Copolymerization of sterically demanding phosphine-olefins and 1-hexene

Jenny S.J. McCahill and Douglas W. Stephan

Abstract: The copolymerization of 1-hexene with *t*-$Bu_2P(CH_2)_3CH{=}CH_2$ **(1)** or *t*-$Bu_2P(CH_2)_9CH{=}CH_2$ **(2)** has been achieved using $CpMe_2Ti(NPt\text{-}Bu_3)$ as the precatalyst and $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, or $[PhNMe_2H][B(C_6F_5)_4]$ as the activator. The resulting polymers are shown to incorporate up to 9% of the phosphine comonomer, albeit with reduced catalyst activity and polymer molecular mass. The cause of the catalyst inhibition is also considered in the light of phosphine–activator interactions.

Key words: titanium phosphinimide, copolymerization, phosphine-containing polymers, phosphine–activator interactions.

Résumé : On a effectué la copolymérisation du hex-1-ène avec le *t*-$Bu_2P(CH_2)_3CH{=}CH_2$ (**1**) ou le *t*-$Bu_2P(CH_2)_9CH{=}CH_2$ (**2**) en utilisant le $CpMe_2Ti(NPt\text{-}Bu_3)$ comme précatalyseur et le $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, ou $[PhNMe_2H][B(C_6F_5)_4]$ comme activateurs. On a montré que les polymères qui en résultent incorporent jusqu'à 9 % du comonomère phosphine, avec une réduction de l'activité du catalyseur et du poids moléculaire du polymère. On considère la cause de cette inhibition du catalyseur en fonction des interactions entre la phosphine et l'activateur.

Mots-clés : phosphinimide de titane, copolymérisation, polymères contenant une phosphine, interaction entre une phosphine et un activateur.

[Traduit par la Rédaction]

Introduction

The development of single-site catalysts for the polymerization of ethylene and other α-olefins has been a major area of research for the past quarter of a century. The specific tuning of defined metal complexes allows strict control over the microstructure of polyolefins produced.[1,2] This rational catalyst development, although extensively studied, continues to be a motivating objective in numerous research endeavors. A driving force behind some of these investigations is the expansion of these systems to incorporate functional moieties into the polymer, to enhance or change the polymer properties and range of applications.

There are two main approaches to the synthesis of functional polyolefins: chain-end functionalization and in-chain functionalization.[3–5] Chain-end functionalization is achieved through reactivity on unsaturated chain-ends or via functionalization of polymer terminae. In-chain functionalization is typically achieved through post-polymerization reactivity, the use of groups to protect the functionality during the polymerization, or via direct polymerization. Of these methods of in-chain functionalization, direct polymerization is preferred, since it requires no post-polymerization modification. Therefore, numerous studies have been carried out to incorporate the functional moieties directly during the polymerization process. Furthermore, it is desirable to add these moieties in a controlled manner without compensation of any desirable properties.

The direct polymerization of functionalized monomers using group-IV transition-metal catalysts has been limited, as many polar monomers poison the catalyst by coordination to the electrophilic metal center. Nonetheless, functionalized monomers containing Si,[6,7] halogens,[8] and N[7,9] have been directly polymerized using group-IV catalysts as such groups afford weak donor interactions.

Previous efforts in our group have shown that activation of $CpMe_2Ti(NPt\text{-}Bu_3)$ with borane and borate activators affords highly active catalysts for olefin polymerization. Moreover, the catalytically active cation can be intercepted with phosphine donors affording species of the form $[CpMeTi(NPt\text{-}Bu_3)(PR_3)]^+$. However, with sterically bulky phosphines (R = Cy, *t*-Bu, and *o*-tolyl) there was no evidence of phosphine binding to Ti and the free phosphine was observed in solution by NMR methods.[10,11] In this paper, we exploit this absence of interaction of bulky phosphines to probe the viability of copolymerization of olefins with olefins containing pendant bulky phosphine fragments.

Experimental section

General considerations

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing Grubbs-type column systems man-

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ufactured by Innovative Technologies. Uninhibited THF purchased from EDM and deuterated benzene, toluene, and methylenechloride purchased from Cambridge Isotopes Laboratories, were dried, distilled, and freeze-pump-thaw degassed (three times) prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers. Trace amounts of protonated solvents were used as references, and ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported relative to $SiMe_4$. ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{19}F NMR spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively. Combustion analyses were performed at the University of Windsor Chemical Laboratories employing a PerkinElmer CHN Analyzer. Molecular mass determinations were performed using a Waters Breeze system GPC using THF as eluent. The detector used was a Waters model 410 refractive index detector at 35 °C, and molecular masses were calibrated using narrow polystyrene standards (Polymer Laboratories Inc.). High-temperature GPC data were provided by the technical staff at NOVA Chemicals Corporation.

