www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 619 (2001) 62–73

Benzyl group abstraction from $Ti(CH_2Ph)_4$ by $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ to form Ziegler–Natta and carbocationic alkene polymerization initiators

Mei Lin, Michael C. Baird *

Department of Chemistry, Queen's University, Kingston, ON, Canada K7L 3N6

Received 2 February 2000; received in revised form 26 June 2000

Abstract

Reaction of $Ti(CH_2Ph)_4$ with $B(C_6F_5)_3$ results in the formation of $[Ti(CH_2Ph)_3][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$, while reactions with $[Ph_3C][B(C_6F_5)_4]$ give either $[Ti(CH_2Ph)_3][B(C_6F_5)_4]$ or $[(CH_2Ph)_3Ti\text{-}\mu\text{-}CH_2PhTi(CH_2Ph)_3][B(C_6F_5)_4]$, depending on the $Ti(CH_2Ph)_4$:$[Ph_3C]$ ratio; NMR evidence is presented that all of these compounds, including $Ti(CH_2Ph)_4$, exhibit multihapto Ti–CH_2Ph bonding. The $Ti(CH_2Ph)_4/B(C_6F_5)_3$ and $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ systems are assessed for their abilities to induce polymerization of ethylene, 1-hexene, isobutylene and ethyl vinylether, and the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ system is found to be able to function as both a Ziegler–Natta catalyst and a carbocationic initiator. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Benzyl group abstraction; Ziegler–Natta catalyst; Carbocationic initiator

The roles of metallocene complexes of the Group 4 elements as the active species in the homogenous catalytic polymerization of ethylene and 1-alkenes via Ziegler–Natta catalytic processes are now well established [1], while more recently monocyclopentadienyl and related 'constrained geometry catalysts' have also been the subject of intense investigations [2]. In both mono- and dicyclopentadienyl Ziegler–Natta systems, the active species are believed to be cationic alkylmetal(IV) complexes, of the types $[Cp'MR_2L]^+$ or $[Cp'_2MRL]^+$ (Cp′ = substituted cyclopentadienyl, M = Ti, Zr, Hf; R = alkyl group; L = labile ligand), respectively. Initiation and propagation steps involve displacement of L and coordination of monomer to give a cationic η^2-alkene intermediates which are subsequently involved in repeated migratory insertion steps [1,2].

While these families of catalysts show great commercial promise, however, it is also becoming ever clearer that the same types of Ziegler–Natta catalyst systems may also behave as initiators of carbocationic polymerizations of e.g. styrene, isobutylene (IB) and vinyl ethers [3a]. The first such multitalented initiator system to be recognized was $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, formed on treating Cp^*TiMe_3 with $B(C_6F_5)_3$ [3b–e], which behaves as a source of the highly electrophilic cation $[Cp^*TiMe_2]^+$. Consistent with carbocationic polymerizations by conventional Lewis acid initiators[1], initiation of, e.g. isobutylene polymerization by $[Cp^*TiMe_2]^+$, is believed to involve η^1-coordination of the alkene as in **A**, where a carbocationic center is stabilized by interaction with a weakly nucleophilic anion and the substituents on the cationic carbon atom. Propagation then involves successive additions of monomer molecules at the carbocationic center, which migrates away from the metal atom. Thus, the metal does not behave as a *catalyst*, but rather as an *initiator* of polymerization.[2]

---

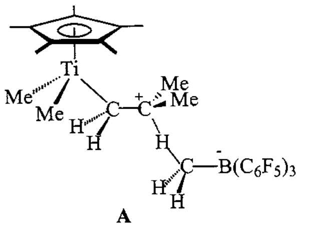
* Corresponding author. Tel.: + 1-613-5452614; fax: + 1-613-5456669.

E-mail address: bairdmc@chem.queensu.ca (M.C. Baird).

[1] For general reviews of carbocationic initiation, see [4].

[2] Use of the terms *catalyst* and *initiator* is confused in the polymerization literature and probably elsewhere; while all catalysts are initiators, not all initiators are catalysts.

PII: S0022-328X(00)00552-0



A

Ziegler–Natta catalysts and carbocationic initiators have generally been used to induce polymerization of rather different classes of alkenes – the key differences being the nature and number of the substituents on the carbon–carbon double bond – and the fields of carbocationic and Ziegler–Natta polymerization have developed almost completely independently. However, successful polymerizations of alkenes via both processes have the same requirements, specifically a vacant site on a highly Lewis acidic metal complex in combination with poorly coordinating solvents and counteranions which do not compete effectively for the metal inner coordination sphere. Thus it might be anticipated that some putative Ziegler–Natta polymerizations may involve, at least in part, carbocationic processes.

Indeed, it has recent been shown that the cationic complexes $[Cp'_2MMe]^+$ (M = Zr, Hf) [5a,b], as well as the complexes obtained on treating $[Cp'_2ZrH_2]_2$ [5c], $[Cp'_2YMe]_2$ [5d] and $ZrMe(N\{SiMe_3\}_2)_3$ [5e] with $B(C_6F_5)_3$ do in fact behave as initiators of carbocationic polymerization of isobutylene. These results may have implications for Ziegler–Natta catalyst systems, although carbocationic polymerization or oligomerization of 1-alkenes has *as yet* not been observed. However, polymers containing vinylidene end groups of the type CH_2=CMe ~ polymer are often formed during Ziegler–Natta processes and might well re-coordinate to the metal cation in η^1 fashion as in **A**. If this were to occur, the catalyst sites would be converted to neutral metal species, cationic metal-centered sites would no longer be available for initiation of the Ziegler–Natta process, and the end result would be cessation of the Ziegler–Natta processes via de facto poisoning of the catalysts. Alternatively, depending on the nature of the monomer(s), carbocationic polymerization could be initiated as in **A**, and possibly a block of a different kind of polymer would be added to any polymer already formed.

In an effort to extend our knowledge of systems which may behave as both Ziegler–Natta and carbocationic initiators, we are investigating a number of putative Ziegler–Natta catalysts for their capacity to also initiate polymerization of, e.g. IB and vinyl ethers. The latter monomers are, for a number of reasons, not generally susceptible to Ziegler–Natta processes [4], and thus successful polymerization of these alkenes may be taken as a signature of a carbocationic polymerization process. In contrast, ethylene, especially, and α-alkenes are much less susceptible to carbocationic initiation because of the lower stabilities of the carbocations which would be produced; thus ethylene polymerization probably implies invariably the relevance of a Ziegler–Natta process.

We have begun this investigation with the long known but, in fact, little studied homoleptic tetrabenzyl compound $Ti(CH_2Ph)_4$ [6]. It has been shown previously that this *neutral* compound and its zirconium analogue $Zr(CH_2Ph)_4$ are essentially unreactive with ethylene, styrene and α-alkenes, but that both promote the polymerization of styrene, ethylene and propene in the presence of conventional activators such as MAO, $[NHMe_2Ph][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ [7]. We describe here an investigation of the properties of $Ti(CH_2Ph)_4$ activated with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ as initiators for polymerization of ethylene, 1-hexene, IB and ethyl vinyl ether (EVE). Although it is clear from our results that $Ti(CH_2Ph)_4/B(C_6F_5)_3$ and $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ can behave, as expected, as Ziegler–Natta catalysts, the system also appears to behave as an active carbocationic initiator.

The polymerization processes presumably involve coordinatively unsaturated, cationic benzyl species of the type $[Ti(CH_2Ph)_3]^+$, but the reactions of $Ti(CH_2Ph)_4$ with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ seem not to have been unexplored in any detail. We therefore also present here a variable temperature NMR investigation of the very unstable complexes formed when $Ti(CH_2Ph)_4$ is treated with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$.

1. Experimental

All operations were performed under purified argon using normal Schlenk techniques or a Vacuum Atmospheres Dry Lab. Solvents were purified by standard methods, and distilled and degassed before use. All 1D-^{1}H-, ^{13}C-, $^{13}C\{^1H\}$- and ^{19}F-NMR spectra and 2D-COSY and HMQC spectra were recorded using Bruker Avance 400 or 500 spectrometers, chemical shifts being determined by reference to residual ^{1}H and ^{13}C solvent peaks for ^{1}H and $^{13}C\{^1H\}$ studies, external $CFCl_3$ for ^{19}F studies. Gel permeation chromatography (GPC) experiments with the polymers were carried out at room temperature (r.t.) using a Waters Model 440 liquid chromatograph with THF as eluant with polystyrene standards. The compounds $Ti(CH_2Ph)_4$ [6], $B(C_6F_5)_3$ [8a,b] and $[Ph_3C][B(C_6F_5)_4]$ [8c] were prepared according to published procedures.

