# Sterically hindered phosphine and phosphonium-based activators and additives for olefin polymerization

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The ability of phosphonium borates of the form $[R_3PH][B(C_6F_5)_4]$, $R_2PHC_6F_4BF(C_6F_5)_2$ and $R_2PHC_4H_8OB(C_6F_5)_3$ as well as the phosphine-boranes $R_2PC_6F_4B(C_6F_5)_2$ to activate $CpTiMe_2(NPtBu_3)$ for olefin polymerization was examined *via* both stoichiometric reactions and catalytic performance. In general these activators resulted in highly active ethylene polymerization catalysts, despite the generation of liberated phosphine donors. Independent experiments in which phosphines were added to the catalyst systems revealed the expected decrease in activity for small phosphines. However in the case of sterically encumbered phosphines, a marked increase in activity was observed. The cause of this increase is considered in the context of the concept of "frustrated Lewis pairs".

## Introduction

Over the last 25 years a great deal of research has focused on the development of homogeneous catalysts for olefin polymerization.[1-6] In these efforts, the primary focus has been on the nature of the metal complex. Thus ligand design has played a principal role in many investigations.[1-6] Indeed, over the last 10 years, we employed this approach to develop active olefin polymerization catalysts based on Ti-phosphinimide complexes.[7-10] A primary example of these systems is the species $(tBu_3PN)_2TiMe_2$ which upon activation is remarkably active under commercially relevant conditions.[9] Typically the activation strategy for olefin polymerization catalysts has been the use of large excesses of methylaluminoxane (MAO). In combination with a metal dihalide species, this reagent acts as both an alkylating and alkyl abstraction reagent to generate cationic metal alkyl species which are catalytically active. Alternatively, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ or $[HNRR'_2][B(C_6F_5)_4]$ have been commonly employed to react with metal-dialkyl derivatives to effect alkyl abstraction. While in general the nature of the cocatalyst has drawn lesser attention than the metal-precursors, the research groups of Marks,[11-19] Piers[20-29] and others[30-34] have developed a variety of Al and B-based cocatalysts and probed the impact of size and charge distribution of the anion on catalyst activity.

In what is seemingly unrelated chemistry, we have recently reviewed a series of reactions of bulky phosphines with $B(C_6F_5)_3$.[35-39] Such "frustrated Lewis pairs" (FLPs) offer unique synthetic routes to a number of phosphonium borates[40-42] and phosphine-boranes[41] that could serve as activators for olefin polymerization catalysts. For example, phosphonium borate salts of the form $[R_3PH][B(C_6F_5)_4]$ R = Cy **1**, Mes[43] **2**, *t*Bu[44] **3**) are readily prepared. Alternatively, heating bulky secondary phosphines with $B(C_6F_5)_3$ results in the substitution of P for F at the *para*-position of one of the $C_6F_5$ rings affording zwitterionic species of the form $R_2PHC_6F_4BF(C_6F_5)_2$ ($R_2$ = $Cy_2$ **4**, $Mes_2$ **5**, *t*Bu(Mes) **6**, $tBu_2$ **7**, Fig. 1(a)). Similarly, the species $Mes_2PHC_6F_4BCl(C_6F_5)_2$ **8**,[45] $Cy_3PC_6F_4BF(C_6F_5)_2$ **9**, subsequent treatment of which with a Grignard reagent affords the corresponding phosphine-boranes, $R_2PC_6F_4B(C_6F_5)_2$ ($R_2$ = $Mes_2$ **10**, *t*Bu(Mes) **11**, $tBu_2$ **12**). Alternatively, an alternative avenue to phosphonium borates, involves the reactions of sterically encumbered phosphines with $(THF)B(C_6F_5)_3$ giving the zwitterions $R_2PHC_4H_8OB(C_6F_5)_3$(R = Mes **13**, *t*Bu **14**). (Fig. 1(b)). These phosphonium borates are of potential interest as activators as these species are expected to activate dialkyl-titanium catalysts *via* protonation of an alkyl group, affording the titanium cation and generating free phosphine. This behavior closely parallels that of ammonium cations $[R_3NH]^+$.[46] However in some cases liberated amine from ammonium-based

