_3CMe$ from Reaction of $Cp^*TiMe_3$ and $Ph_3C^+B(C_6F_5)_4^-$.** A J. Young NMR tube was charged with $Cp^*TiMe_3$ (3.0 mg, 0.013 mmol), $Ph_3C^+B(C_6F_5)_4^-$ (12.1 mg, 0.013 mmol), and an internal standard consisting of either $Ph_3SiMe$ (3.6 mg, 0.013 mmol) or $Si(SiMe_3)_4$ (2.1 mg, 0.0060 mmol). Toluene-$d_8$ (0.60 mL) was added either in the glovebox or by vacuum transfer at −78 °C. The tube was sealed and vigorously agitated for 2 min at room temperature, resulting in an orange-red solution. A $^1$H NMR spectrum recorded in <5 min at room temperature showed complete consumption of $Cp^*TiMe_3$ as evidenced by the complete disappearance of resonances at $\delta$ 1.75 (Cp*) and 0.96 (Me). Moreover, complete disappearance of the distinctive $Ph_3C^+$ cation resonances at $\delta$ 7.33 and 6.77 was observed, and the signals were replaced by the phenyl resonances of $Ph_3CMe$ (at $\delta$ 7.00−7.05). A comparison of the integrated intensities of the resonance at $\delta$ 2.01 (for Me protons of $Ph_3CMe$) versus that of the internal standard (either $Ph_3SiMe$ ($\delta_H$ = 0.72 for Me) or $Si(SiMe_3)_4$ ($\delta_H$ = 0.26 for Me)) revealed the quantitative formation of methyl-abstraction product $Ph_3CMe$. The $^{19}$F NMR spectrum ($\delta_F$ −131.4, −165.6, −167.7) showed the anion $B(C_6F_5)_4^-$ to be free and noncoordinating. Attempts were not made to identify the exact nature of the organotitanium species formed due to their instability and substantial decomposition over time.

**NMR-Scale Reaction of α-Chlorononorbornene with $Cp^*TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$.** In the glovebox, a J. Young NMR tube was charged with $Cp^*TiMe_3$ (3.0 mg, 0.013 mmol), $Ph_3C^+B(C_6F_5)_4^-$ (12.1 mg, 0.013 mmol), and benzene-$d_6$ (0.60 mL). The tube was sealed and vigorously agitated for 2 min at room temperature, and then 10.0 equiv of α-chlorononorbornene (20.0 μL) was added. An immediate dark-red solution was obtained. A $^1$H NMR spectrum recorded in <5 min revealed complete consumption of α-chlorononorbornene (as evidenced by the disappearance of the olefinic proton resonance at $\delta$ 5.58) and afforded *exo*-1-chloro-2-phenyl-$d_5$-norbornane-7-$d_1$ (**1a-$d_6$**) quantitatively. Similarly, the activation reaction of $Cp^*TiMe_3$ with 0.92 equiv of $Ph_3C^+B(C_6F_5)_4^-$ in benzene-$d_6$ (0.6 mL), followed by addition of 10.0 equiv of α-chlorononorbornene at room temperature, leads to the quantitative formation of **1a-$d_6$** in <5 min.

**Preparative-Scale Synthesis of *exo*-1-Chloro-2-phenylnorbornane (1a).** A 50 mL Schlenk flask was charged in the glovebox with $Cp^*TiMe_3$ (5.0 mg, 0.022 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (20.2 mg, 0.022 mmol). The flask was then attached to the vacuum line, benzene (15.0 mL) was condensed in at −78 °C, and the contents of the flask were warmed to room temperature and stirred for 2 min. A portion of α-chlorononorbornene (0.50 g, 3.9 mmol; α-chlorononorbornene:Ti = 177:1 molar ratio) was measured in the glovebox and was added to the reaction flask by gastight syringe. An immediate red color was observed. The reaction mixture was then allowed to stir at room temperature, and after 5 h, the reaction was quenched with methanol (5.0 mL). No polymeric materials were precipitated from the solution; however, analysis of an aliquot by GC−MS showed complete consumption of α-chlorononorbornene. The volatiles were next removed in vacuo, resulting in an oily residue, which was subjected to chromatographic workup (silica gel column, followed by TLC) to yield **1a** as a colorless liquid (0.65 g, 81.0%). In addition, small quantities of 1,4-bis(*exo*-1-chlorononorbornyl)benzene (**2a**) were also isolated as a white solid (0.20 g, 7.0%). Crystals of **2a** suitable for single-crystal X-ray diffraction study were obtained from pentane/$CH_2Cl_2$ (4:1) solution at room temperature.

**Data for 1a**. $^1$H NMR ($CDCl_3$): $\delta$ 7.28−7.32 (m, 2H, *m*-C*H*Ph), 7.22−7.24 (m, 3H, *o*- and *p*-C*H*Ph), 2.98 (dd, $J$ = 8.5 and 6.0, 1H, allylic C*H*), 2.33 (br s, 1H, C*H*), 2.14 (dd, $J$ = 10.0 and 2.0, 1H), 1.84−2.12 (m, 5H), 1.65 (dd, $J$ = 10.0 and 1.0, 1H), 1.47−1.54 (m, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 144.1 (s, quart. phenyl *C*), 129.1 (s, *o*-*C*HPh), 128.1 (s, *m*-*C*HPh), 126.8 (s, *p*-*C*HPh), 74.1 (s, *C*Cl), 52.8 (s, *C*HPh), 43.9 (s, *C*H$_2$), 41.2 (s, *C*H$_2$), 40.3 (s, *C*H$_2$), 34.0 (s, *C*H), 30.9 (s, *C*H$_2$). GC−MS: *m*/*z* 208 ($M^+$ + 2), 206 ($M^+$), 170 ($M^+$ − 36 (HCl)). Anal. Calcd for $C_{13}H_{15}Cl$: C, 75.54; H, 7.31; Cl, 17.15. Found: C, 75.69; H, 7.40; Cl, 17.35.

**Data for 2a.** $^1$H NMR ($CDCl_3$): $\delta$ 7.19 (s, 4H, phenyl C*H*), 2.98 (dd, $J$ = 8.5 and 6.0, 2H, allylic C*H*), 2.35 (br s, 2H, C*H*), 1.86−2.15 (m, 12H), 1.65 (d, $J$ = 10.0, 2H), 1.48−1.55 (m, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 142.3 (s, quart. phenyl *C*), 128.7 (s, phenyl *C*H), 74.2 (s, *C*Cl), 52.4 (s, *C*HPh), 43.9 (s, *C*H$_2$), 41.2 (s, *C*H$_2$), 40.2 (s, *C*H$_2$), 34.1 (s, *C*H), 30.9 (s, *C*H$_2$). GC−MS: *m*/*z* 338 ($M^+$ + 4), 336 ($M^+$ + 2), 334 ($M^+$), 298 ($M^+$ − 36 (HCl)). Anal. Calcd for $C_{20}H_{24}Cl_2$: C, 71.64; H, 7.21; Cl, 21.15. Found: C, 71.82; H, 7.32; Cl, 21.32.

**Synthesis of *exo*-1-Chloro-2-phenyl-$d_5$-norbornane-7-$d_1$ (1a-$d_6$).** The analogous deuterium-labeled benzene-addition adduct of α-chlorononorbornene was prepared in a procedure similar to the synthesis of **1a** described above using benzene-$d_6$ as the aromatic reagent. The product **1a-$d_6$** (>98% deuterium labeled) was characterized using $^2$H NMR and spectroscopic techniques.

**Data for 1a-$d_6$.** $^2$H NMR ($CDCl_3$): $\delta$ 7.44 (br s, 2D, *m*-C*D*Ph), 7.36 (br s, 3D, *o*- and *p*-C*D*Ph), 2.23 (br s, 1D, CH*D*). $^2$H NMR ($CD_2Cl_2$): $\delta$ 8.25 (br s, 2D, *m*-C*D*Ph), 8.17 (br s, 3D, *o*- and *p*-C*D*Ph), 2.96 (br s, 1D, CH*D*). $^1$H NMR ($CDCl_3$): $\delta$ 2.98 (dd, $J$ = 8.5 and 6.0, 1H, allylic C*H*), 2.33 (virtual triplet, $J$ = 3.75, 1H, C*H*), 1.84−2.12 (m, 5H), 1.63 (br s, 1H, C*H*D), 1.47−1.54 (m, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 143.9 (s, quart. phenyl *C*), 128.7 (t, $J_{C-D}$ = 23.7, *o*-*C*Dph), 127.6 (t, $J_{C-D}$ = 24.2, *m*-*C*Dph), 126.3 (t, $J_{C-D}$ = 24.2, *p*-*C*Dph), 74.1 (s, *C*Cl), 52.7 (s, *C*HPh), 43.5 (t, $J_{C-D}$ = 20.8, *C*HD), 41.2 (s, *C*H$_2$), 40.2 (s, *C*H$_2$), 33.9 (s, *C*H), 30.9 (s, *C*H$_2$). GC−MS: *m*/*z* 214 ($M^+$ + 2), 212 ($M^+$), 176 ($M^+$ − 36 (HCl)).

**Synthesis of *exo*-1-Chloro-2-tolylnorbornane (1b).** Similar to the procedure described above for the synthesis of **1a**, the reaction product of $Cp^*TiMe_3$ (5.0 mg, 0.022 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (20.2 mg, 0.022 mmol) in toluene (15.0 mL) was treated with α-chlorononorbornene (2.0 g, 15.6 mmol; α-chlorononorbornene:Ti = 709:1 molar ratio) at room temperature. The reaction mixture was stirred for 12 h at room temperature and then quenched with methanol (5.0 mL). After removal of solvent in vacuo, followed by chromatographic workup, **1b** was obtained as a colorless liquid (3.0 g, 87.0%). The product is a mixture of positional isomers with *ortho*:*meta*:*para* = 28:30:42.