Ethylene was purified by passing through a column containing 3 Å molecular sieves. Isobutylene (IB) was purified by passing through a barium oxide column and two columns containing 3 Å molecular sieves. 1-Hexene and EVE were purified by stirring over CaH_2 followed by vacuum distillation.

1.1. General polymerization procedures

The monomers were either bubbled through or, alternatively, measured aliquots were added to stirred solutions of $Ti(CH_2Ph)_4$ (25 mg, 0.06 mmol) in 5 ml of toluene or methylene chloride at the desired temperatures. Polymerizations were normally initiated by rapid addition of $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) or $[Ph_3C][B(C_6F_5)_4]$ (46 mg, 0.05 mmol) in the same solvent. In addition, some polymerization experiments were carried out using different initiator:co-initiator ratios. Reactions were terminated after varying periods of time by the addition of methanol, the residual initiators were removed by column chromatography with pentane as eluant, and the polymers were characterized by NMR spectroscopy and GPC analysis.

1.2. Preparation of $Ti(CH_2Ph)_3[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$

An NMR tube containing 17 mg (0.04 mmol) of $Ti(CH_2Ph)_4$ and 21 mg (0.04 mmol) $B(C_6F_5)_3$ was cooled to − 78°C and 0.5 ml of pre-cooled CD_2Cl_2 was added. All the material dissolved at − 78°C to give a dark-red solution of $Ti(CH_2Ph)_3[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$, which was characterized spectroscopically at − 78°C. ^{1}H-NMR (500 MHz, CD_2Cl_2, − 78°C): δ 7.00–7.33 (m, 9H, $TiCH_2$-*m*, *p-Ph*), 6.76 (m, 4H, BCH_2-*o*, *m-Ph*), 6.69 (br, 1H, BCH_2-*p-Ph*), 6.62 (d, 6H, $TiCH_2$-*o-Ph*), 2.98 (br s, 2H, B*CH*$_2$Ph), 2.79 (s, 6H, Ti*CH*$_2$Ph). ^{13}C-NMR (125 MHz, CD_2Cl_2, − 78°C, ^{1}H coupled): δ 130.0 (d, *J* 160 Hz, $TiCH_2$-*m*-Ph), 129.7 (d, *J* 157 Hz, $TiCH_2$-*o*-Ph), 127.3 (d, *J* 154 Hz, $TiCH_2$-*o*-Ph), 105.5 (t, *J* 137 Hz, Ti-CH_2). Resonances of the BCH_2Ph and C_6F_5 groups were observed, but were relatively weak and could not be identified unambiguously. The ^{1}H and ^{13}C assignments made were confirmed by complementary 2D-COSY and HMQC experiments, while integrations relative to the resonance of the residual protons of the solvent showed that the reaction proceeded essentially quantitatively and without loss of overall intensity. ^{19}F-NMR (400 MHz, CD_2Cl_2, − 50°C): δ − 168.6 (br s, 6F, *o*-C_6F_5), − 138.8 (t, *J* 22 Hz, 3F, *p*-C_6F_5), − 134.8 (t, J 22 Hz, 6F, *m*-C_6F_5).

1.3. Preparation of $[Ti(CH_2Ph)_3][B(C_6F_5)_4]$

An NMR tube containing 11 mg (0.025 mmol) of $Ti(CH_2Ph)_4$ and a slight excess of $[Ph_3C][B(C_6F_5)_4]$ (23 mg, 0.025 mmol) was cooled to − 78°C, and 0.5 ml of pre-cooled CD_2Cl_2 was added. All the material dissolved at − 78°C to give a dark-red solution of $[Ti(CH_2Ph)_3]$-$[B(C_6F_5)_4]$, which was characterized spectroscopically. ^{1}H-NMR (400 MHz, CD_2Cl_2, − 50°C): δ 7.06 (t, $J = 7.0$ Hz, *m-Ph*; *p-Ph* resonance obscured), 5.49 (d, $J = 7.2$ Hz, 6H, *o-Ph*), 3.54 (s, 6H, *CH*$_2$Ph). In addition, there were resonances attributable to 1,1,1,2-tetraphenylethane at δ 6.9–7.22 (m, CH_2-*m-Ph* and C*Ph*$_3$), 6.92 (t, CH_2-*m-Ph*), 6.55 (d, 2H, CH_2-*o-Ph*) and 3.90 (s, 2H, *CH*$_2$), and to unreacted $[Ph_3C][B(C_6F_5)_4]$ (δ 8.24 (t, *p-H*), 7.85 (t, *m-H*) and 7.64 (d, *o-H*). ^{19}F-NMR (400 MHz, CD_2Cl_2, − 78°C): δ − 166.8 (br m, 6F, *m*-C_6F_5), − 163.0 (br s, 3F, *p*-C_6F_5), −134.1 (br m, 6F, *o*-C_6F_5). The stoichiometry of the overall reaction was determined on the basis of integrations relative to the resonance of the residual protons of the solvent, and it was found that the reaction proceeded essentially quantitatively and without loss of overall intensity.

The ^{1}H spectrum also exhibited weak resonances attributable to bibenzyl (δ 2.85) and toluene (δ 2.31) respectively. These become stronger at the expense of the resonances attributed to $[Ti(CH_2Ph)_3]^+$ when the temperature of the solution was raised above − 50°C. However, if the ^{1}H-NMR spectrum of the initially formed red solution was examined at − 78°C, weak, ephemeral resonances of $[Ti(CH_2Ph)_3(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3]^+$ (see below) were also observed.

1.4. Preparation of $[Ti(CH_2Ph)_3(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3][B(C_6F_5)_4]$

An NMR tube containing 21 mg of $Ti(CH_2Ph)_4$ (0.05 mmol) and 23 mg of (0.025 mmol) $[Ph_3C][B(C_6F_5)_4]$ was cooled to − 78°C and 0.5 ml of pre-cooled CD_2Cl_2 was added. All of the material dissolved at − 78°C to give a dark-red solution of $[Ti(CH_2Ph)_3(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3]^+$, characterized spectroscopically. ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2, − 78°C): δ 7.10–7.45 (m, $TiCH_2$-*m*, *p*-Ph, Ph_3C of Ph_3CCH_2Ph, traces of bibenzyl and toluene), 6.82 (br s, 2H, μ-CH_2-*m-Ph*), 6.61 (br s, 7H: 6H of μ-CH_2-*o-Ph*, 1H of μ-CH_2-*p-Ph* partially obscured by Ph_3CCH_2-*o-Ph* at 6.52), 6.38 (br s, 6H, $TiCH_2$-*o-Ph*), 6.23 (br s, 2H, μ-CH_2-*o-Ph*), 2.77 (s, 6H, Ti*CH*$_2$), 2.29 (s, 6H, Ti*CH*$_2$), 0.97 (s, 2H, μ-*CH*$_2$). In addition, resonances were observed of 1,1,1,2-tetraphenylethane (one equivalent; δ 7.02–7.22, 6.92, 6.52, 3.88) and traces of bibenzyl (δ 2.82) and toluene (δ 2.31), but not of $[Ph_3C][B(C_6F_5)_4]$ (δ 8.24, 7.85, 7.64). Assignments of the resonances of $[Ti(CH_2Ph)_3(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3]^+$ were confirmed by 2D-COSY and HMQC experiments and by the multiplicities exhibited on warming (see below), while the stoichiometry of the overall reaction was determined using integrations relative to the resonance of the residual protons of the solvent. It was found that the reaction proceeded essentially quantitatively and without loss of overall intensity.