HP*t*-Bu_2, $Br(CH_2)_3CHCH_2$, $Br(CH_2)_4CH_3$, $Br(CH_2)_9CH_3$, and anhydrous MeOH were purchased from Sigma-Aldrich Chemical Company, and $[Me_2PhNH][B(C_6F_5)_4]$ was purchased from Strem Chemical Inc.; all were used as received. 1-Hexene was purchased from Sigma-Aldrich Chemical Company and distilled from Na/benzophenone. $B(C_6F_5)_3$, and $[Ph_3C][B(C_6F_5)_4]$ were generously donated by NOVA Chemicals Corp. $CpTiMe_2(NPt\text{-}Bu_3)$ was prepared via literature methods.[12]

Synthesis of *t*-$Bu_2P(CH_2)_3CH{=}CH_2$ (1), *t*-$Bu_2P(CH_2)_9CH{=}CH_2$ (2), *t*-$Bu_2P(CH_2)_4CH_3$ (3)

These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of $Br(CH_2)_3CH{=}CH_2$ (4.829 g 32.40 mmol) in THF (5 mL) was added to a solution of *t*-Bu_2PLi (4.392g, 28.87 mmol) in THF (50 mL) cooled to 0 °C. The solution was stirred and warmed to room temperature for 12 h. The solvent was removed in vacuo, and hexanes were added to precipitate LiBr. The solution was filtered through Celite and vacuum-distilled (58–62 °C) to yield a clear liquid.

(1): Yield: 4.89 g (79%). ^{1}H NMR (C_6D_6) δ: 5.71–5.85 (m, 1H, C*H*=CH_2), 4.97–5.08 (m, 2H, CH=CH_2), 2.13 (q, 2H, $^3J_{H-H}$ = 7 Hz, CH_2CHCH_2), 1.65 (sextet, 2H, $^2J_{H-H}$ = 7 Hz, $CH_2CH_2CH_2$), 1.22–1.33 (m, 2H, PCH_2CH_2), 1.07 (d, 18H, $^3J_{H-P}$ = 10 Hz, *t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6) δ: 139.20 (s, *C*H=CH_2), 115.39 (s, CH=*C*H_2), 36.06 (d, $^3J_{C-P}$ = 13 Hz, CH_2CH_2CH), 31.66 (d, $^1J_{C-P}$ = 23 Hz, *t*-Bu), 30.65 (s, PCH_2CH_2), 30.25 (d, $^2J_{C-P}$ = 15 Hz, *t*-Bu), 21.46 (d, $^1J_{C-P}$ = 22 Hz, P*C*H_2). ^{31}P{^{1}H} NMR (C_6D_6) δ: 27.82 (s). Anal. calcd. for $C_{13}H_{27}P$: C 72.85, H 12.70; found: C 72.73, H 12.43.

(2): Yield: 2.70 g (66%) ^{1}H NMR (C_6D_6) δ: 5.73–5.87 (m, 1H, C*H*=CH_2), 4.98–5.09 (m, CH=CH_2), 1.99 (q, 2H, CH_2CH=CH_2), 1.29–1.66 (m, 14H, CH_2), 1.16 (d, 18H, $^3J_{H-P}$ = 11 Hz, *t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6) partial δ: 139.59 (s, *C*H=CH_2), 114.86 (s, CH=*C*H_2), 34.57 (s, CH_2), 32.27 (d, $^2J_{C-P}$ = 13 Hz, CH_2), 31.58 (d, $^1J_{C-P}$ = 23 Hz, *t*-Bu), 31.56 (s, *C*H_2), 22.13 (d, $^1J_{C-P}$ = 23 Hz, *t*-Bu). ^{31}P{^{1}H} NMR (C_6D_6) δ:27.82 (s). Anal. calcd. for $C_{19}H_{39}P$: C 76.45, H 13.17; found: C 76.25, H 13.00.