**Data for 1b.** $^1$H NMR ($CDCl_3$): $\delta$ 7.03−7.30 (m, 3 × 4H, C*H* of phenyl), 3.34 (dd, $J$ = 8.75 and 6.25, 1H, allylic C*H*), 2.96 (dd, $J$ = 8.6 and 5.8, 2 × 1H, allylic C*H*), 2.39, 2.36, 2.33 (s, 3 × 3H, C*H*$_3$), 1.86−2.22 (m, 3 × 7H, C*H*), 1.48−1.68 (m, 3 × 2H, C*H*). $^{13}$C NMR ($CDCl_3$): $\delta$ 144.0, 142.3, 141.1, 137.8, 137.5, 136.3 (s, 6 × 1 quart. Ph *C*), 130.2, 130.0, 128.0, 127.6, 126.6, 126.4, 126.1, 125.9 (s, 8 × 1 *C*H of phenyl), 129.0, 128.8 (s, 2 × 2 *C*H of phenyl), 74.2, 74.1, 74.0 (s, 3 × 1 *C*Cl), 52.7 (s, *C*HPh), 52.3 (s, 2 × 1 *C*HPh), 46.4 (s, *C*H), 44.0, 43.9, 43.8 (s, 3 × 1 *C*H$_2$), 41.4, 41.2, 41.1 (s, 3 × 1 *C*H$_2$), 40.3, 40.2, 40.0 (s, 3 × 1 *C*H$_2$), 34.0 (s, 2 × 1 *C*H), 30.9, 30.8, 30.7 (s, 3 × 1 *C*H$_2$), 21.8 (s, CH$_3$), 21.2 (s, 2 × 1 *C*H$_3$). GC−MS: *m*/*z* 222 ($M^+$ + 2), 220 ($M^+$), 184 ($M^+$ − 36 (HCl)). Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.18; H, 7.76; Cl, 16.06. Found: C, 76.35; H, 7.63; Cl, 16.39.

**Data for *exo*-1-Chloro-2-tolyl-$d_7$-norbornane-7-$d_1$ (1b-$d_8$).** The characteristic signal in the $^1$H-decoupled $^{13}$C NMR of **1b-$d_8$** displays multiple peaks at $\delta$ 43.2−43.7 for *C*HD groups due to the presence of three different positional isomers. GC−MS: *m*/*z* 230 ($M^+$ + 2), 228 ($M^+$), 192 ($M^+$ − 36 (HCl)).

**Reaction of α-Chlorononorbornene with the $Cp^*ZrMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ Activated System.** In the glovebox, a J. Young NMR tube was charged with $Cp^*ZrMe_3$ (3.6 mg, 0.013 mmol), $Ph_3C^+B(C_6F_5)_4^-$

(12.1 mg, 0.013 mmol), and toluene-$d_8$ (0.60 mL). The tube was sealed and vigorously agitated for 2 min at room temperature, and 10.0 equiv of α-chloronorbornene (20.0 μL) was added. The progress of the reaction was monitored periodically by $^1$H NMR spectroscopy. After 14 h at room temperature, the $^1$H NMR spectrum showed quantitative conversion to **1b-*d*$_8$**. The *ortho*:*meta*:*para* ratio was 29:29:42.

**Reaction of α-Chloronorbornene with the (CGC)MMe$_2$ (M = Zr, Ti)/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ Activated System.** In the glovebox, a J. Young NMR tube was charged with (CGC)ZrMe$_2$ (4.9 mg, 0.013 mmol), Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (12.1 mg, 0.013 mmol), and toluene-$d_8$ (0.60 mL). The tube was sealed and vigorously agitated for 2 min at room temperature, and 10.0 equiv of α-chloronorbornene (20.0 μL) was added. The progress of the reaction was monitored periodically by $^1$H NMR spectroscopy. A 63% conversion to **1b-*d*$_8$** was observed after 41 h at room temperature. The *ortho*:*meta*:*para* ratio was 29:28:43. Similarly, the reaction product of (CGC)TiMe$_2$ and Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ in toluene-$d_8$ (0.60 mL) was reacted with 10.0 equiv of α-chloronorbornene (20.0 μL). A $^1$H NMR spectrum recorded after 48 h at room temperature showed an 81% conversion to **1b-*d*$_8$**. The ratio of three arene positional isomers was *ortho*:*meta*:*para* = 28:30:42.

**Reaction of the Isolated Ion Pair (CGC)ZrMe(toluene)$^+$B(C$_6$F$_5$)$_4^-$ with α-Chloronorbornene.** In the glovebox, a J. Young NMR tube was charged with the isolated complex (CGC)ZrMe(toluene)$^+$B(C$_6$F$_5$)$_4^-$ (5.0 mg, 0.0050 mmol) and toluene-$d_8$ (0.60 mL). Then α-chloronorbornene (20.0 μL, 0.13 mmol) was added to the tube, and the tube was sealed and vigorously agitated. The progress of the reaction was monitored periodically at room temperature by $^1$H NMR spectroscopy. A 32% conversion to **1b-*d*$_8$** was observed after 110 h at room temperature. The *ortho*:*meta*:*para* ratio was 33:31:36.

**Reaction of α-Chloronorbornene with the Cp$_2$ZrMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ Activated System.** In the glovebox, a J. Young NMR tube was charged with Cp$_2$ZrMe$_2$ (3.3 mg, 0.013 mmol), Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (12.1 mg, 0.013 mmol), and toluene-$d_8$ (0.60 mL). The tube was sealed and vigorously agitated for 2 min at room temperature, and 1.0 equiv of α-chloronorbornene (1.7 μL) was added. Complete conversion to **1b-*d*$_8$** was observed after 4 h at room temperature. Another 10.0 equiv of α-chloronorbornene (20.0 μL) was then added to the tube inside the glovebox and the progress of the reaction monitored periodically by $^1$H NMR spectroscopy. Compound **1b-*d*$_8$** was formed quantitatively after 24 h at room temperature. The *ortho*:*meta*:*para* ratio was 32:30:38.

**Reaction of Cp*$_2$ThMe$^+$B(C$_6$F$_5$)$_4^-$ with α-Chloronorbornene.** In the glovebox, a J. Young NMR tube was charged with Cp*$_2$ThMe$^+$B(C$_6$F$_5$)$_4^-$ (5.0 mg, 0.004 mmol) and toluene-$d_8$ (0.60 mL). Then, α-chloronorbornene (20.0 μL, 0.13 mmol) was added to the tube, and the tube was sealed and vigorously agitated. The progress of the reaction was monitored periodically at room temperature by $^1$H NMR spectroscopy. A 48% conversion to **1b-*d*$_8$** was observed after 110 h at room temperature. The *ortho*:*meta*:*para* ratio was 31:31:38.

**Control Reactions of α-Chloronorbornene with Radical Initiators.** In the glovebox, a J. Young NMR tube was charged with TEMPO (6.1 mg, 0.039 mmol) and toluene-$d_8$ (0.60 mL). Next, α-chloronorbornene (5.0 μL, 0.039 mmol) was added to the tube, and the tube was sealed and vigorously agitated. The mixture was then monitored by $^1$H NMR. No reaction was detected over a period of 24 h, either at 25 °C or at 110 °C. Experiments using AIBN as the initiator also resulted in negligible reaction between α-chloronorbornene and toluene under similar reaction conditions.

**Reaction of α-Chloronorbornene with Cp*TiMe$_3$/MAO (Al:Ti = 10).** In the glovebox, a J. Young NMR tube was charged with Cp*TiMe$_3$ (3.0 mg, 0.013 mmol), vacuum-dried MAO (10.0 equiv, 7.6 mg, 0.13 mmol), and toluene-$d_8$ (0.60 mL). The tube was then sealed and vigorously agitated to yield an orange-colored solution. Next, 10.0 equiv of α-chloronorbornene (20.0 μL) was added to the tube, and the reaction was monitored periodically by $^1$H NMR spectroscopy. Formation of **1b-*d*$_8$** was not observed over a period of 24 h either at 25 °C or at 90 °C.

**Effect of 2,6-Di-*tert*-butylphenol on Cp*TiMe$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-Catalyzed Arylation of α-Chloronorbornene.** In the glovebox, a J. Young NMR tube was charged with Cp*TiMe$_3$ (3.6 mg, 0.013 mmol), Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (12.1 mg, 0.013 mmol), and toluene-$d_8$ (0.60 mL). The tube was sealed and vigorously agitated for 2 min at room temperature, and then 1.1 equiv of 2,6-di-*tert*-butylphenol (3.0 mg, 0.014 mmol) was added. The tube was then vigorously shaken for 2 min followed by addition of 10.0 equiv of α-chloronorbornene (20.0 μL). A $^1$H NMR spectrum recorded after 5 min showed no significant inhibition of the rate of the arylation reaction, and quantitative conversion to **1b-*d*$_8$** was ultimately observed. Alternatively, to the activated Cp*TiMe$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ system in toluene-$d_8$ (0.60 mL) was added 10.0 equiv of α-chloronorbornene (20.0 μL) at 25 °C. A $^1$H NMR spectrum showed **1b-*d*$_8$** had formed quantitatively in <5 min. Next, 1.1 equiv of 2,6-di-*tert*butylphenol (3.0 mg, 0.014 mmol) was added to the reaction mixture, and the resulting mixture was vigorously agitated, followed by addition of another 10 equiv of α-chloronorbornene (20.0 μL) at room temperature. A $^1$H NMR spectrum recorded immediately thereafter showed complete α-chloronorbornene conversion to **1b-*d*$_8$**. Control studies showed that both the Cp*TiMe$_3$ and Cp*TiMe$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ systems react with 2,6-di-*tert*-butylphenol very slowly at 25 °C. For example, when Cp*TiMe$_3$ was reacted with 1.0 equiv of di-*tert*-butylphenol in toluene-$d_8$ at 25 °C, $^1$H NMR revealed the generation of Cp*Ti(O-2,6-$^t$Bu$_2$C$_6$H$_3$)Me$_2$ in only trace amounts after 1 h, and in 30% yield only after 6 h. Similarly, when 1.0 equiv of di-*tert*-butylphenol was combined with the Cp*TiMe$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ activated system in toluene-$d_8$ at 25 °C, the $^1$H NMR revealed the presence of >80% unreacted phenol after 2 h. In addition, the spectrum exhibited a signal for methane, but no Ti−Me signal corresponding to a cationic species such as Cp*Ti(O-2,6-$^t$BuC$_6$H$_3$)Me$^+$B(C$_6$F$_5$)$_4^-$ was detected.