2. Results and discussion

2.1. NMR spectrum of $Ti(CH_2Ph)_4$

The variable temperature ^{1}H-NMR spectrum of $Ti(CH_2Ph)_4$ does not appear to have been reported

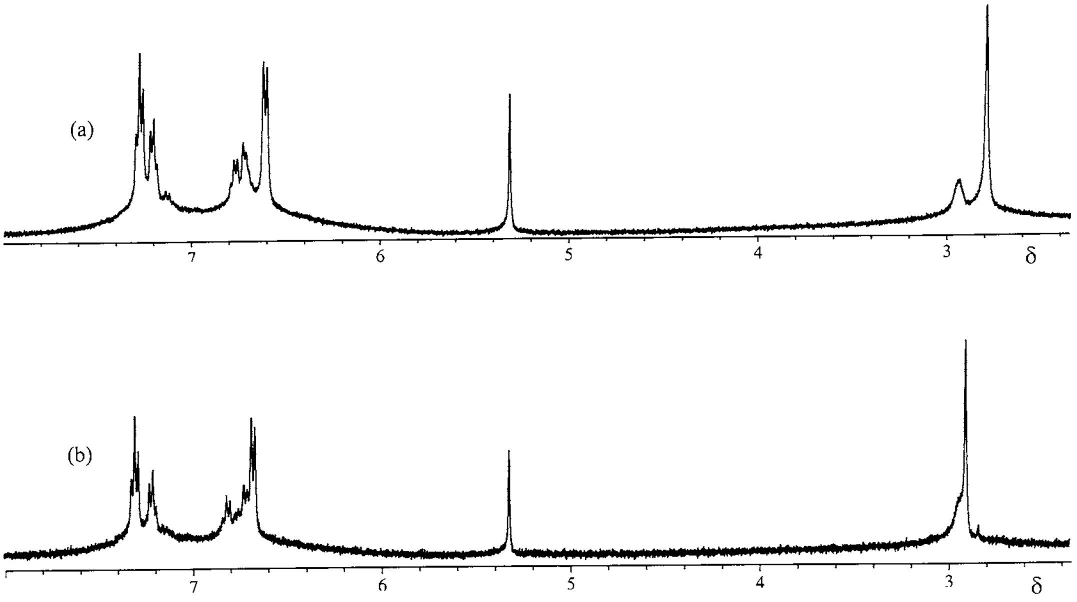
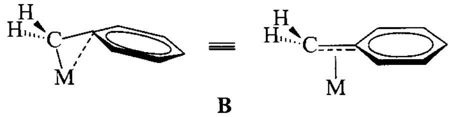


Fig. 1. ^{1}H-NMR study of the reaction of $Ti(CH_2Ph)_4$ with an equimolar amount of $B(C_6F_5)_3$ in CD_2Cl_2 at (a) −78°C, (b) −50°C.

previously. In contrast to $Sn(CH_2Ph)_4$, which exhibits a regular tetrahedral structure about the tin, essentially identical η^1-Sn-CH_2Ph bonds and Sn–CH_2–Ph bond angles all ~112°, the analogous, homoleptic tetrabenzyl compounds of titanium, zirconium and hafnium exhibit varying degrees of η^2-metal-CH_2Ph bonding in which the compounds appear to be stabilized by overlap of the ring π electron cloud on a phenyl *ipso*-carbon atom with a vacant orbital on the metal [9]. The result is contraction of the metal–CH_2–Ph bond angles to ~90° and much reduced M-*ipso*-carbon atom internuclear distances, as represented by **B** [9].



B

Such η^2-coordination of benzyl groups to transition metals is also known for other types of compounds[3], and generally results in both increases of $^1J_{CH}$ from about 120–125 to >130 Hz and shifting of the *o*-H resonance upfield of the normal aromatic region, δ 6.8–7.5 [10d], i.e. 0.5–1 ppm upfield of the corresponding *m*-H and *p*-H resonances [11b]. In cases of compounds for which both η^1 and η^2 structures are present in solution, exchange between the two types of sites is generally rapid on the NMR time scale [10d].

In the case of $Ti(CH_2Ph)_4$, the structure in the solid state contains a range of Ti–CH_2–Ph bond angles and Ti-*ipso*-C distances [9a], suggesting varying degrees of Ti-*ipso*-C interactions within the molecule. Anticipating that changes in the mode of bonding might be reflected in NMR spectra of the compound, we carried out variable temperature ^{1}H and $^{13}C\{^1H\}$ in CD_2Cl_2. The ^{1}H-NMR spectrum of a solution of $Ti(CH_2Ph)_4$ in CD_2Cl_2 at −50°C exhibits resonances attributable to methylene (δ 2.32, s), *o*-phenyl (δ 6.47, d, *J* 0.7 Hz) and *m*-, *p*-phenyl (7.1–7.3, m) hydrogen atoms. On warming to 27°C, the methylene and *o*-phenyl resonances shift to δ 2.64 and δ 6.54, respectively, while the *m*-, *p*-phenyl multiplet remains essentially unchanged. The change in methylene chemical shift in particular is consistent with a subtle variation in the position of equilibrium between various η^1- and multihapto structures [9]. Unfortunately the methylene carbon resonance (125 MHz) did not undergo decoalescence, but remained a sharp singlet δ 94.4 even at −50°C and thus the ground state structure in solution cannot be ascertained.

2.2. NMR investigation of the reaction between $Ti(CH_2Ph)_4$ and $B(C_6F_5)_3$; formation of $Ti(CH_2Ph)_3[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$

The resonances of $Ti(CH_2Ph)_4$ disappear on addition of an equimolar amount of $B(C_6F_5)_3$ at −78°C, and the methylene resonance (δ 2.32) in particular is replaced by a narrow singlet at δ 2.75 (6H) and a broad singlet at δ 2.98 (2H) (Fig. 1). The latter resonance is presumably broadened because of the quadrupolar boron, and thus the data are consistent with the anticipated abstraction of a benzyl group from titanium by boron. As the analogous reaction of $Zr(CH_2Ph)_4$ results in a zwitterionic η^6-arene structure as in **C** (M = Zr) [11], we expect that an analogous complex (**C**, M = Ti) is obtained with $Ti(CH_2Ph)_4$.

---

[3] References for other types of η^2 benzyl complexes, NMR, see [10].

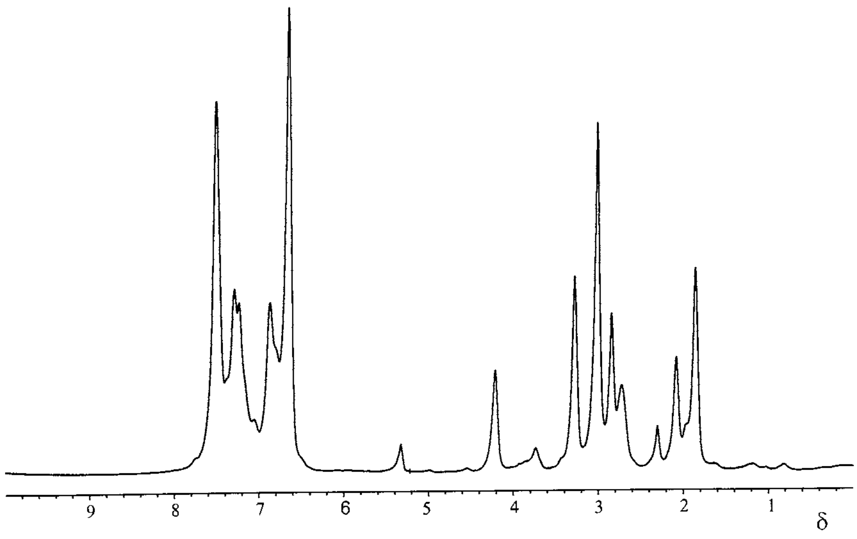
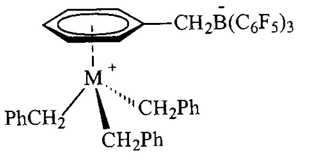


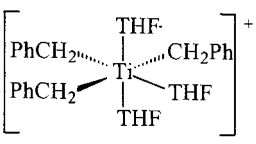
Fig. 2. ^{1}H-NMR spectrum of *mer*-$[Ti(CH_2Ph)_3(THF)_3]^+$ from the reaction of $Ti(CH_2Ph)_4$ with $B(C_6F_5)_3$ and THF at −78°C.