(3): Yield: 0.71 g (51%). ^{1}H NMR (C_6D_6) δ: 1.27–1.54 (m, 8H, CH_2), 1.11 (d, 18H, $^3J_{H-P}$ = 11 Hz, *t*-Bu), 0.97 (t, 3H, $^3J_{H-H}$= 7 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ: 34.41 (d, $^3J_{C-P}$ = 12 Hz, $CH_2CH_2CH_2$), 31.56 (d, $^1J_{C-P}$ = 23 Hz, *t*-Bu), 31.02 (d, $^2J_{C-P}$ = 12 Hz, PCH_2CH_2), 30.19 (d, $^2J_{C-P}$ = 14 Hz, *t*-Bu), 23.26 (s, $CH_2CH_2CH_3$) 22.03 (d, $^1J_{C-P}$ = 22 Hz, P*C*H_2), 14.68 (s, *C*H_3). ^{31}P{^{1}H} NMR (C_6D_6) δ: 27.84 (s). Anal calcd. for $C_{14}H_{39}P$: C 76.45, H 13.17; found: C 76.13, H 13.13.

Synthesis of *t*-$Bu_2P((CH_2)_9CHCH_2)C_6F_4BF(C_6F_5)_2$ (5)

To a solution of $B(C_6F_5)_3$ (0.254 g, 0.50 mmol) in CH_2Cl_2 (10 mL) **2** (0.156 g, 0.52 mmol) was added. The solution was stirred overnight, and the solvent was removed in vacuo. The residue was dissolved in 3 mL of CH_2Cl_2 and hexanes were added to precipitate an off-white solid. The solid was filtered and washed with pentanes several times to give a white solid. Yield: 0.198 g (50%). ^{1}H NMR (CD_2Cl_2) δ: 5.74–5.88 (m, 1H, C*H*=CH_2), 4.89–5.01 (m, 2H, CH=CH_2), 2.51–2.63 (br m, 2H, CH_2), 1.99–2.08 (br m, 2H, CH_2), 1.62–1.79 (br, m, 2H, CH_2), 1.51 (d, 18H, $^3J_{H-P}$ = 13 Hz, *t*-Bu_2), 1.25–1.36 (br, 12H, CH_2). ^{11}B{^{1}H} NMR (CD_2Cl_2) δ: –0.16 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial δ: 148.41 (dm, $^1J_{C-F}$ = 238 Hz, *C*F), 139.77 (s, *C*H=CH_2), 139.53 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 137.15 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 114.39 (s, CH=*C*H_2), 38.37 (d, $^1J_{C-P}$ = 32 Hz, *t*-Bu), 34.27 (s, CH=*C*H_2), 32.12 (s, *C*H_2), 31.94 (s, *C*H_2), 29.91 (s, *C*H_2), 29.53 (s, *C*H_2), 29.42 (s, *C*H_2), 29.27 (s, *C*H_2), 27.92 (s, *t*-Bu_2), 20.00 (dd, $^1J_{C-P}$ = 40 Hz, $^3J_{C-F}$ = 13 Hz, *C*H_2). ^{19}F NMR (CD_2Cl_2) δ: –119.93 to –119.73 (m, 1F, C_6F_4), –125.24 (s, 1F, C_6F_4), –125.82 (s, 1F, C_6F_4), –130.28 to –130.06 (m, 1F, C_6F_4), –132.54 (t, 4F, $^3J_{F-F}$ = 12 Hz, *o*-C_6F_5), –158.28 (t, 2F, $^3J_{F-F}$ = 20 Hz , *p*-C_6F_5), –163.78 to –163.22 (m, 4F, *m*-C_6F_5), –190.87 (br s, BF). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 54.98 (s). Anal. calcd. for $C_{37}H_{39}BP$: C 54.83, H 4.85; found: C 54.72, H 4.65.

Generation of [*t*-$Bu_2PH((CH_2)_3CH{=}CH_2)][B(C_6F_5)_4]$ (6)

A solution of **1** (0.021 g, 0.100 mmol) in C_6D_5Br (0.5 mL) was added to a solution of $[Me_2PhNH][B(C_6F_5)_4]$ (0.079 g, 0.100 mmol) in C_6D_5Br. Quantitative product formation was observed by NMR. ^{1}H NMR (C_6D_5Br) δ: 7.22 (t, $^3J_{H-H}$ = 7 Hz, 2H, Ph), 6.75 (t, $^3J_{H-H}$ = 7 Hz, 1H, Ph), 6.65 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ph), 5.50–5.54 (m, 1H, C*H*=CH_2), 4.96–5.08 (m, 2H, CH=CH_2), 4.22 (d, $^1J_{H-P}$ = 444 Hz, P*H*), 2.69 (s, 6H, Me_2), 1.93–1.95 (m, 2H, CH_2), 1.29–1.61 (m, 4H, CH_2), 0.87 (d, $^3J_{H-P}$ = 17 Hz, 18H, *t*-Bu). ^{11}B NMR (C_6D_5Br) δ: –16.70 (s). ^{19}F NMR (C_6D_5Br) δ: –132.37 (s, 8F, *o*-C_6F_5), –162.76 (t, 4F, $^3J_{F-F}$ = 19 Hz, *p*-C_6F_5), –166.46 (t, 8F, $^3J_{F-F}$ = 18 Hz, *m*-C_6F_5). ^{31}P NMR (C_6D_5Br) δ: 53.26 (d, $^1J_{P-H}$ = 438 Hz).