**Reaction of Brønsted Acids (Anhydrous HCl Gas, BF$_3$·OEt$_2$) with α-Chloronorbornene.** In the glovebox, a J. Young NMR tube was charged with toluene-$d_8$ (0.60 mL) and α-chloronorbornene (10.0 μL). The tube was connected to the high-vacuum line, and anhydrous HCl gas was condensed in at −78 °C. The tube was then sealed and vigorously agitated, and the ensuing reaction was monitored periodically by $^1$H NMR spectroscopy. Formation of **1b-*d*$_8$** was not observed over the course of 12 h at 25 °C. Similarly, to a solution of α-chloronorbornene (5.0 μL, 0.039 mmol) in toluene-$d_8$ (0.60 mL) was added BF$_3$·OEt$_2$ (3.6 μL, 0.039 mmol), and the reaction was monitored by $^1$H NMR. Negligible formation of **1b-*d*$_8$** was detected over a period of 12 h, either at 25 °C or at 90 °C.

**Control Reaction of α-Chloronorbornene with Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$.** In the glovebox, a J. Young NMR tube was charged with Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (35.9 mg, 0.039 mmol) and toluene-$d_8$ (0.60 mL). Next, 1.0 equiv of α-chloronorbornene (5.0 μL, 0.039 mmol) was added to the tube, and the tube was sealed and vigorously agitated. The reaction mixture was then monitored at 25 °C by $^1$H NMR. A reaction time of 12 h at 25 °C was required for complete conversion of the α-chloronorbornene, and **1b-*d*$_8$** was formed quantitatively. In a separate experiment, 1.1 equiv of 2,6-di-*tert*-butyl-phenol (8.0 mg, 0.039 mmol) was mixed with Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (35.9 mg, 0.039 mmol) in toluene-$d_8$ (0.60 mL), and then α-chloronorbornene (5.0 μL, 0.039 mmol) was added to the reaction mixture. No reaction was detected over a period of 24 h at 25 °C. Control studies indicated no reaction between Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ and 2,6-di-*tert*-butyl-phenol in toluene-$d_8$ over 12 h at 25 °C.

**Reaction of Lewis Acids (B(C$_6$F$_5$)$_3$, MAO, SnCl$_4$, Cp*TiCl$_3$, TiCl$_4$) with α-Chloronorbornene.** A series of control experiments involving the reaction of α-chloronorbornene with conventional strong Lewis acids (B(C$_6$F$_5$)$_3$, MAO, SnCl$_4$) and Ti-based Lewis acids (Cp*TiCl$_3$, TiCl$_4$) was conducted using 1:1 stoichiometric ratios. A representative example is given here. To a Wilmad screw-capped NMR tube were added toluene-$d_8$ (0.60 mL) and α-chloronorbornene (1.5 μL, 0.012

***Table 1.*** Crystal Data and Structure Refinement for **2a**

| | |
|---|---|
| empirical formula | $C_{20}H_{24}Cl_2$ |
| fw | 335.29 |
| temp | 153(2) K |
| wavelength | 0.71073 Å |
| cryst syst, space group | orthorhombic, *Pbca* |
| unit cell dimensions | $a = 11.931(3)$ Å |
| | $b = 11.152(2)$ Å |
| | $c = 12.3422(13)$ Å |
| $V$ | 1642.2(5) Å$^3$ |
| $Z$, calcd density | 4, 1.356 g/m$^3$ |
| abs coeff | 0.390 mm$^{-1}$ |
| $F$(000) | 712 |
| cryst size | 0.320 × 0.250 × 0.190 mm |
| $\theta$ range for data collection | 3.00−29.04° |
| limiting indices | $-16 < h < +15$, $-14 < k < +14$, $-15 < l < +16$ |
| no. of reflns collected/unique | 14374/2066 [$R$(int) = 0.0348] |
| completeness to $\theta = 29.04°$ | 94.1% |
| abs correction | integration |
| max and min transmission | 0.9387 and 0.9036 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 2066/0/100 |
| goodness-of-fit on $F^2$ | 1.061 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0381, wR2 = 0.1071 |
| $R$ indices (all data) | R1 = 0.0438, wR2 = 0.1134 |
| largest diff peak and hole | 0.579 and −0.210 e$^-$/Å$^{-3}$ |

mmol) in the glovebox. Next, $TiCl_4$ (1.3 μL, 0.012 mmol) was added by microsyringe, and the reaction was monitored by $^1$H NMR. No reaction was observed over the course of 24 h at room temperature and at 90 °C for 6 h. Similarly, when $B(C_6F_5)_3$, MAO, $SnCl_4$, and Cp*$TiCl_3$ were added to α-chloronorbornene in toluene-$d_8$, no reaction was observed over the course of 12 h, either at 25 °C or at 90 °C.

**Crystal Structure Determination for 2a.** Suitable single crystals of **2a** were obtained by slow evaporation from a $CH_2Cl_2$/pentane (1:4) solution at room temperature. A colorless block crystal of **2a**, covered in Infineum V8512 (aka Paratone-N) oil was mounted on a goniometer head. Data were collected under a cold (−120 °C) $N_2$ stream using a Bruker SMART-1000 CCD area detector with graphite-monochromated Mo Kα radiation. Compound **2a** crystallizes in the space group *Pbca*. The structure was solved by direct methods[24] and expanded using Fourier techniques.[24] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in $F_{calcd}$;[26] the values for Df′ and Df″ were those of Creagh and McAuley.[27] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[28] All calculations were performed using the Shelxtl for WindowsNT software package.[29] The ORTEP diagram and the bond distances and bond angles of **2a** were obtained using the program ORTEP-3 for Windows.[30] Crystal data and details of data collection and structure refinement parameters are given in Table 1. Atomic coordinates and a complete listing of bond lengths and bond angles are available as Supporting Information.

## Results and Discussion

The goal of this investigation was to examine the reactivity patterns with respect to single-site group 4 polymerization catalysts of a conformationally rigid α-chloroalkene monomer in which the transition state for β-Cl elimination is inaccessible. In the first section, we examine the reactivity of α-chloronorbornene with single-site group 4 complexes using $B(C_6F_5)_3$ as the cocatalyst; the resulting $M^+-Me$ species are known to undergo insertion of vinyl chloride.[5] We then focus on the chloronorbornene reaction scope using $Ph_3C^+B(C_6F_5)_4^-$ as a methide abstractor for the activation of single-site catalysts. Finally, a number of control experiments are conducted to gain further insight into the reaction pathway, and we propose a plausible mechanism to explain the results.

**(A) Reaction of Well-Defined, Isolable Contact Ion Pairs with α-Chloronorbornene.** Halide-containing vinyl monomers ($CH_2$═$CHX$; X = F, Cl, Br) are known to coordinate to cationic late-transition-metal centers via the olefinic bond rather than via the halogen atom,[5c,31] and such C−X bonds are in general not readily susceptible to nucleophilic substitution reactions.[32] For group 4 and other early-transition metal single-site catalysts, such π-coordination of vinyl halides has not been detected using spectroscopic techniques.[5] However, facile displacement of $MeB(C_6F_5)_3^-$ from in situ generated $L_nMMe^+MeB(C_6F_5)_3^-$ contact ion pairs by vinyl chloride and subsequent insertion of olefin into the metal−alkyl bond is observed, leading to transient $L_nMCH_2CHCl^+$ species, which undergo rapid, exothermic[10] β-Cl elimination to yield catalytically inactive $L_nMCl_2$ products, thus preventing further insertion of vinyl chloride (eq 1).[5]

We therefore examined NMR-scale reactions of isolated and well-characterized contact ion pairs such as $Cp_2ZrMe^+$-$MeB(C_6F_5)_3^-$,[21] $Me_2SiCp_2ZrMe^+MeB(C_6F_5)_3^-$,[22] and (CGC)-$TiMe^+MeB(C_6F_5)_3^-$,[23] having differing steric and electronic characteristics, with α-chloronorbornene. We hypothesized that α-chloronorbornene, once inserted into a metal−$Me^+$ bond, would be resistant to β-Cl elimination processes. Reaction of $Cp_2ZrMe^+MeB(C_6F_5)_3^-$ in toluene-$d_8$ with 1.0 equiv of α-chloronorbornene was monitored by NMR over time at room temperature. No perceptible change in the chemical shifts of the Zr−$Me^+$ (δ 0.27) and $MeB(C_6F_5)_3^-$ (δ 0.11) signals in $Cp_2ZrMe^+MeB(C_6F_5)_3^-$, nor of the α-chloronorbornene olefinic C−H signal (δ 5.58), was observed in the $^1$H NMR, and the $^{19}$F NMR showed only the presence of coordinated $MeB(C_6F_5)_3^-$, indicating that no reaction had occurred. The reaction mixture was then heated to 60 °C and monitored by NMR for 2 h, again indicating no detectable reaction. Similarly, no reaction is observed for $Me_2SiCp_2ZrMe^+MeB(C_6F_5)_3^-$ or (CGC)$TiMe^+$-$MeB(C_6F_5)_3^-$ with α-chloronorbornene in toluene-$d_8$ using either 1:1 or 1:10 catalyst:chloroolefin molar ratios, either at room temperature or at 60 °C. The use of chlorinated polar solvents