C

Unfortunately, the compound formed decomposes in solution on warming to ∼ −10°C, and identification therefore rests completely on the NMR spectroscopic data. In addition to the two resonances attributable to the methylene protons of the benzyl groups bound to titanium and boron, the spectrum at −78°C exhibits resonances at δ 6.62 (6H, d, *J* 7.2 Hz), attributable to the $TiCH_2$-*o-Ph* hydrogens, at δ 7.22 (6H, t, *J* 7.4 Hz) and δ 7.28 (3H, t, *J* 6.4 Hz), attributable to the $TiCH_2$-*m-Ph* and the $TiCH_2$-*p-Ph* hydrogens, respectively. Thus, the *ortho* hydrogen resonance lies about 0.6 ppm upfield shift from the resonances of the corresponding *meta* and *para* hydrogens, similar to observations on the zirconium analogue [11b]. In the latter case, the chemical shift difference was attributed to interactions of the phenyl π-system with a metal vacant metal d orbital. The Ti–CH_2 ^{13}C resonance is shifted significantly downfield, from δ 94 in the precursor $Ti(CH_2Ph)_4$ to δ 105.5. There were also observed a broad four hydrogen resonance at δ 6.76 and a broad one hydrogen resonance at δ 6.69, attributable to the *ortho* and *meta* hydrogens and the *para* hydrogen of the benzyl group bound to boron, respectively. The pattern of arene chemical shifts of the BCH_2Ph group, with the *meta* and *para* hydrogen resonances shifted upfield relative to the resonance of the *ortho* hydrogens, is consistent with structure **C**. The electronic deficiency of the titanium is thus relieved by the coordination of the phenyl ring of $[B(CH_2Ph)(C_6F_5)_3]^-$ counterion. The chemical shifts of the titanium- and boron-bonded methylene resonances vary somewhat with temperature, suggesting a degree of fluxionality of the groups. The complex decomposes completely at −10°C, a resonance attributable to toluene appearing at δ 2.31.

The $[Ti(CH_2Ph)_3^+]$–$[B(CH_2Ph)(C_6F_5)_3^-]$ interaction is weak since addition of THF results in the displacement of anion by THF coordination; a similar result has been reported for the zirconium analogue [11b]. In an NMR experiment carried out in CD_2Cl_2 at −78°C, addition of a slight excess of THF resulted in complete disappearance of the ^{1}H resonances of $[Ti(CH_2Ph)_3]$–$[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$. Resonances for coordinated THF were observed at δ 4.20, 3.26, 2.07, 1.84 at −78°C, with approximate intensity ratios of 1:2:1:2 (Fig. 2), respectively, consistent with a six-coordinate meridional structure **D**.



D

In addition, resonances attributable to the Ti–CH_2 (δ 2.99) and *m*-H (δ 7.49) positions of the benzyl groups were shifted significantly (∼ 0.2 ppm) downfield from those of $Ti(CH_2Ph)_3[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$, consistent with the weak donor abilities of the THF ligands compared with the η^6-borate ligand. In contrast the *o*-H resonance (δ 6.86) was relatively little shifted, possibly suggesting a greater degree of η^2 bonding in **D** than in $[Ti(CH_2Ph)_3][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$.

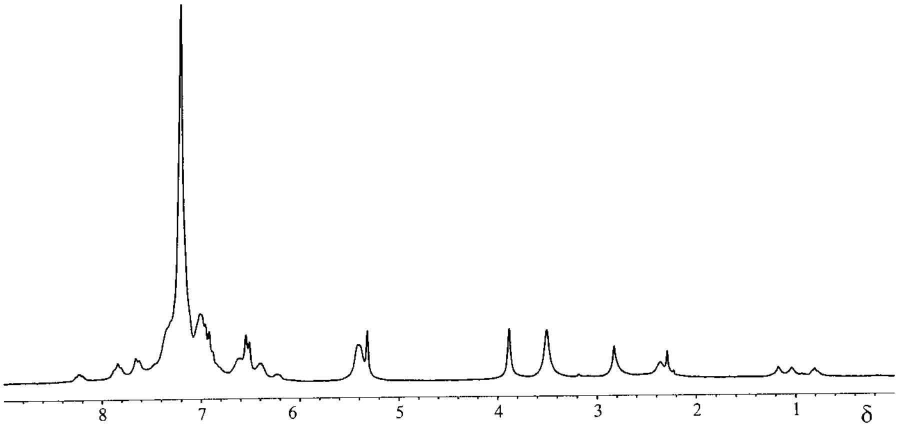


Fig. 3. ^{1}H-NMR spectrum of the reaction of $Ti(CH_2Ph)_4$ with one molar equivalent of $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at −78°C.

2.3. NMR investigation of the reaction between $Ti(CH_2Ph)_4$ and $[Ph_3C][B(C_6F_5)_4]$

The $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ system does not appear to have yet been investigated even for its catalytic properties, and while the analogous zirconium system, $Zr(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$, has been shown to induce polymerization of ethylene [7l], the nature of the species in solution has not been reported. The reaction of $Ti(CH_2Ph)_4$ with $[Ph_3C][B(C_6F_5)_4]$ is expected, by analogy with metallocene systems [1,2], to proceed as in Eq. (1) and to involve abstraction of a benzyl anion and formation of Ph_3CCH_2Ph and the electron deficient species $[Ti(CH_2Ph)_3]^+$. The latter might be expected to be stabilized via multihapto bonding of one or more of the benzyl groups and/or by η^6 coordination of either the Ph_3CCH_2Ph or the counteranion.

$$Ti(CH_2Ph)_4 + [Ph_3C][B(C_6F_5)_4] \rightarrow [Ti(CH_2Ph)_3][B(C_6F_5)_4] + Ph_3CCH_2Ph \quad (1)$$

Low temperature NMR scale reactions between $Ti(CH_2Ph)_4$ and $[Ph_3C][B(C_6F_5)_4]$ were carried out several times in CD_2Cl_2, at various temperatures and with varying ratios of reagents, and the formation of about one equivalent Ph_3CCH_2Ph was confirmed generally by ^{1}H-NMR spectroscopy and GC–MS analyses. Small, variable resonances of presumed decomposition products bibenzyl and toluene were also identified, and sometimes rendered satisfactory spectral integrations difficult.

The ^{1}H-NMR spectrum of a solution containing $Ti(CH_2Ph)_4$ and a slight molar excess of $[Ph_3C][B(C_6F_5)_4]$ at −78°C exhibited relatively weak resonances of unreacted trityl cation at δ 8.24, 7.85 and 7.64 (see Section 1), in addition to methylene or methyl singlets attributable to Ph_3CCH_2Ph (δ 3.90), bibenzyl (δ 2.85) and toluene (δ 2.31) (Fig. 3). Replacing the methylene resonance of $Ti(CH_2Ph)_4$ at δ 2.32 was a new singlet Ti−*CH*$_2$Ph resonance at δ 3.54, integrating to about 6H atoms relative to the 2H atoms of the Ph_3CCH_2Ph resonance at δ 3.90[4] and shifted downfield ~1.2 ppm from the chemical shift of the neutral precursor as a consequence of cation formation. The spectrum also exhibited a broad resonance at δ 5.49, also integrating for 6H and attributable to the *ortho*-Ph hydrogen atoms of the newly formed cationic species. The *ortho*-Ph chemical shift of the latter is almost 1 ppm upfield from that of the *ortho*-Ph hydrogen resonance of $Ti(CH_2Ph)_4$, and presumably implies strong η^n interaction of the benzyl ligands with the highly electrophilic titanium in the cation [12]. The chemical shifts of the methylene and *ortho*-Ph resonances were temperature dependent, moving downfield δ 0.1 ppm and ~0.3 ppm, respectively, on changing the temperature from −78°C to −50°C to −30°C (Fig. 4). The *ortho*-Ph resonance also decoalesced to a doublet as the temperature was increased, and both the broadening and the chemical shift changes were found to be reversible between −78°C and −30°C in CD_2Cl_2. Our investigation was hampered, however, by slow decomposition which was suggested by slight increases in the intensities of the bibenzyl methylene and toluene methyl resonances during the course of the variable temperature NMR experiments. Thus, the product could not be isolated as the dark-red solution turned black and a dark-brown precipitate formed.

The NMR results suggest that a single major species was formed, although clearly a reversible exchange between η^1- and η^2- and/or η^3-benzyl ligands occurs in solution. The resonances of the primary product Ph_3CCH_2Ph [13] and of the secondary products bibenzyl and toluene are identical to those of the pure materials, while the addition of excess toluene has no

---

[4] The ratio of resonances was generally <3:1, but inclusion of the intensities of the resonances of the bibenzyl and toluene, presumed decomposition products during the abstraction reaction, brought the ratio close to 3:1.