Polymerization procedures

A 20 mL vial with a propylene top closure with TFE–silicone septa was equipped with a magnetic stir bar. 0.673 g of 1-hexene (8 mmol), 0.015 g of $CpMe_2Ti(NPt\text{-}Bu_3)$ (0.04 mmol) and 6 mL of toluene were added to the vial. The vial was then immersed in a bath of desired temperature and stirred for 5 min at the polymerization temperature. A syringe containing 0.020 g of $B(C_6F_5)_3$ (0.04 mmol) dissolved in 4 mL of toluene was then brought out of the glovebox,

and its contents were injected into the vial. After a desired time interval, polymerizations were quenched by injection of 1 mL of MeOH. Volatiles were removed in vacuo. 1 mL of toluene was added and 5 mL MeOH was added to precipitate the polymer. Polymer was washed two times with 5 mL MeOH and dried in vacuo.

The % P incorporation is based on the relative integrals of the ^{13}C resonances attributable to methyl groups from the *t*-Bu groups on P and methyl groups of the hexene side chains. While differences in the T_1 relaxation times are expected to be small, a 10 s relaxation delay was employed to record these spectra. This delay was selected based on previously determined T_1 experiments on polyhexene.[13]

Results and discussion

In designing an appropriate phosphine-containing monomer for the polymerization with the $CpTiMe_2(NPt\text{-}Bu_3)$/$B(C_6F_5)_3$ system, we noted the previous studies by Waymouth and co-workers in which polymerization incorporated amine-functionalized olefin.[7,14] It was shown that the steric bulk of amine substituents correlated with the resulting activity of the catalyst. Similar results were also observed by Hakala et al. for the copolymerization of oxygen-functionalized olefins.[15] In addition to the influence of the steric properties of the functional group, the length of the spacer between the functional group and the olefinic residue was also seen to have a profound impact on polymerization. For example, reducing the spacer to two carbons from three carbons to the 4-amino-1-butene, resulted in a decreased polymerization activity.[14] Gianni et al.[16] also observed this trend for the polymerization of amino-functionalized olefins using Ziegler catalysts. Lofgren and co-workers have also reported the increased incorporation of oxygen-functionalized monomers into the polyethylene chain with the increase of the spacer group.[17]

In our efforts to incorporate phosphine residues into polyolefins, these earlier results prompted us to target a sterically encumbered phosphine with the pendant olefinic substituent, $t\text{-}Bu_2P(CH_2)_3CH{=}CH_2$ (**1**). This species was readily prepared via treatment of the corresponding halide derivative with lithium phosphide (Scheme 1). Employing the same methodology, the species $t\text{-}Bu_2P(CH_2)_9CH{=}CH_2$ (**2**) and $t\text{-}Bu_2P(CH_2)_4CH_3$ (**3**) were also prepared.