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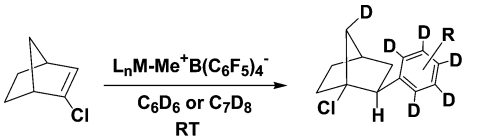
such as methylene chloride or chlorobenzene also has no effect on the inertness of α-chloronorbornene with respect to $Cp_2ZrMe^+MeB(C_6F_5)_3^-$. The unreactive nature of α-chloronorbornene vs vinyl chloride with respect to metallocenium contact ion pairs presumably reflects steric characteristics of the encumbered monomer, and the relatively strong coordination of the $MeB(C_6F_5)_3^-$ counteranion.[33] A similar manifestation of $MeB(C_6F_5)_3^-$ tight binding to a cationic Zr center is observed in the relative inertness of $(CGC)ZrMe^+MeB(C_6F_5)_3^-$ with respect to ethylene polymerization[34] and of most metallocenium $MeB(C_6F_5)_3^-$ ion pairs toward silane chain transfer in olefin polymerization.[35]

**(B) Reaction of α-Chloronorbornene with Group 4 Ion Pairs Having Weakly Coordinating Anions.** The nature of the cation−anion interactions in homogeneous single-site olefin polymerization has attracted considerable attention and clearly plays an important role in modulating activity as well as the product molecular weight and microstructure.[33a,36,37] Systems containing the weakly basic, weakly coordinating $B(C_6F_5)_4^-$ counteranion exhibit significantly enhanced polymerization activity,[20] likely reflecting the lack of significant cationic metal center−anion covalent interactions, the more dispersed anion negative charge, and anion steric encumberance.[33a] It is generally accepted that the activation reaction of metallocene dimethyls with $Ph_3C^+B(C_6F_5)_4^-$ leads to the formation, inter alia, of dinuclear $\mu$-methyl cations, formed in situ by the coordination of the highly electrophilic metallocene monomethyl cation with unreacted neutral metallocene dimethyl.[36c] Most $B(C_6F_5)_4^-$-based ion pairs are thermally unstable, and it is presumed that the subsequent reaction of the $\mu$-methyl dinuclear cations with substrate leads to substrate (e.g., olefin)-coordinated metallocene monomethyl cation or a combination of both substrate- and solvent-coordinated metallocene monomethyl cation. Therefore, in the following studies, the cationic metal species were generated in situ in either benzene or toluene solution using $Ph_3C^+B(C_6F_5)_4^-$ as the activator, and α-chloronorbornene was then added. Three important classes of group 4 single-site catalysts were investigated: half-sandwich catalyst systems based on $Cp^*MMe_3$ (M = Ti, Zr), constrained-geometry catalyst systems based on $(CGC)MMe_2$ (M = Ti, Zr), and $Cp_2ZrMe_2$. The isolable salts $(CGC)ZrMe(toluene)^+B(C_6F_5)_4^-$ [20] and $Cp^*_2ThMe^+B(C_6F_5)_4^-$ [20] were also used as single-component reagents in reactivity studies with α-chloronorbornene.

**(i) Reaction of Activated $Cp^*MMe_3$ (M = Ti, Zr) Complexes with α-Chloronorbornene.** Reaction of $Cp^*TiMe_3$ with 1.0 equiv of $Ph_3C^+B(C_6F_5)_4^-$ in either $C_6D_6$ or toluene-$d_8$ at room temperature immediately generates an orange-red solution. The $^1$H NMR spectrum of the reaction mixture reveals quantitative formation of the methide abstraction product $Ph_3CMe$. The $^{19}$F NMR spectrum reveals negligible decomposition of the $B(C_6F_5)_4^-$ anion and that it is essentially free and noncoordinating.[20] From these spectroscopic data, the organometallic species formed in this process is plausibly formulated as a cation of the type "$Cp^*TiMe_2^+$" (Chart 1). However, the exact nature of the Ti species in this activated system is still a topic of debate among several research laboratories.[38] It is believed and reasonably accepted that Ti(IV) is responsible for the oligomerization/polymerization of propylene/α-olefins, whereas, for an activated, conjugated nonpolar monomer such as styrene, it is more likely that a Ti(III) species mediates the polymerization.[39,40] In a separate experiment, $Cp^*TiMe_3$ was mixed with 1.0 equiv of $Ph_3C^+B(C_6F_5)_4^-$ in $C_6D_6$ and vigorously agitated at room temperature for 2 min, and then 10.0 equiv of α-chloronorbornene was added. A $^1$H NMR spectrum recorded in <5 min at 25 °C showed complete consumption of α-chloronorbornene (evidenced by the disappearance of the olefinic CH signal at $\delta_H$ 5.58), and the $^{19}$F NMR spectrum exhibited only the free $B(C_6F_5)_4^-$ anion. The result is a net catalytic cycle with a turnover frequency >120 $h^{-1}$ (eq 2; see below for product characterization).




(2)

Similar results are also obtained by activating $Cp^*TiMe_3$ with 0.92 equiv of $Ph_3C^+B(C_6F_5)_4^-$ in $C_6D_6$ (to ensure complete $Ph_3C^+$ consumption), followed by addition of α-chloronorbornene, supporting a rapid, metal center-catalyzed reaction. In stoichiometric reactions of 1:1 α-chloronorbornene−$Cp^*TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ at 25 or −20 °C, we were unsuccessful in detecting an olefin $\pi$-complex[41] or an initial insertion product by $^1$H NMR. Instead, the reaction of eq 2 was found to be very rapid, and only formation of the final product (**1a-*d*$_6$**/**1b-*d*$_8$**) is observed.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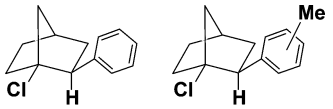
(41) The coordination of vinyl chloride to cationic late-metal catalysts via the C=C $\pi$-bond can be detected and characterized at low temperatures,[5b] whereas such $\pi$-coordination is postulated for group 4 single-site catalysts in olefin insertion/polymerization processes. For evidence of olefin $\pi$-coordination in $d^0/f^n$ model compounds see: (a) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222−3223. (b) Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898−909. (c) Brandow, C. G.; Mendiratta, A.; Bercaw, J. E. *Organometallics* **2001**, *20*, 4253−4261. (d) Casey, C. P.; Carpenetti, D. W., II.; Sakurai, H. *Organometallics* **2001**, *20*, 4262−4265 and references therein. (e) Casey, C. P.; Klein, J. F.; Fagan, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 4320−4330. (f) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750−7767.

To characterize the nature of the organic product formed from the catalytic reaction in eq 2, a preparative-scale reaction involving 0.5 g of α-chloronorbornene was carried out with the $Cp^*TiMe_3/Ph_3C^+B(C_6F_5)_4^-$ activated system (α-chloronorbornene:Ti molar ratio = 178:1) in benzene at 25 °C for 5 h. The reaction was then quenched with MeOH, and analysis of the reaction mixture by GC−MS showed complete consumption of the monomer. No polymeric material is produced in this reaction. After removal of the solvent, further purification by chromatographic techniques (silica gel column, followed by TLC) yielded a colorless liquid that was characterized by spectroscopic techniques and elemental analysis. The data are consistent with a net benzene addition product, *exo*-1-chloro-2-phenylnorbornane (**1a**; 81% yield). In addition, a small amount of the 1,4-bis(*exo*-1-chloronorbornyl)benzene adduct (**2a**; 7% yield) was also isolated as a white solid and characterized.




**1a** **1b**

Key NMR parameters for product **1a** include the following: (i) Aromatic ($\delta$ 7.22−7.32) and alicyclic ($\delta$ 1.49−2.99) protons are present with an intensity ratio of 1:2. In addition, a downfield signal with distinctive multiplicity at $\delta$ 2.98 (dd, $J$ = 8.5 and 6.0 Hz) is assigned to a benzylic proton. (ii) $^1$H-decoupled $^{13}$C and DEPT $^{13}$C NMR confirm the presence of a quaternary *C*Cl signal at $\delta_C$ 74.1, indicating that the Cl moiety remains on the norbornyl skeleton. Moreover, the presence of four $CH_2$ carbon signals (vs three $CH_2$ groups in the starting molecule) suggests rearrangement of the norbornyl skeleton. (iii) $^1$H−$^{13}$C HMQC and HMBC experiments reveal that the Cl moiety is bonded to a bridgehead quaternary carbon atom and that the phenyl group is attached to a CH unit. In the $^1$H−$^{13}$C HMBC spectrum, the C*H* proton signal ($\delta_H$ 2.98) correlates with the *C*Cl signal ($\delta_C$ 74.1) and the *o*-*C*H signal ($\delta_C$ 129.1) of the phenyl group. No correlation is observed between the *C*Cl signal and the *o*-C*H* proton signals of the phenyl group, confirming that the Cl moiety and the phenyl group are not attached to the same carbon atom. (iv) The combination of $^1$H−$^1$H COSY, $^1$H−$^{13}$C HMQC and HMBC, and $^1$H−$^1$H NOESY spectra suggest an *exo*-selectivity of the phenyl ring placement at the α-position of the chloronorbornyl ring. This stereochemical assignment is further corroborated in the X-ray structure of the 1,4-bis(1-chloronorbornyl)-benzene adduct (**2a**) as described below. The analogous deuterium-labeled compound *exo*-1-chloro-2-phenyl-$d_5$-norbornane-7-$d_1$ (**1a-*d*$_6$**) was characterized by $^2$H NMR and conventional analytical techniques.[42] Additionally, the GC−MS data for **1a-*d*$_6$** show that the mass of the parent ion peak is increased by 6 units ($m/z$($M^+$) 212 (**1a-*d*$_6$**) vs 206 (**1a**)).