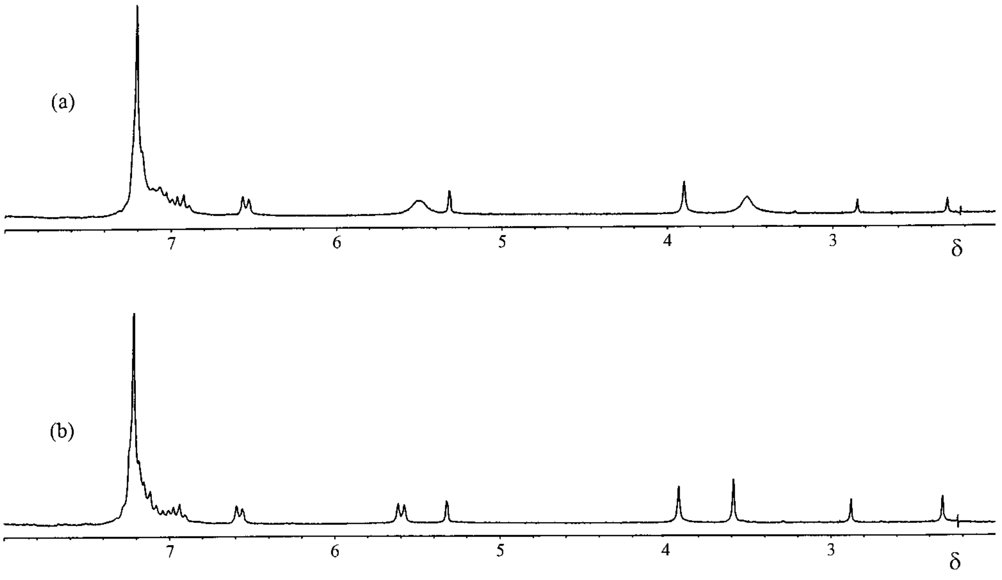
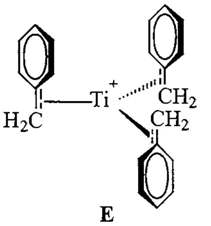


Fig. 4. ^{1}H-NMR spectrum of the reaction of $Ti(CH_2Ph)_4$ with one molar equivalent of $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at (a) −50°C, (b) −30°C.

effect on the resonances of the titanium complex formed. It is thus clear that these potential aromatic ligands are not involved in e.g. η^6 bonding. The methylene or methyl resonances of these compounds would be expected to shift considerably on coordination; for instance, the toluene methyl resonance of the complex $[Cp^*TiMe_2(\eta^6\text{-toluene})]^+$ is deshielded ~0.4 ppm relative to the methyl resonance of free toluene [14].

The ^{19}F-NMR spectrum of a freshly prepared reaction mixture at −78°C gave no indication that the borate anion was coordinating via a fluorine to titanium, and thus the complex formed appears to be the bare $[Ti(CH_2Ph)_3]^+$ cation. The latter probably contains all three benzyl ligands at least η^2-bound, but the temperature dependence of the methylene and *ortho*-Ph resonances suggests strongly an exchange between two or more isomers such as **E**.

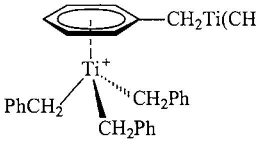


E

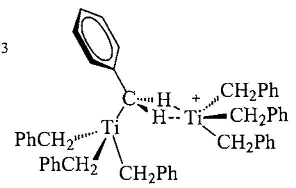
The exchange may involve interchange between 'up' and 'down' benzyl groups, or between η^1, η^2 and/or η^n ($n > 2$) benzyl groups [10f,15].

Reaction of two equivalents of $Ti(CH_2Ph)_4$ with one of $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at −78°C resulted again in the formation of one equivalent of Ph_3CCH_2Ph per mole of $[Ph_3C][B(C_6F_5)_4]$, as well as small amounts of bibenzyl and toluene. Although the ^{1}H-NMR spectrum (Fig. 5(a)) run immediately after the reactants had been combined exhibited resonances of $[Ph_3C][B(C_6F_5)_4]$, indicating that the reaction was not instantaneous at this temperature, the resonances of this starting material did disappear after a few minutes, to be replaced by strong, broad phenyl resonances in the region δ 7.1–7.45 and medium, broad phenyl resonances in the region δ 6.23–6.82 (see Section 1). In addition to the methylene singlet of Ph_3CCH_2Ph at δ 3.88 (2H), the ^{1}H-NMR spectrum at −78°C also exhibited rather broad, apparent Ti–CH_2Ph singlets at δ 0.97 (2H), 2.3 (6H but overlapping with toluene methyl resonance) and 2.78 (6H but overlapping with bibenzyl methylene resonance).

The spectrum may be tentatively interpreted in terms of dititanium structures **F** or **G**, although the observation of the high field methylene resonance (δ 0.97) argues in favour of the latter (see below).



F



G

On the basis of the NMR evidence, it seems likely the initial benzyl abstraction reaction (Eq. (1)) was followed by reaction of the newly formed $[Ti(CH_2Ph)_3]^+$ with a second mole of $Ti(CH_2Ph)_4$ to give a μ-benzyl complex $[(CH_2Ph)_3Ti\text{-}\mu\text{-}CH_2PhTi(CH_2Ph)_3]^+$ (Eq. (2)):

$$[Ti(CH_2Ph)_3][B(C_6F_5)_4] + Ti(CH_2Ph)_4$$
$$\rightarrow [(CH_2Ph)_3Ti(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3][B(C_6F_5)_4] \qquad (2)$$

It is interesting to note that a ^{1}H-NMR spectrum recorded at −78°C immediately after the combining of equivalent amounts of $Ti(CH_2Ph)_4$ and $[Ph_3C][B$-

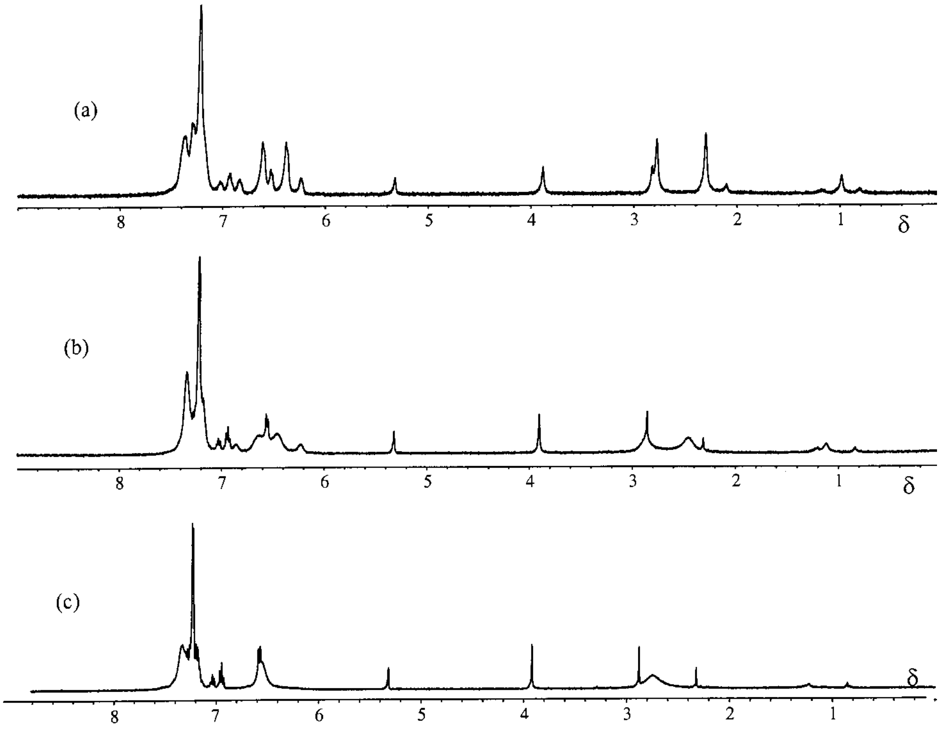


Fig. 5. VT ^{1}H-NMR of the reaction of $Ti(CH_2Ph)_4$ with $[Ph_3C][B(C_6F_5)_4]$, 2:1 ratio in CD_2Cl_2 at (a) −78°C, (b) −50°C, (c) −30°C.

$(C_6F_5)_4]$ exhibited *temporarily* the resonances of $[(CH_2Ph)_3Ti(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3]^+$, in addition to those of $[Ph_3C][B(C_6F_5)_4]$. After completion of the reaction, only the resonances of $[Ti(CH_2Ph)_3]^+$ remained, suggesting that the two cationic titanium complexes are indeed related and possibly involved in a facile equilibrium.