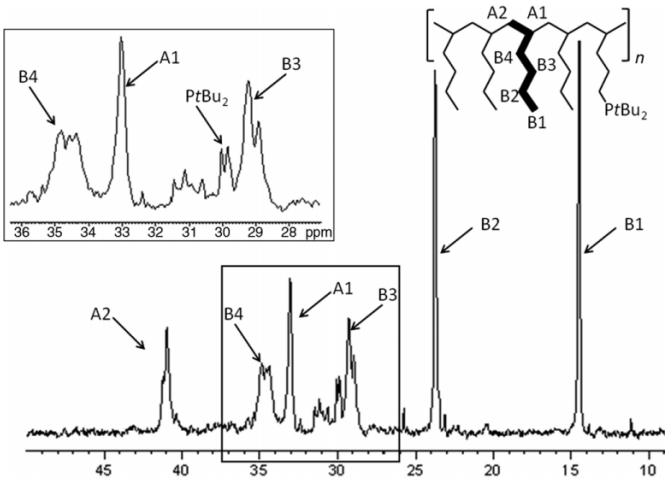
Initial attempts to effect the homopolymerizations of the phosphine-functionalized monomer were unsuccessful as no polymer was formed. However, copolymerization using 1, 5, and 10 mol% of (**1**) with 1-hexene did yield isolable polymeric products. In the cases where 5 and 10 mol% of the phosphine-functionalized monomer were used (Table 1), this resulted in a marked suppression of yield and molecular mass of the resulting polymers. The PDI of these polymers were typical of the single-site phosphinimide catalyst[12] used, ranging between 1.0 and 4.2. The degree of comonomer incorporation was determined by analysis of the $^{13}C\{^1H\}$ NMR spectra of the polymers. Specifically, the ratio of the integrals of signal attributable to the terminal methyl group of the hexyl residue was compared with that ascribed to the *tert*-butyl fragment (Fig. 1). The level of comonomer incorporation ranges between 3% and 5% with use of 5–10 mol% of comonomer **1**. While these values vary

Table 1. Copolymerizations of 1-hexene and **1**–**2** using the catalyst precursor $CpMe_2Ti(NPt\text{-}Bu_3)$.

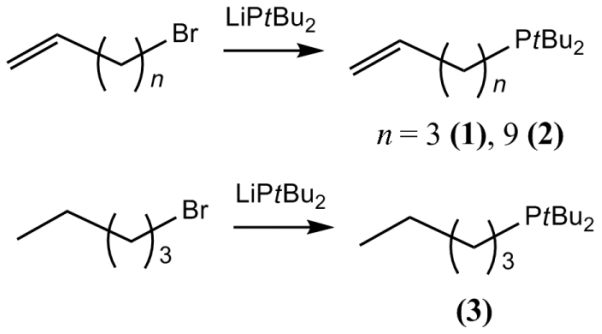
% 1-Hexene	Co-monomer	Catalyst (mmol)	Activator	Time (h)	Temperature (°C)	Yield (%)	MM (M_n)	PDI	% Incorporation
100		0.16	$B(C_6F_5)_3$	16	0	94	7980	1.28	
100		0.04	$B(C_6F_5)_3$	5	30	98	3230	1.82	
99	**1**	0.16	$B(C_6F_5)_3$	16	0	93	7740	1.37	n/a
95	**1**	0.16	$B(C_6F_5)_3$	16	0	21	1140	1.02	4
95	**1**	0.04	$B(C_6F_5)_3$	5	30	23	1065	3.18	3
95	**1**	0.04	$[Ph_3C][B(C_6F_5)_4]$	5	30	19	1125	3.65	4
95	**1**	0.04	$[Me_2PhNH][B(C_6F_5)_4]$	5	30	18	916	4.21	4
95	**1**	0.04	$B(C_6F_5)_3$	5	30	59	1480	3.30	3
90	**1**	0.16	$B(C_6F_5)_3$	16	0	21	2650	1.40	5
90	**1**	0.04	$B(C_6F_5)_3$	5	30	44	1590	n/a	4
90	**2**	0.04	$B(C_6F_5)_3$	5	30	51	n/a[a]		9
75	**1**	0.04	$B(C_6F_5)_3$	5	30	36	1800	2.91	n/a

[a]n/a: Not applicable.

Fig. 1. ^{13}C NMR spectrum of copolymer of 1-hexene–(**1**).



Scheme 1. Synthesis of **1**–**3**.

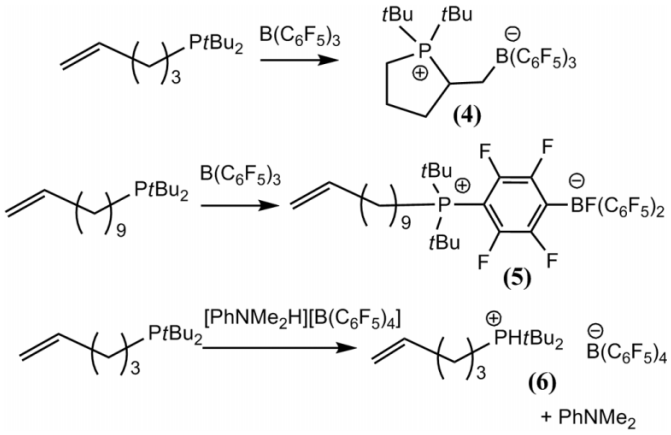


slightly with co-catalyst used, in general the level of incorporation of comonomer into the polymer increase with increased comonomer concentration. Use of 5 mol% comonomer results in less than 5 mol% incorporation, reflecting the differing steric demands of comonomer and hexene. In the case where 10 mol% of **2** is employed, incorporation rises to 9%, reflecting the decreased steric influence of the P*t*-Bu_2 fragment with the increase chain length in **2**. This result is consistent with observations made for N- and O-containing functional monomers where longer spacers between the heteroatom and the olefinic fragment were used.[18]