The reaction of $Cp^*ZrMe_3$ with $Ph_3C^+B(C_6F_5)_4^-$ in $C_6D_6$, followed by addition of 10.0 equiv of α-chloronorbornene under similar reaction conditions as described above, requires 14 h at 25 °C to reach completion, with the reaction affording **1a-*d*$_6$** quantitatively. Similar reactivity differences between the Cp*Ti- and Cp*Zr-catalyzed polymerization of styrene have been previously reported.[34]

(42) The $^2$H NMR spectrum of *exo*-1-chloro-2-phenyl-$d_5$-norbornane-7-$d_1$ (**1a-*d*$_6$**) displays a singlet at $\delta$ 2.23, and its $^1$H-decoupled $^{13}$C NMR spectrum exhibits a signal at $\delta$ 43.54 (triplet, $J_{C-D}$ = 20.8 Hz) which correlates with the $^1$H NMR signal at $\delta$ 1.63 through the $^1$H−$^{13}$C HMQC spectrum, and is assigned to the CHD group at the bridging C7 position of the norbornyl skeleton. In the $^1$H−$^1$H NOESY spectrum, the signal at $\delta$ 1.63 correlates weakly with the proton at the bridgehead carbon (C4, $\delta$ 2.33) and two *exo*-protons at C5 and C6. A comparison of the corresponding signal in the $^1$H−$^1$H NOESY spectrum of **1a** suggests that the deuterium at the C7 position of the labeled compound **1a-*d*$_6$** is oriented toward the phenyl substituent.

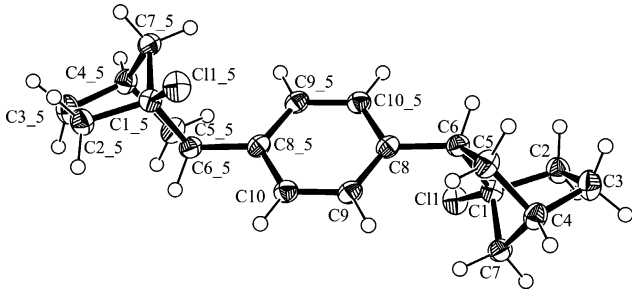
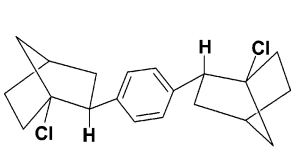



***Figure 2.*** Molecular structure of 1,4-bis(1-chloronorbornyl)benzene (**2a**) with hydrogen atoms shown. Thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): C(1)−Cl(1) = 1.7940(13), C(9)−C(10) = 1.3907(19), C(9)−C(8) = 1.3937(18), C(1)−C(7) = 1.5267(17), C(1)−C(2) = 1.5350(17), C(1)−C(6) = 1.5568(18), C(6)−C(8) = 1.5167(17), C(6)−C(5) = 1.5597(18), C(2)−C(3) = 1.5472(19), C(4)−C(5) = 1.5349(18), C(4)−C(7) = 1.5372(19), C(4)−C(3) = 1.5381(19), C(8)−C(10)#1 = 1.3927(18), C(10)−C(8)#1 = 1.3927(18), C(1)−C(7)−C(4) = 93.09(10), C(10)−C(9)−C(8) = 120.94(11), C(9)−C(10)−C(8)#1 = 121.89(12), C(10)#1−C(8)−C(9) = 117.17(12).

Reaction of α-chloronorbornene with the $Cp^*MMe_3$ (M = Zr, Ti)/$Ph_3C^+B(C_6F_5)_4^-$ activated system in toluene under similar reaction conditions yields the corresponding toluene-addition products. Thus, in the presence of a catalytic quantity of $Cp^*TiMe_3/Ph_3C^+B(C_6F_5)_4^-$, 10.0 equiv of α-chloronorbornene reacts instantaneously with excess toluene-$d_8$, whereas, for the corresponding $Cp^*ZrMe_3/Ph_3C^+B(C_6F_5)_4^-$ active species, the net addition reaction of toluene-$d_8$ to α-chloronorbornene with complete conversion requires 14 h under similar reaction conditions. Both reactions yield *exo*-1-chloro-2-tolyl-$d_7$-norbornane-7-$d_1$ (**1b-*d*$_8$**; eq 2) quantitatively. The *ortho*:*meta*:*para* ratios for **1b-*d*$_8$** obtained in both reactions are very similar. The toluene-addition product *exo*-1-chloro-2-tolylnorbornane (**1b**) was isolated as a colorless liquid after workup from a preparative scale-up reaction, similar to the procedure for **1a** above, and was characterized by conventional spectroscopic/analytical techniques. In addition, a small quantity of 1,4-bis(chloronorbornyl)toluene (**2b**; 8% yield) was isolated from the preparative-scale reaction, and GC−MS data reveal a mixture of positional isomers.

**(1) Characterization of 1,4-Bis(1-chloronorbornyl)benzene (2a).** The $^1$H and $^{13}$C NMR spectra of product **2a** display sets of signals with chemical shifts very similar to those of **1a**, except for the resonances of the phenyl group. In **2a**, a single aromatic resonance at $\delta$ 7.19 in $^1$H NMR correlates with the $^{13}$C NMR signal at $\delta$ 128.7 for the four equivalent protons of the phenyl group.



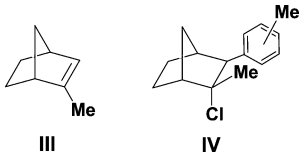

2a

**(2) X-ray Structure of 2a.** An ORTEP diagram of the molecular structure of **2a** is shown in Figure 2. The structure consists of two chloronorbornyl units connected to the 1- and

4-positions of a phenylene moiety such that the entire molecule is centrosymmetric with a crystallographic inversion center along the axis bisecting the centers of the C(8)−C(9) and C(8−5)−C(9−5) bonds. The Cl moiety is bonded to the bridgehead C(1) carbon of the norbornyl skeleton, and the phenylene moiety occupies an *exo* site at the α-position of each chloronorbornyl ring system. The C(1)−Cl(1) bond distance of 1.7940 (13) Å in **2a** is similar to the corresponding distances at the bridgehead cyclic system observed in 3,6-dichloro-11,12-benzotetracyclododecan-9-one (av C−Cl = 1.807(5) Å).[43] The C−C bond distances in the norbornyl skeleton and phenyl ring in **2a** are in the range of 1.535(2)−1.560(2) Å (av 1.542(2) Å) and 1.391(2)−1.394(2) Å (av 1.392(2) Å), respectively. These distances are comparable to the corresponding distances in numerous norbornyl and substituted norbornyl derivatives.[44] As expected, the C−C−C bond angles of the norbornyl segment in **2a** are all less than the tetrahedral angle, reflecting the strain within the molecular skeleton, with a C(1)−C(7)−C(4) bridge angle of 93.09 (10)°.

**(ii) Reaction of Activated Constrained-Geometry Catalysts (CGC)$MMe_2$ (M = Zr, Ti) with α-Chloronorbornene.** Although half-sandwich complexes are known for their coordinatively open structures and high reactivity with respect to specific monomers (e.g., styrene),[38−40] the optimal balance between electronic stabilization and a sterically open coordination sphere imbue catalyst systems of the type (CGC)-$MMe^+$ (M = Zr, Ti) with unique and high reactivity toward ethylene and α-olefin polymerization, as well as ethylene copolymerization with encumbered comonomers as bulky as isobutylene.[18,45,46] The reactions of vinyl chloride with (CGC)$ZrMe(C_6H_6)^+B(C_6F_5)_4^-$ and (CGC)$TiMe_2/Ph_3C^+B(C_6F_5)_4^-$ were reported by Jordan and co-workers.[5] Only 1.0 equiv of vinyl chloride undergoes insertion into the $M-Me^+$ bond, followed by rapid $\beta$-Cl elimination to yield either propylene or *atactic* polypropylene (PP) as noted above. Insertion of vinyl chloride was further substantiated by (a) derivatization of the organometallic species formed with vinyl chloride, affording the corresponding (CGC)$MCl_2$ complex, and (b) analysis of the allylic and vinylidene polymer end groups on homo-PP, resulting from propylene polymerization in the presence of vinyl chloride.[5,47] Here we investigate the reaction of α-chloronorbornene with in situ generated (CGC)$MMe^+B(C_6F_5)_4^-$ (M = Ti, Zr) ion pairs. In addition, the isolated (CGC)$ZrMe(toluene)^+B(C_6F_5)_4^-$ [20] ion-pair complex was also used as a single-component system for comparative reactions with α-chloronorbornene.