When the temperature was raised to −50°C (Fig. 5(b)), the *o*-, *m*- and *p*-$CH_2\mathit{Ph}$ resonances of Ph_3CCH_2Ph at δ 6.55 (d), 6.93 (t) and 7.03 (t), respectively, narrowed considerably and were readily identified. However, the remaining phenyl resonances at δ 6.24, 6.38, 6.61 and 6.83 broadened at −50°C and coalesced into a single broad ($\Delta\nu_{1/2}$ ~0.2 ppm) resonance at δ ~6.55 at −30°C (Fig. 5(c)). Furthermore, the methylene resonances at δ 2.77 (6H, Ti$\mathit{CH_2}$) and 2.29 (6H, Ti$\mathit{CH_2}$) had both broadened significantly ($\Delta\nu_{1/2}$ ~0.2 ppm) at −50°C while that at 0.97 (2H, μ-$\mathit{CH_2}$) had broadened and shifted downfield ~0.17 ppm. On warming to −30°C, the two resonances at δ 2.77 and 2.29 appear to have coalesced into a very broad resonance at δ 2.75 (~12H, $\Delta\nu_{1/2}$ ~0.4 ppm) while that at δ 0.97 had shifted downfield to δ 1.23. Because of continual decomposition, indicated by growing resonances of toluene and bibenzyl, the system was difficult to characterize properly. An HMQC experiment at −50°C indicated that the putative Ti–CH_2 resonances at δ 2.77, 2.29 and 0.97 correlated with apparent Ti–$^{13}CH_2$ resonances at δ 112, 98, 49, and respectively, confirming the assignments. The high-field ^{1}H chemical shifts of the μ-CH_2 resonances are consistent with assignments to a bridging benzyl group.[5]

3. Alkene polymerizations

As indicated in Section 1 and Tables 1–3, we have assessed the ability of $Ti(CH_2Ph)_4$, activated by $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$, to act both as a Ziegler–Natta catalyst (with ethylene and 1-hexene) and as a carbocationic initiator (IB, EVE). As expected, both $B(C_6F_5)_3$ and the trityl cation abstract a benzyl group from $Ti(CH_2Ph)_4$, giving $Ti(CH_2Ph)_3[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ in the case of the former, either $[Ti(CH_2Ph)_3][B(C_6F_5)_4]$ or $[(CH_2Ph)_3Ti(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3][B(C_6F_5)_4]$ in the latter. All are potential sources of the cationic species $[Ti(CH_2Ph)_3]^+$, which should in principle be capable of inducing Ziegler–Natta or carbocationic polymerization processes.

3.1. Ethylene polymerization

Ethylene polymerizations were performed in both toluene and chlorobenzene, and with results as shown in Table 1 where comparisons are also made with

---

[5] The μ-methyl resonance in $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][BMe(C_6F_5)_3]$ is observed ~1.3 ppm upfield of the terminal methyl resonance, see [16].

Table 1
Ethylene polymerization of $Ti(CH_2Ph)_4$ and $Zr(CH_2Ph)_4$ with various co-catalysts

Run [a]	Catalyst [d] (mmol)	Co-catalyst [d] (mmol)	Solvent	Time (min)	Temperature (°C)	Yield (g)	Activity (kg PE $(mol{\cdot}cat{\cdot}h)^{-1}$)
1 [b] [7j]	$ZrBz_4$ (0.035)	MAO (10.0)	Toluene	30	50	3.2	18.3
2 [b] [7j]	$ZrBz_4$ (0.2)	AFPB (0.035)	Toluene	60	50	5.0	28.6
3 [b] [7k]	$ZrBz_4$ (0.15)	$B(C_6F_5)_3$ (0.1)	Toluene	15	50	1.8	14.4
4 [b] [7k]	$TiBz_4$ (0.15)	$B(C_6F_5)_3$ (0.1)	Toluene	15	50	0.2	1.6
5 [a]	$TiBz_4$ (0.025)	$B(C_6F_5)_3$ (0.025)	Toluene	15	50	0.004	0.64
6 [b] [12]	$ZrBz_4$ (0.05)	$B(C_6F_5)_3$	Toluene	30	50	0.048	1.9
7 [a] [12]	$ZrBz_4$ (0.025)	$B(C_6F_5)_3$	Toluene	30	26	Trace	–
8 [a]	$ZrBz_4$ (0.05)	$[Ph_3C][B(C_6F_5)_4]$	Toluene	8	50	0.078	28
9 [a]	$TiBz_4$ (0.06)	$[Ph_3C][B(C_6F_5)_4]$ (0.05)	Toluene	15	25	Trace	–
10 [a]	$TiBz_4$ (0.06)	$[Ph_3C][B(C_6F_5)_4]$ (0.05)	Chlorobenzene	15	25	0.056	4.48
11 [c]	$TiBz_4$ (0.06)	$[Ph_3C][B(C_6F_5)_4]$ (0.05)	Toluene	15	50	0.012	0.96

[a] $P(C_2H_4) = 1$ atm.
[b] $P(C_2H_4) = 5$ atm.
[c] $P(C_2H_4) = 3$ atm.
[d] Bz, benzyl, MAO, methylaluminoxane, AFPB, *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate.

Table 2
1-Hexene oligomerization initiated by $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$

Run [a]	Solvent	Time (time)	Temperature (°C)	Yield (g)	Conversion (%)	M_w	M_w/M_n
1 [b]	CH_2Cl_2	30	50	0.28	16.5	854	1.10
2 [b]	CH_2Cl_2	60	25	2.0	66.7	1200	1.20
3 [c]	CH_2Cl_2	60	25	0.08	<1	–	–
4 [b]	CH_2Cl_2	60	0	2.2	73.3	1320	1.24
5 [b]	CH_2Cl_2	60	−30	Trace	–	–	–
6 [b]	Toluene	30	0	0.23	8	1000	1.10
7 [d]	Toluene	30	0	0.67	22	1250	1.14
8 [b]	Toluene	30	−50	Trace	–	–	–

[a] 3 g of 1-hexene.
[b] 0.06 mmol $Ti(CH_2Ph)_4$; the ratio $Ti(CH_2Ph)_4{:}[Ph_3C][B(C_6F_5)_4] = 1.2{:}1$.
[c] 0.05 mmol $[Ph_3C][B(C_6F_5)_4]$.
[d] Ratio $Ti(CH_2Ph)_4{:}[Ph_3C][B(C_6F_5)_4] = 2{:}1$.

Table 3
Polymerization of IB and EVE with $Ti(CH_2Ph)_4$ activated by $[Ph_3C][B(C_6F_5)_4]$

Run [a]	Alkene	Solvent	Time (min)	Temperature (°C)	Monomer weight (g)	Yield (g)	Conversion (%)	M_w	M_w/M_n
1	IB	CH_2Cl_2	20	25	–	3.8	–	979	1.19
2	IB	CH_2Cl_2	20	0	–	3.4	–	19 400	1.78
3	IB	CH_2Cl_2	10	−15	2.7	2.4	90	20 800	1.84
4	IB	Toluene	10	25	–	Trace	–	47 800	1.27
5	IB	Toluene	10	0	–	Trace	–	50 500	1.48
6	IB	Toluene	10	−15	2.5	0.4	16	203 000	1.51
7	IB	CH_2Cl_2	5	−50	3.1	2.9	92	4300	1.38
8	IB	Toluene	5	−50	2.7	0.26	10	230 800	1.89
9	EVE	CH_2Cl_2	10	25	2.0	2.0	$\sim$100	33 900	1.82
10	EVE	Toluene	10	25	2.0	2.0	$\sim$100	73 100	2.06

[a] 0.06 mmol $Ti(CH_2Ph)_4$; ratio $Ti(CH_2Ph)_4{:}[Ph_3C][B(C_6F_5)_4] = 1.2{:}1$, except for runs 7, 8, for which $Ti(CH_2Ph)_4{:}[Ph_3C][B(C_6F_5)_4] = 2{:}1$.