Competitive reactions

The reduced catalyst activity observed in the presence of the phosphine-olefin comonomers could be attributed to competitive and independent interactions of these species with the activators. For example, the independent reaction of **1** with $B(C_6F_5)_3$ has been previously reported to effect addition of P and B to the olefinic fragment to give the cyclic phosphonium borate *t*-$Bu_2P((CH_2)_4CHCH_2B(C_6F_5)_3$ (**4**). This yields a cyclic phosphonium borate (Scheme 2). In contrast, as a result of the longer chain in **2**, it is unlikely to undergo such cyclization. However, reaction of $B(C_6F_5)_3$ with **2** does proceed to give a new species **5** in 50% isolated yield. This species exhibits a $^{31}P\{^1H\}$ NMR signal at 54.98 ppm. Perhaps most diagnostic, however, is the ^{19}F NMR data. Here signals at –119.8, –125.24, –125.82, and –130.1 ppm are

Scheme 2. Reactions of olefinic phosphines with activators.



consistent with the presence of a C_6F_4 fragment in addition to signals attributable to C_6F_5 rings. As well, the signal at –190.87 ppm is attributable to a B–F residue. These data together with the ^1H and ^{13}C data confirm the formulation of **5** as *t*-$Bu_2P((CH_2)_9CH{=}CH_2)C_6F_4BF(C_6F_5)_2$ (Scheme 2). This species forms by para-attack on a C_6F_5 ring by the sterically encumbered P center. We have previously documented such reactivity of bulky phosphines with $B(C_6F_5)_3$.[19,20]

Such reactions of comonomer with the activator could compete with the precatalyst and thus account for the lesser activity observed. Similarly, in the case of the activator $[Ph_3C][B(C_6F_5)_4]$, interactions of phosphines are known to form traditional acid–base adducts affording the corresponding phosphonium salts. Alternatively, bulky phosphines are also known to effect nucleophilic aromatic substitution of a ring of $[Ph_3C]^+$ yielding cations of the form $[R_3PC_6H_4CH(C_6H_5)_2]^+$.[21] In the case of the activator $[Me_2PhNH]$ $[B(C_6F_5)_4]$, it is operative via protonation of the Ti–Me fragment. Clearly, the basicity of the phosphine centers in **1** or **2** could compete for this proton, affording the corresponding phosphonium salt. Indeed, independent reaction of **1** with $[Me_2PhNH][B(C_6F_5)_4]$ generated [*t*-$Bu_2P(H)((CH_2)_3CH{=}CH_2)][B(C_6F_5)_4]$ (**6**) (Scheme 2) and free amine Me_2PhN as evidenced by the NMR data, and in particular, the ^{31}P NMR signal at 52.5 ppm which exhibits P–H coupling of 438 Hz. Such phosphonium salts have been shown ineffective activators. Thus, such competitive side reactions could also slow catalyst generation.

The yields of polymerizations conducted in the presence of **1** or **3** were also compared. The yield of polymer generated, under otherwise identical conditions was significantly reduced when **1** was employed. This suggests the possibility that an intramolecular interaction of inserted comonomer could inhibit catalyst activity. This proposition is consistent with observations made by Waymouth and co-workers,[18] where the aminopentene, *i*$Pr_2N(CH_2)_3CHCH_2$, was found to be a more potent inhibitor than the amine, *i*$Pr_2N(CH_2)_4CH_3$, which lacks an olefinic group.[18] Nonetheless, the yield was also seen to decrease with increasing concentration of **3**, albeit to a lesser extent, suggesting that intermolecular coordination of the phosphine to the Ti cation could also diminish polymerization to some extent.

Conclusions

Copolymerization of 1-hexene and phosphine functionalized monomers is possible, although the catalyst activity is diminished. The cause of this diminished reactivity could be competitive reactions of the comonomer with the activator or the Ti catalyst. This issue can be mitigated to some extent by increasing the separation of the functional group from the double bond. Presumably, increased steric bulk at the heteroatom and decreased nucleophilicity would also facilitate comonomer incorporation.

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