Activation of (CGC)$TiMe_2$ with $Ph_3C^+B(C_6F_5)_4^-$ in toluene-$d_8$, followed by addition of 10.0 equiv of α-chloronorbornene, was monitored by $^1H$ NMR at room temperature. After 48 h at room temperature, an 81% conversion to **1b-$d_8$** was observed. The *ortho*:*meta*:*para* ratio in **1b-$d_8$** is 28:31:41. Similarly, the reaction of the (CGC)$ZrMe_2/Ph_3C^+B(C_6F_5)_4^-$ catalytic system with α-chloronorbornene in toluene-$d_8$ afforded **1b-$d_8$** in 63% yield after 41 h at room temperature. The ratio of the three arene positional isomers (*ortho*:*meta*:*para* = 29:28:43) is virtually identical to the distribution found with the corresponding Ti system. Note that reaction of the isolated ion pair (CGC)$ZrMe(toluene)^+B(C_6F_5)_4^-$ with α-chloronorbornene is also catalytic. Thus, reaction of (CGC)$ZrMe(toluene)^+B(C_6F_5)_4^-$ with α-chloronorbornene in toluene-$d_8$ selectively yields the net toluene addition product **1b-$d_8$**. A 32% conversion is observed at 25 °C after 110 h. The *ortho*:*meta*:*para* ratio is 33:31:36. No Me-inserted products such as methylnorbornene (formed by C=C insertion, followed by Cl elimination, **III**) or methyl-inserted **1b** (formed by $M^+-Me$ addition to α-chloronorbornene followed by toluene addition to the resulting M−carbon bond, **IV**) are detected by GC-MS, from either a 1:1 stoichiometric or a catalytic-scale reaction. These results argue against direct involvement of the metal−$Me^+$ bond in the catalytic cycle for **1a**/**1a-$d_6$** or **1b**/**1b-$d_8$** product formation.[48]




III IV

**(iii) Reaction of Metallocenium Ion Pairs with α-Chloronorbornene.** Activation of metallocene dialkyls with $Ph_3C^+B(C_6F_5)_4^-$ generates catalytic systems which are known to be highly active for olefin polymerization.[1] Activation of $Cp_2ZrMe_2$ with 1.0 equiv of $Ph_3C^+B(C_6F_5)_4^-$ in toluene-$d_8$, followed by addition of either 1.0 or 10.0 equiv of α-chloronorbornene, is catalytic, similar to the other catalytic systems discussed above. However, the progress of the aromatic addition reaction is slow compared to that of the aforementioned $Cp^*TiMe_3$ system, but much more rapid than that of the constrained-geometry catalyst systems. Thus, the reaction of α-chloronorbornene with excess toluene-$d_8$ catalyzed by the $Cp_2ZrMe_2/Ph_3C^+B(C_6F_5)_4^-$ system at room temperature affords **1b-$d_8$** in quantitative yield after 24 h. The ratio of positional isomers is *ortho*:*meta*:*para* = 32:30:38.

The only isolable and well-characterized, base/solvent-free metallocene ion pair with a minimally coordinating counteranion is $Cp^*_2ThMe^+B(C_6F_5)_4^-$.[20] Room temperature reaction of $Cp^*_2ThMe^+B(C_6F_5)_4^-$ in toluene-$d_8$ with an excess of α-chloronorbornene is catalytic and affords **1b-$d_8$** in 48% yield after 110 h. The ratio of *ortho*:*meta*:*para* = 33:31:36 is very similar to the results found with the (CGC)$ZrMe(toluene)^+B(C_6F_5)_4^-$ catalytic system described above.

**(C) Mechanistic Experiments and Proposed Reaction Pathway.** A series of control experiments was performed to investigate whether any of the established free radical or ionic pathways for the addition of aromatics to olefins are operative in the present chloronorbornene arylation process. Radical

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(48) This is further supported by the observation that activation of $Cp'_2ZrMeCl$ (Cp′ = $C_5H_4Me$) with $Ph_3C^+B(C_6F_5)_4^-$ in toluene-$d_8$ (yielding $Ph_3CMe$ among other products), followed by the addition of α-chloronorbornene (10.0 equiv), produces the same product, **1b-$d_8$**, in quantitative yield.

initiators such as AIBN and TEMPO were found to be completely ineffective with respect to α-chlorononorbornene addition to toluene-$d_8$ at either 25 or 110 °C. However, the reactivity of conventional organic radical initiators may not be strictly comparable to that of metal-centered radical initiators if such a mechanism is operative in the present catalytic synthesis of **1a**/**1a-*d*$_6$** or **1b**/**1b-*d*$_8$**. As an example, radical-initiated polymerization of vinyl chloride by Cp*$TiX_3$ + MAO (X = Cl or $OCH_3$; MAO = methylaluminoxane) has recently been reported.[5a,49] For optimal PVC yields, the polymerization must be carried out with low Al:Ti ratios.[50] If the polymerization is carried out at high Al:Ti ratios in benzene at 80 °C, the only product observed is the coordinative/insertive (coupled with β-chloride elimination) product, atactic oligopropylene. In the present work, the product of the Cp*$TiMe_3$ + MAO reaction (Al:Ti = 10) in toluene-$d_8$ was combined with α-chlorononorbornene under anaerobic conditions, and the reaction progress monitored by $^1$H NMR. No reaction was observed either at 25 °C or at 90 °C over a period of 24 h.

The effect of a free radical inhibitor on the reaction rate of the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$-catalyzed arene−α-chlorononorbornene addition process was also examined. To an activated Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ catalyst system in toluene-$d_8$ was added 1.1 equiv of the vacuum-dried inhibitor 2,6-di-*tert*-butylphenol[51] with vigorous agitation, followed by 10.0 equiv of α-chlorononorbornene.[52] The reaction is rapid, and complete consumption of α-chlorononorbornene is observed in <5 min—a result similar to those observed in the absence of the phenol. Additionally, in a separate experiment, an additional 1.1 equiv of 2,6-di-*tert*-butylphenol was added to the reaction mixture after the first aliquot of 10.0 equiv of α-chlorononorbornene had been consumed. This was followed by the addition of another 10.0 equiv of α-chlorononorbornene, and no significant inhibition of the catalytic synthesis of **1b-*d*$_8$** was detected. Control studies also revealed that both Cp*$TiMe_3$ and the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ activated system react with 2,6-di-*tert*-butylphenol slowly in toluene-$d_8$, and after 2 h at 25 °C, >80% of the phenol remains *unreacted*. The high reactivity of the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ catalytic system in the presence of 2,6-di-*tert*-butylphenol for the synthesis of **1b-*d*$_8$** (5 min, 99% yield) vs the lower reactivity of the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ system with respect to 2,6-di-*tert*-butylphenol (2 h, 20% conversion) argues against a significant radical pathway in the synthesis of **1a**/**1a-*d*$_6$** and **1b**/**1b-*d*$_8$**.

The reaction of the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ catalytic system with adventitious traces of water present in the aromatic reagents or α-chlorononorbornene could conceivably generate protons which might act as carbocationic initiators.[53−55] In such a scenario, a reasonable explanation for the formation of **1a-*d*$_6$**/**1b-*d*$_8$** in eq 2 is that generated $H^+$ adds to the α-chlorononorbornene olefinic bond to form an electrophilic carbocationic moiety which then reacts with aromatics (benzene or toluene)[56] to yield **1a**/**1a-*d*$_6$** or **1b**/**1b-*d*$_8$** in a catalytic cycle such as shown in Scheme 1. As noted in the Experimental Section, all experiments were carried out with rigorous exclusion of oxygen and moisture. Reaction of Cp*$TiMe_3$ or $Cp_2ZrMe_2$ in toluene-$d_8$ with an excess of α-chlorononorbornene (25.0 equiv) was examined by in situ $^1$H NMR. Evolution of $CH_4$[57] was not detected over the course of 12 h at 25 °C. Similarly, when extremely sensitive Cp*$_2$La[$CH(SiMe_3)_2$] was combined with an excess of α-chlorononorbornene in toluene-$d_8$, no evidence for the formation of the protonolysis product $CH_2(SiMe_3)_2$[58] was detected by $^1$H NMR over the course of 12 h at 25 °C. Additionally, the reaction of α-chlorononorbornene in toluene-$d_8$ with either $BF_3$·$OEt_2$ (a $H^+$ source in the presence of water) or anhydrous HCl gas was monitored by $^1$H NMR at 25 and 90

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(52) Reaction of 2,6-di-*tert*-butylphenol with the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ activated catalyst system in toluene-$d_8$ is slow, and with time is expected to yield the corresponding phenoxide-substituted cations of the type Cp*Ti(OAr)$Me^+B(C_6F_5)_4^-$ (Ar = O-2,6-$^t$Bu$C_6H_3$). The exact nature of species generated from reaction of Cp*Ti(OAr)$Me_2$ with $Ph_3C^+B(C_6F_5)_4^-$ remains ill-defined. For examples of the use of such catalysts, see: (a) Nomura, K.; Fudo, A. *J. Mol. Catal. A* **2004**, *209*, 9−17. (b) Nomura, K.; Fudo, A. *Inorg. Chim. Acta*. **2003**, *345*, 37−43. (c) Nomura, K.; Fudo, A. *Catal. Commun*. **2003**, *4*, 269−274. (d) Nomura, K.; Oya, K.; Komatsu, T.; Imanishi, Y. *Macromolecules* **2000**, *33*, 3187−3189. (e) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152−2154.

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(54) Carbocationic species derived from trityl salts are known to add directly to double bonds as well as to initiate cationic oligomerization/polymerization of α-olefins.[55] A control reaction involving $Ph_3C^+B(C_6F_5)_4^-$ with 1.0 equiv of α-chlorononorbornene in toluene-$d_8$ was also examined by $^1$H NMR, and complete consumption of α-chlorononorbornene to form **1b-*d*$_8$** required 12 h at 25 °C (as opposed to consumption of ∼700.0 equiv of α-chlorononorbornene by the Cp*$TiMe_3$/$Ph_3C^+B(C_6F_5)_4^-$ activated system over the same time period and at comparable concentrations). Addition of 1.1 equiv of 2,6-di-*tert*-butylphenol to $Ph_3C^+B(C_6F_5)_4^-$ in toluene-$d_8$, followed by addition of 1.0 equiv of α-chlorononorbornene, showed complete inhibition of **1b-*d*$_8$** formation. Control NMR studies also revealed negligible reaction between $Ph_3C^+B(C_6F_5)_4^-$ and 2,6-di-*tert*-butylphenol in toluene-$d_8$ at 25 °C. Although the exact pathway for the above reaction leading to **1b-*d*$_8$** formation is not completely clear, the complete lack of reactivity in the presence of a radical scavenger possibly argues for the involvement of a trityl radical. One-electron reduction of the $Ph_3C^+$ cation to the trityl radical, which undergoes subsequent dimerization to Gomberg's dimer, has been reported: Hembre, R. T.; McQueen, J. S. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 65−67. For reactions involving generation of the trityl radical from the $Ph_3C^+$ cation, see: (a) Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747−751. (b) Zador, E.; Warman, J. M.; Hummel, A. *J. Chem. Soc., Faraday Trans*. **1979**, *75*, 914−920. (c) Berlin, K. D.; Shupe, R. D.; Grigsby, R. D. *J. Org. Chem*. **1969**, *34*, 2500−2503.