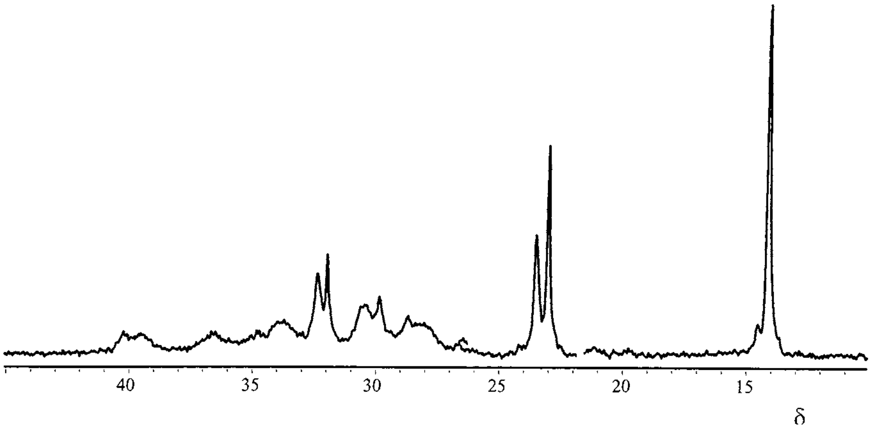


Fig. 6. ^{1}H-NMR spectrum of oligomer of 1-hexene.

similar systems involving $Zr(CH_2Ph)_4$. While comparisons with investigations carried out elsewhere are difficult, the catalytic activities of the $Ti(CH_2Ph)_4/B(C_6F_5)_3$ and $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ systems for ethylene polymerization are both very low, indeed lower than activities of the similar zirconium systems [7j,k,12]. While the $Ti(CH_2Ph)_4/B(C_6F_5)_3$ system also appears to be much less active than the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ system, consistent with observations that the poorly coordinating anion $[B(C_6F_5)_4]^-$ generally gives more active catalysts [4,11], ethylene polymerization clearly does not warrant further comment except to note that the activity of the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ system is higher in chlorobenzene than in toluene, possibly because of toluene coordination [14] which would hinder monomer coordination. The polyethylene products were in all cases too insoluble for molecular weights to be determined, and thus were presumably essentially linear.

3.2. 1-Hexene polymerization

The results of polymerizations of 1-hexene by the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ system are shown in Table 2; as with ethylene, the $Ti(CH_2Ph)_4/B(C_6F_5)_3$ system was relatively inactive and was little studied. In a typical experiment, a solution of $[Ph_3C][B(C_6F_5)_4]$ was added to a mixture of $Ti(CH_2Ph)_4$ and 1-hexene in methylene chloride or toluene; there was invariably an immediate color change accompanied by evolution of heat. Termination of the reaction after 30–60 min resulted in moderate conversions ($\sim 70\%$) at both room temperature and 0°C, the products formed being oligomeric and exhibiting narrow molecular weight distributions. Conversion decreased significantly at temperatures $> 50°C$ and $< -30°C$ in CH_2Cl_2. Polymerizations in toluene resulted in lower conversions compared with methylene chloride, while $[Ph_3C][B(C_6F_5)_4]$ alone was relatively ineffective. Thus, the polymerizations were not induced by protons resulting from reaction of the trityl cation with adventitious water [4a,b].

The oligomers obtained were characterized by their $^{13}C\{^1H\}$-NMR spectra (Fig. 6), which were found to differ greatly from the much simpler spectra of atactic poly-1-hexenes formed via normal 1,2-inserted 1-hexene units, obtained using Ziegler–Natta catalysts such as $Cp^*TiMe_3/B(C_6F_5)_3$ [17]. Although the latter catalyst can also produce polymers containing significant amounts of regioirregularities arising from 2,1-insertions, the $^{13}C\{^1H\}$-NMR spectra of such materials nonetheless indicate that they are essentially linear polymers containing almost exclusively butyl branching [17]. In contrast, the $^{13}C\{^1H\}$-NMR spectra of the materials formed by the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ initiator system indicate that they contain branches of varying lengths [18], and are in fact rather similar to the low molecular weight, highly branched products of carbocationic oligomerization of 1-hexene induced by $AlCl_3$ [18a]. Our finding that the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ initiator system is significantly more active for 1-hexene than for ethylene polymerization is also consistent with carbocationic rather than Ziegler–Natta polymerization of the 1-hexene; while 1-hexene is not *readily* polymerized via a carbocationic mechanism, it is *more* amenable to this type of process than is ethylene [3a,4].

Interestingly, the ^{1}H-NMR spectra of the oligomers also exhibited very weak phenyl resonances, indicating the presence of benzyl end groups. The latter could be incorporated via the initial insertion step of a Ziegler–Natta process (as in Eq. (1)), or via either intra- or intermolecular transfer of benzyl groups from a titanium to a carbocationic center of intermediates of the type $[(PhCH_2)_3Ti(C_6H_{12})_nCH_2-{}^+CH(n\text{-}Bu)]$. To test for the possibility that a neutral titanium species can transfer a benzyl group to a distant carbocationic center, we carried out oligomerization experiments in the presence of excess $Ti(CH_2Ph)_4$ (two equivalents per $[Ph_3C][B(C_6F_5)_4]$) in toluene at 0°C (Table 2, compare runs 6, 7). The products formed exhibited essentially identical molecular weight distributions and ^{1}H-NMR spectra, suggesting that the presence of excess $Ti(CH_2Ph)_4$ had little effect on the oligomerization process. Unfortunately, the relative intensities of the weak phenyl resonances varied erratically and we were unable to confirm or deny a correlation with the presence of excess $Ti(CH_2Ph)_4$. Thus, the possibility that a Ziegler–Natta process pertains to a slight degree remains moot.

3.3. Polymerization of IB and EVE

These two monomers are prototypical alkenes for carbocationic processes [4], and no unambiguous examples of their homopolymerization via Ziegler–Natta processes are known. Polymerizations of the two alkenes by the $Ti(CH_2Ph)_4/[Ph_3C][B(C_6F_5)_4]$ system were carried out largely as described for 1-hexene, although in some cases IB was just bubbled through a solution of $Ti(CH_2Ph)_4$ as co-initiator was added; the results are indicated in Table 3. Addition of $[Ph_3C][B(C_6F_5)_4]$ to the reaction mixtures resulted in all cases in rapid polymerization of IB and EVE, with concurrent heating and immediate color changes. High conversions are obtained in polymerization of IB in CH_2Cl_2 and of EVE in both solvents (~ 90–100%). Polymerizations of IB in toluene give only trace yields at temperatures higher than 0°C and moderate to low conversions at low temperature, although reasonably high molecular weights and quite narrow molecular weight distributions were obtained. Rather lower molecular weights were obtained in methylene chloride for both monomers.

That the polymerizations of IB and EVE proceed by carbocationic processes was confirmed by the ^{1}H-NMR spectra of the products, as no phenyl resonances were observed in any cases. The observations of higher activities and molecular weights for PIB formation with decreases in temperature are also consistent with carbocationic processes [4], and suggest a different polymerization mechanism from that which applies for 1-hexene.

4. Summary

Treatment of $Ti(CH_2Ph)_4$ with an equimolar amount of $B(C_6F_5)_3$ results in benzyl group abstraction to give $Ti(CH_2Ph)_3[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$, in which the resulting benzylborate anion $[BCH_2Ph(C_6F_5)_3]^-$ is η^6-coordinated to the $[Ti(CH_2Ph)_3]^+$ moiety. Analogous reactions involving one and two molar equivalents of the trityl salt, $[Ph_3C][B(C_6F_5)_4]$, also result in benzyl group abstraction to give 1,1,1,2-tetraphenylethane and the complex $[Ti(CH_2Ph)_3]^+$, and the latter appears to be capable of existence as such, stabilized by multihapto benzyl coordination. In the presence of excess $Ti(CH_2Ph)_4$, however, a μ-benzyl dititanium complex is formed, apparently with the structure $[(CH_2Ph)_3Ti(\mu\text{-}CH_2Ph)Ti(CH_2Ph)_3]^+$. All of these species are thermally unstable above about − 10°C in methylene chloride, forming dark solutions and precipitates. However, the species $[Ti(CH_2Ph)_3]^+$ is sufficiently stable in the presence of alkenes in toluene that solutions do not darken or throw precipitates, but instead can initiate oligomerization or polymerization of ethylene, 1-hexene, isobutylene and ethyl vinyl ether over a range of temperatures. An alternative possibility, that proton sources such as residual water could be the actual initiator, is quite unlikely since the benzyl-titanium complexes react rapidly with water. NMR studies of the oligomeric poly-1-hexene show that this material is highly branched, similar to the similar material produced via a carbocationic process, but contains minor amounts of benzyl end groups; thus it may be formed in part via a Ziegler–Natta process. In contrast, the polyisobutylene and polyethyl vinyl ether products do not contain benzyl end groups, consistent with the anticipated carbocationic process for these polymerizations.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (Research and Strategic Grants to M.C.B.) and Queen's University (Queen's scholarship to M.L.) for financial support of this research, and to Dr. M. Parent for assistance with GPC measurements, Dr. F. Sauriol and Ms S. Blake for assistance with NMR measurements.