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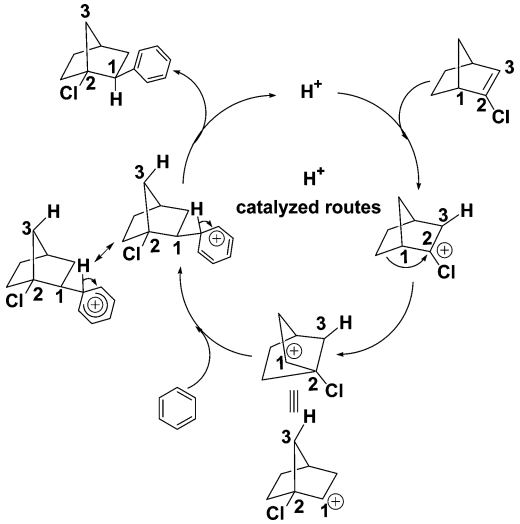
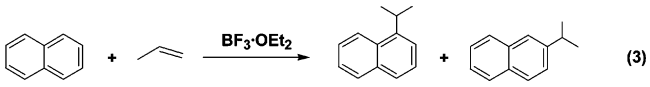
***Scheme 1.*** Plausible Proton ($H^+$)-Catalyzed Arylation of α-Chloronorbornene



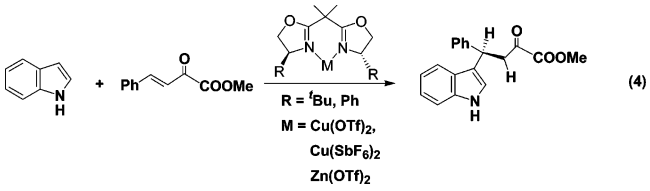

°C. Formation of **1b-*d*$_8$** was not observed. These results argue against the possibility of initiation by trace (or larger) amounts of $H^+$ generated by adventitious water, in the catalytic formation of product **1a/1a-*d*$_6$** or **1b/1b-*d*$_8$**.[59]

Lewis acid-mediated Friedel−Crafts alkylation of aromatics by olefins and alkyl halides is well-documented.[60] Commonly used Lewis acids (e.g., $SnCl_4$, $FeCl_3$, $AlCl_3$, etc.) or proton acids (e.g., HF, $BF_3{\cdot}OEt_2$, $H_2SO_4$, $H_3PO_4$, etc.) are usually used in 1:1 stoichiometric ratios with the alkylating agents for such transformations (eq 3).[60e] More recently, the catalytic enantio-



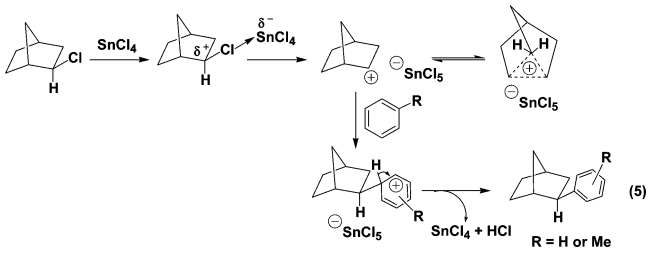

(3)

selective addition of aromatic C−H bonds to $\beta,\gamma$-unsaturated α-ketoesters, mediated by chiral transition-metal Lewis acids (e.g., (bisoxazoline)copper(II) and -zinc(II)), was reported (eq 4).[61]




(4)

Olah and co-workers reported the Friedel−Crafts alkylation of aromatics with chloronorbornanes using a 1:1 stoichiometric ratio of $SnCl_4$ or $AlCl_3$ to chloronorbornane (eq 5).[62] It was proposed that the reaction proceeds via a carbocationic inter-




(5)

mediate, ultimately leading to the corresponding chlorine-free, aryl-substituted norbornanes.

It was observed in the $SnCl_4$ reaction with toluene that the *para* isomer is the major product, while the *meta* isomer (with no trace of *ortho* isomer) is the major product in the corresponding $AlCl_3$-mediated reactions. In the present study, the possible reaction of α-chloronorbornene with toluene was investigated in the presence of strong Lewis acids such as MAO, $B(C_6F_5)_3$, $SnCl_4$, $Cp^*TiCl_3$, and $TiCl_4$. No reaction is observed at either 25 or 90 °C. In the group 4 metal alkyl/$Ph_3C^+B(C_6F_5)_4^-$-catalyzed reactions with α-chloronorbornene, note that the only products formed are aryl-substituted chloronorbonanes (**1a/1a-*d*$_6$** or **1b/1b-*d*$_8$**). No detectable quantities of bis-aryl-substituted norbornanes are observed. These would result from abstraction of the chloride at the bridgehead carbon if the catalytic system behaved as a conventional Lewis acid.[63] In addition, the present metal-catalyzed reaction is catalytic and exhibits turnover numbers ranging from 10 to 700, whereas, for the above Lewis acid alkylation reaction,[62] a 1:1 stoichiometric alkylating agent:initiator ratio is required.

On the basis of the reactivity differences among the present single-site group 4 complexes having differing ancillary ligation, and the control experiments discussed above, a plausible mechanism for the organometal/$Ph_3C^+B(C_6F_5)_4^-$-catalyzed reaction of α-chloronorbornene with aromatics is shown in Scheme 2. The first step in the catalytic cycle involves coordination of α-chloronorbornene to the electron-deficient, unsaturated cationic metal center via a plausible but transitory[41] $\pi$-olefin complex (**A**). This is followed by addition of the

(59) Addition of 2,6-di-*tert*-butylpyridine to the $Cp^*TiMe_3/Ph_3C^+B(C_6F_5)_4^-$ activated system in a 1:1 stoichiometric molar ratio followed by addition of 1.0 equiv of α-chloronorbornene evidences no inhibition of catalytic turnover and thus argues against any significant role of $H^+$ initiation as a competing pathway to product formation. For related studies, see: (a) Barsan, F.; Karam, A. R.; Parent, M. A.; Baird, M. C. *Macromolecules* **1998**, *31*, 8439−8447. (b) Shaffer, T. D.; Ashbaugh, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 329−344.

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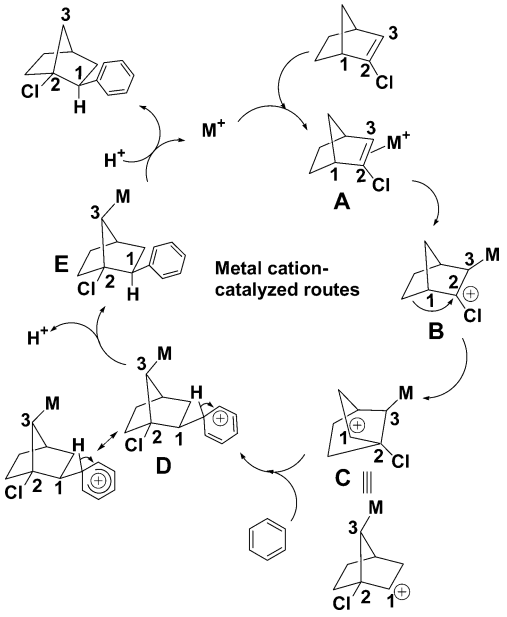
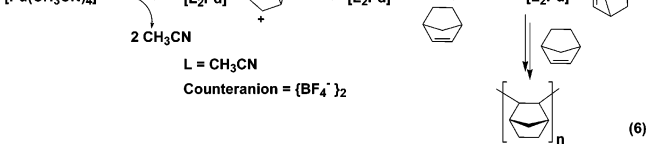
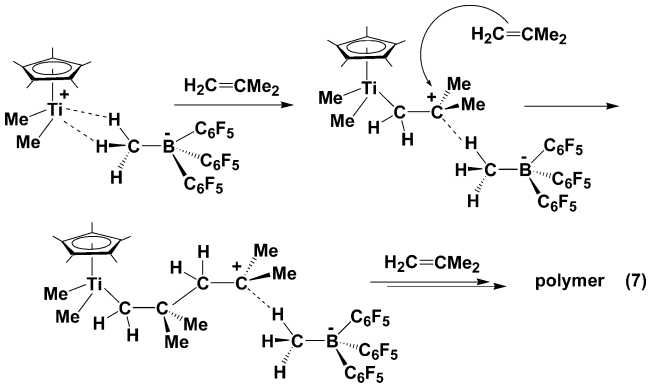
***Scheme 2.*** Plausible Mechanism for $L_nMMe^+B(C_6F_5)_4^-$-Catalyzed Arylation of α-Chloronorbornene




cationic metal moiety to the sterically less hindered and presumably more electron-rich olefinic site, generating an $\eta^1$-metal-coordinated, α-tertiary carbocationic intermediate (**B**; Scheme 2). An analogous addition of an electron-deficient cationic metal species to the olefinic bond of norbornene is proposed in the homopolymerization of norbornene to produce a saturated homopolymer (eq 6)[64] as well as in the copolymerization of norbornene with ethylene.[65] Moreover, similar pathways have been proposed in cases where addition of single-site group 4 catalysts to substituted olefins (styrene, isobutene, vinyl ethers, etc.) leads to stable carbocations that initiate further monomer addition to yield polyolefins (eq 7).[53,66]

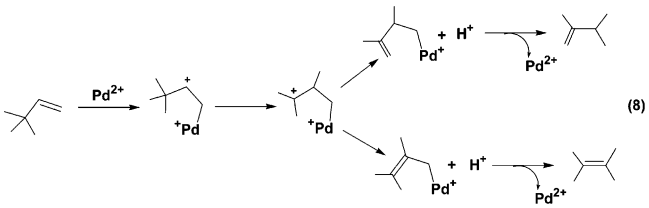



(6)



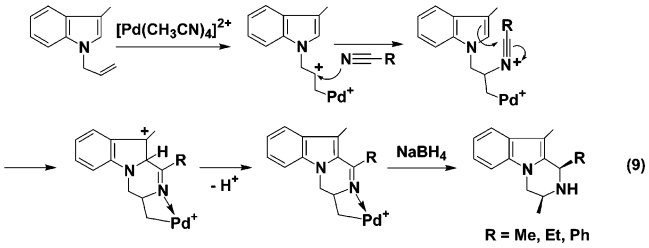

(7)

Perhaps reflecting destabilization by the electron-withdrawing Cl substituent,[67] intermediate **B** (Scheme 2) is postulated to undergo rapid alkyl migration/skeletal rearrangement to yield carbocationic species **C**, via a nonclassical carbocationic pathway.[68] Such rearrangements of carbocationic species are commonly observed in norbornyl systems[62,68] as well as in $Pd(CH_3CN)_4^{2+}[BF_4^-]_2$-catalyzed oligomerization of olefins[69] and isomerization of *tert*-butylethylene[69] (eq 8). For comparison,




(8)

the catalytic isomerization/disproportionation of olefins mediated by cationic group 4 benzamidinate complexes is proposed to occur through either metal−alkyl insertion/β-H elimination (for aliphatic olefins) or allylic proton activation (for cyclic olefins).[70] Moreover, the very similar ratios of positional isomers in product **1b-*d*$_8$** (eq 2) produced from the various organometal/$Ph_3C^+B(C_6F_5)_4^-$-catalyzed reactions of α-chloronorbornene with toluene-$d_8$ further argue for a similar, metal-independent intermediate in each catalytic system preceding product formation. The greater presumed reactivity at carbocationic vs metal centers leads to attack by even weaker nucleophiles as shown in the synthesis of indole derivatives (eq 9)[71] as well as in the $Pd(CH_3CN)_4^{2+}[BF_4^-]_2$-catalyzed reaction of propylene with aromatics.[72]




(9)

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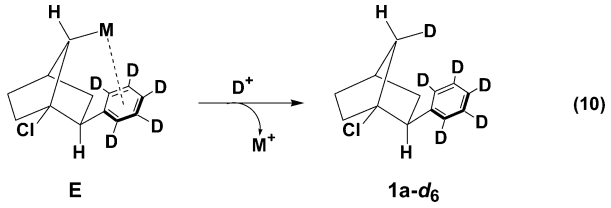
Similarly, a conventional aromatic electrophilic substitution reaction[56] at the α-position of intermediate **C** (Scheme 2), followed by $H^+$ elimination (possibly concerted with M−C cleavage),[73] may lead to a species such as **E**, in which the neutral metal moiety at the bridging position is located proximate to, and possibly within π-bonding distance of, the phenyl substituent (eq 10).[74] This stereochemistry is further supported by Spartan-




**E** **1a-$d_6$** (10)

level, energy-minimized molecular modeling of such a species,[75] as well as by establishing the stereochemistry of deuterium introduced at the bridging C7 position (Scheme 2) in the labeled product *exo*-1-chloro-2-phenyl-$d_5$-norbornane-7-$d_1$ (**1a-$d_6$**), using $^2$H NMR and $^1$H−$^1$H NOESY.[42] Similar retention of configuration at the metal−C centers is observed on protonolysis/deuteriolysis or electrophilic cleavage of alkyl and vinyl groups in many early- and late-transition-metal complexes.[76] Protonolysis of the M−C bond in **E** yields the final *exo*-1-chloro-2-aryl-substituted norbornane and regenerates a cationic active metal species.[77]

## Conclusions

A wide variety of $B(C_6F_5)_4^-$-stabilized single-site cationic polymerization catalysts are found to efficiently mediate the arylation of α-chloronorbornene under mild catalytic reaction conditions to selectively yield the corresponding *exo*-1-chloro-2-arylnorbornanes. The results presented here illustrate the diverse nonclassical reactivity patterns of highly electrophilic single-site catalysts toward nonpolar/polar vinyl monomers. For example, vinyl halides undergo 1,2-insertion into M−alkyl species followed by β-Cl elimination, while norbornene adds to cationic metal moieties to effect vinyl-addition polymerization. Similarly, isobutylene undergoes polymerization via metal-mediated carbocationic routes. In the present study, we show that α-chloronorbornene undergoes a novel transformation involving olefin addition to the cationic metal moiety and then skeletal rearrangement, followed by reaction with aromatic reagents to yield the corresponding aryl-substituted chloronorbornanes. To the best of our knowledge, this is the first report concerning addition of cationic single-site catalysts to α-haloalkenes in which β-Cl elimination is blocked. Instead of enchaining a second α-chloronorbornene molecule, presumably for steric reasons, the metallocarbocation undergoes reaction with aromatic reagents to effect what is essentially a conventional electrophilic substitution. This finding lays the groundwork necessary to understand how to prevent β-Cl elimination and also shows the importance of the delicate balance between the nature of the functional group directly bound to a vinyl monomer and its electronic/steric influence in determining the reaction pathway. Further extension of the scope of such functionalized monomers and the design of catalysts to obtain interesting new polymers is under investigation.

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**Supporting Information Available:** NMR spectra ($^1$H, $^{13}$C, $^1$H−$^{13}$C HMQC and HMBC, and $^1$H−$^1$H NOESY) for product **1a/1a-$d_6$/1b** as well as details of the structure determinations for product **2a**, including listings of atomic coordinates, thermal parameters, bond distances, and bond angles (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(72) In the oligomerization of propylene in aromatic solvents (benzene or toluene) catalyzed by $Pd(CH_3CN)_4^{2+}[BF_4^-]_2$, substantial amounts (>15% compared to the yield of propylene oligomers) of isopropyl-substituted benzene or toluene are observed due to competition between arene alkylation (reaction at the carbocationic center) and olefin oligomerization (reaction at the metal center).[69]

(73) A competition experiment (to identify possible kinetic isotope effects) involving a 1:1 mixture of $C_6H_6/C_6D_6$ with either the $Cp_2ZrMe_2/Ph_3C^+B(C_6F_5)_4^-$ or the $Cp^*TiMe_3/Ph_3C^+B(C_6F_5)_4^-$ activated system was examined in the presence of 10.0 equiv of α-chloronorbornene at 25 °C. The reaction was quenched after 5 min with methanol. GC−MS of an aliquot revealed complete deuterium scrambling within the aryl portions of the reaction product ($m/z(M^+)$ 206−212), consistent with a rapid, reversible C−H bond breaking process. See ref 56 for other examples of such processes.

(74) Such a scenario is observed in Ti−benzyl complexes, where the Ti moiety is coordinated to the *ipso*-carbon of the phenyl group, and is confirmed by solid-state X-ray structures. For examples, see: (a) Cotton, F. A.; Murillo, C. A.; Petrukhina, M. A. *J. Organomet. Chem.* **1999**, *573*, 78−86. (b) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562−569. (c) Bassi, I. W.; Allegra, G.; Scordamaglia, R.; Chioccola, G. *J. Am. Chem. Soc.* **1971**, *93*, 3787−3788.

(75) An energy-minimized molecular mechanics Spartan-level geometry calculation of species **E** with M = $Cp^*Ti(IV)Me_2$ or $Cp^*Ti(III)Me$ shows that the Ti center is oriented toward the phenyl substituent with Ti−C(phenyl) contact distances in the range of 4.269−6.271 Å (for Ti(IV)) and 3.753−5.556 Å (for Ti(III)). These distances are comparable to, and within, the range of Ti−C(phenyl) contact bond distances {3.135−5.558 Å (for Ti(IV)); 3.111−5.560 Å (for Ti(III))} generated from Spartan-level calculations for the corresponding styrene-inserted Ti species (two distances from the Ti center), where 2,1-insertion of Ti−Me species into styrene occurs preferentially via multihapto coordination with the phenyl substituent during syndiospecific styrene polymerization.[39,40]

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(77) An alternative pathway would invoke a C−H activation process in which the cationic metal−Me species undergoes reaction with benzene to yield a cationic M−H or M−phenyl species. This species would then add to the α-chloronorbornene olefinic bond, followed by rearrangement (to explain the position/stereochemistry of the Cl and phenyl group in **1a**) and reaction with another molecule of benzene to yield the final product and regenerate the cationic M−H or M−phenyl species.


**1a**

Control studies were carried out in which the $Cp_2ZrMe_2/Ph_3C^+B(C_6F_5)_4^-$ activated system in either $C_6H_6$ or $C_6D_6$ was reacted with α-chloronorbornene (10.0 equiv) in the presence of 1.0 atm of $D_2$ or $H_2$ gas, respectively, with vigorous stirring. No deuteriolysis/hydrogenolysis interception products were detected; i.e., no deuterium-incorporated chloronorbornanes (resulting from deuteriolysis of the M−carbon bond) were detected by GC−MS. These results argue that such a C−H activation route is not a major competing pathway in product formation. For recent examples of similar C−H activation processes, see: (a) Hoyt, H. M.; Michael, F. E.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 1018−1019. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870−8888. (c) Lail, M.; Arrowood, B. N.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2003**, *125*, 7506−7507. (d) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633−639 and references therein. (e) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 10846−10855.