References

[1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (b) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255. (c) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143. (d) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1. (e) V.K. Gupta, S. Satish, I.S. Bhardwaj, J. Macromol. Sci. C34 (1994) 439.

[2] (a) S.W. Ewart, M.C. Baird, in: J. Scheirs, W. Kaminsky (Eds.), Preparation, Properties and Technology of Metallocene-based Polyolefins, Vol. 1, 1999, John Wiley and Son, UK, pp. 119–141. (b) N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, J. Molec. Catal. 128 (1998) 167. (c) A.L. McNight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[3] (a) M.C. Baird, Chem. Rev. 100 (2000) 1471. (b) F. Barsan, M.C. Baird, J. Chem. Soc. Chem. Commun. (1995) 1065. (c) Q. Wang, M.C. Baird, Macromolecules. 28 (1995) 8021. (d) Q.-Y. Wang, D.J. Gillis, R. Quyoum, D. Jeremic, M.-J. Tudoret, B.K. Hunter, M.C. Baird, Organometallics 15 (1996) 693. (e) F. Barsan, A.R. Karam, M.A. Parent, M.C. Baird, Macromolecules 31 (1998) 8439.

[4] (a) J.P. Kennedy, E. Maréchal, Carbocationic Polymerization, John Wiley and Sons, New York, 1982. (b) J.P. Kennedy, B. Iván, Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice, Hanser Publishers, Munich, 1991. (c) M. Sawamoto, Prog. Polym. Sci. 16 (1991) 111. (d) G. Sauvet, P. Sigwalt, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 3, Pergamon Press, New York, 1989, p. 579. (e) O. Nuyken, S.D. Pask, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 3, Pergamon Press, New York, 1989, p. 619. (f) K. Matyjaszewski, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 3, Pergamon Press, New York, 1989, p. 639. (g) T. Higashimura, M. Sawamoto, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 3, Pergamon Press, New York, 1989, p. 673. (h) J.M. Rooney, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 3, Pergamon Press, New York, 1989, p. 697. (i) J.P. Kennedy, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 3, Pergamon Press, New York, 1989, p. 705. (j) A.R. Padwa, Prog. Poly. Sci. 14 (1989) 811.

[5] (a) T.D. Shaffer, J.R. Ashbaugh, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 329. (b) A.G. Carr, D.M. Dawson, M. Bochmann, Macromolecules 31 (1998) 2035. (c) A.G. Carr, D.M. Dawson, M. Thornton-Pett, M. Bochmann, Organometallics 18 (1999) 2933. (d) X. Song, M. Thornton-Pett, M. Bochmann, Organometallics 17 (1998) 1004. (e) A.G. Carr, D.M. Dawson, M. Bochmann, Macromol. Rapid Commun. 19 (1998) 205.

[6] (a) U. Zucchini, E. Albizzati, U. Giannini, J. Organomet. Chem. 26 (1971) 357. For detailed NMR characterization, see (b) L. Zetta, G. Gatti, Org. Magn. Res. 4 (1972) 585. (c) J. Scholz, M. Schlegel, K.-H. Thiele, Chem. Ber. 120 (1987) 1369.

[7] (a) U. Gianinni, U. Zucchini, E. Albizzati, J. Polym. Sci. Part B 8 (1970) 405. (b) D.G.H. Ballard, P.W. Van Lienden, Makromol. Chem. 154 (1972) 177. (c) D. Martineau, P. Dumas, P. Sigwalt, Makromol. Chem. 184 (1983) 1389. (d) D. Martineau, P. Dumas, P. Sigwalt, Makromol. Chem. 184 (1983) 1397. (e) A. Zambelli, P. Longo, C. Pellecchia, A. Grassi, Macromolecules 20 (1987) 2035. (f) L. Oliva, P. Longo, C. Pellecchia, Makromol. Chem., Rapid Commun. 9 (1988) 51. (g) A. Zambelli, L. Oliva, C. Pellecchia, Macromolecules 22 (1989) 2129. (h) P. Longo, A. Grassi, L. Oliva, Makromol. Chem. 191 (1990) 2387. (i) J.C.W. Chien, Z. Salajka, J. Polym. Sci. Part A. 29 (1991) 1243. (j) C. Pellecchia, A. Proto, P. Longo, A. Zambelli, Makromol. Chem., Rapid Commun. 12 (1991) 663. (k) C. Pellecchia, P. Longo, A. Proto, A. Zambelli, Makromol. Chem. Rapid Commun. 13 (1992) 265. (l) C. Pellecchia, A. Proto, P. Longo, A. Zambelli, Makromol. Chem. Rapid Commun. 13 (1992) 277. (m) M. Bochmann, S.J. Lancaster, Organometallics 12 (1993) 633.

[8] (a) A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245. (b) R. Uson, A. Laguna, Inorg. Syntheses 21 (1982) 72. (c) J.C.W. Chien, W.-M. Tsai, M.D. Rausch, J. Am. Chem. Soc. 113 (1991) 8570.

[9] (a) I.W. Bassi, G. Allegra, R. Scordamaglia, G. Chioccola, J. Am. Chem. Soc. 93 (1971) 3787. (b) B.T. Kilbourn, G.R. Davies, J.A.J. Jarvis, A.J.P. Pioli, J. Chem. Soc. D (1971) 677. (c) G.R. Davies, J.A.J. Jarvis, B.T. Kilbourn, J. Chem. Soc. D (1971) 1511. (d) C. Tedesco, A. Immirzi, A. Proto, Acta Crystallogr. Sect. B 54 (1998) 431.

[10] (a) M. Mena, P. Royo, R. Serrano, M.A. Pellinghelli, A. Tiripicchio, Organometallics 8 (1989) 476. (b) R.F. Jordan, R.E. LaPointe, C.S. Bajgur, S.F. Echols, R. Willett, J. Am. Chem. Soc. 109 (1987) 4111. (c) R.F. Jordan, R.E. LaPointe, N. Baenziger, G.D. Hinch, Organometallics 9 (1990) 1539. (d) S.L. Latesky, A.K. McMullen, G.P. Niccolai, I.P. Rothwell, J.C. Huffman, Organometallics 4 (1985) 902. (e) G.J. Pindado, M. Thornton-Pett, M.B. Hursthouse, S.J. Coles, M. Bochmann, J. Chem. Soc. Dalton Trans. (1999) 1663. (f) C. Pellecchia, A. Grassi, A. Zambelli, Organometallics 13 (1994) 298. (g) A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936. (h) Y.-M. Jeon, J. Heo, W.M. Lee, T. Chang, K. Kim, Organometallics 18 (1999) 4107.

[11] (a) C. Pellecchia, A. Grassi, A. Immirzi, J. Am. Chem. Soc. 115 (1993) 1160. (b) C. Pellecchia, A. Grassi, A. Zambelli, J. Mol. Catal. 82 (1993) 57.

[12] C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, Organometallics 12 (1993) 4473.

[13] (a) H.-D. Beckhuns, B. Dogan, J. Schaetzer, S. Hellmann, C. Rüchardt, Chem. Ber. 123 (1990) 137. (b) H.E. Zieger, I. Angres, D. Mathisen, J. Am. Chem. Soc. 98 (1976) 2580.

[14] D.J. Gillis, R. Quyoum, M.-J. Tudoret, Q. Wang, D. Jeremic, A. Roszak, M.C. Baird, Organometallics 15 (1996) 3600.

[15] (a) C. Pellecchia, A. Grassi, A Zambelli, J. Chem. Soc. Chem. Commun. (1993) 947. (b) C. Pellecchia, A. Immirzi, D. Pappalardo, A. Peluso, Organometallics 13 (1994) 3773.

[16] Q. Wang, D.J. Gillis, R. Quyoum, D. Jeremic, M.C. Baird, J. Organomet. Chem. 527 (1997) 7.

[17] (a) M.C. Murray, M.C. Baird, J. Mol. Catal. 128 (1998) 1. (b) M.C. Murray, M.C. Baird (unpublished results).

[18] (a) S. Nemes, J. Borbély, J. M. S. Pure Appl. Chem. A34 (1997) 2355. (b) W. Liu, D.G. Ray, P.L. Rinaldi, Macromolecules 32 (1999) 3817.