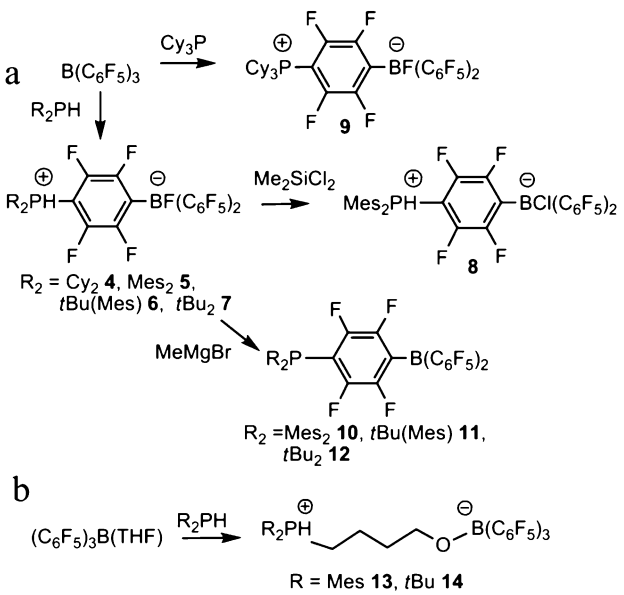


**Fig. 1** Preparative routes to phosphonium-borates and phosphine-boranes.

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activators has been shown to coordinate to the metal cation supressing activity to some extent.[46] While small phosphines have been shown to sequester the Ti cation as $[CpTiMe(NPtBu_3)(PR_3)]^+$ (R = Me, Bu, Ph, $C_6H_4Me$) (Fig. 2),[47] the present phosphonium-borates will liberate sterically encumbered phosphines. Such donors have been shown not to coordinate to main group Lewis acids, affording uniquely reactive FLPs. In this manuscript we explore the viability of these phosphonium borate and phosphine-borane species for use as activators. The impact on the activity of the resulting catalysts is examined.

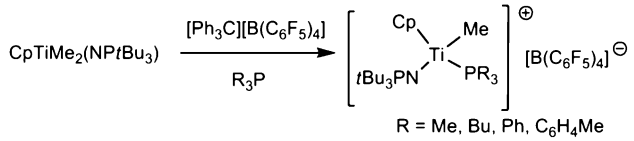


**Fig. 2** Complexation of $[CpTiMe(NPtBu_3)]^+$ by small phosphines.

## Experimental

### 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 glove box. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under $N_2$. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers. Deuterated benzene, toluene and methylene-chloride were purchased from Cambridge Isotopes Laboratories, vacuum distilled from the appropriate drying agents and freeze–pump–thaw degassed (3 times). Trace amounts of protonated solvents were used as references, and $^1H$ and $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and $^{19}F$ NMR spectra were referenced to external 85% $H_3PO_4$, $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively. NMR data were acquired at 300 K unless otherwise noted. Ethylene was purchased from BOC gases and was degassed and dried over Q5 copper deoxygenation material and 3 Å molecular sieves. MeOH was purchased from Aldrich Chemical Co. HCl was purchased from EM Science; all were used as received. $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ and $AliBu_3$ (TiBAl) were generously donated by Nova Chemicals Corp. and were used without further purification. $CpTiMe_2(NPtBu_3)$,[7] $[R_3PH][B(C_6F_5)_4]$ (R = Cy **1**, Mes[43] **2**, *t*Bu[44] **3**), $R_2PHC_6F_4BF(C_6F_5)_2$ (R = Cy **4**, Mes **5**, *t*Bu **7**; $R_2$ = *t*BuMes **6**), $Mes_2PHC_6F_4BCl(C_6F_5)_2$ **8**,[45] $Cy_3PC_6F_4BF(C_6F_5)_2$ **9**, $R_2PC_6F_4B(C_6F_5)_2$ (R = Cy **10**, *t*Bu **12**; $R_2$ = *t*BuMes **11**) and $R_2PHC_4H_8OB(C_6F_5)_3$ (R = Mes **13**, *t*Bu **14**) were prepared as previously reported.[35,36,40-42]

### Generation of $[CpTiMe(NPtBu_3)][B(C_6F_5)_4]$ 15

This species was generated using varying activators and thus only one preparation is detailed. To an orange solution of $[Cy_3PH][B(C_6F_5)_4]$ (0.057 g, 0.059 mmol) in $C_6D_5Br$ (0.4 mL) was added dropwise a solution of $CpTiMe_2(NPtBu_3)$ (0.021 g, 0.058 mmol) in $C_6D_5Br$ (0.3 mL). The solution was stirred for 5 min. Quantitative product formation was observed by NMR spectroscopy. **15**: $^1H$ NMR ($C_6D_5Br$): 7.18–7.09 (m, 15 H, PhCMe), 6.09 (s, 5H, Cp), 2.07 (s, 3H, PhCMe), 1.18 (d of d, $^3J_{HP}$ = 14 Hz, 30 Hz, *t*Bu, TiMe). $^{11}B$ NMR ($C_6D_5Br$): −16.7 (s). $^{13}C$ NMR ($C_6D_5Br$): 149.07 (s, quat, Ph), 148.66 (d, $^1J_{CF}$ = 236 Hz, CF), 138.44 (d, $^1J_{CF}$ = 245 Hz, CF), 136.56 (d, $^1J_{CF}$ = 242 Hz, CF), 128.81 (s, CH, Ph), 127.96 (s, CH, Ph), 136.03 (s, CH, Ph), 116.10 (s, Cp), 61.29 (s, TiMe), 52.53 (s, quat, $Ph_3CMe$), 41.19 (d, $^1J_{CP}$ = 41 Hz, quat, $tBu_3$), 30.51 (s, $Ph_3CMe$), 28.93 (s, *t*Bu) $^{19}F$ NMR ($C_6D_5Br$): −132.29 (s, 8F, *o*-$C_6F_5$), −162.67 (t, 4F, $^3J_{FF}$ = 20 Hz, *p*-$C_6F_5$), −166.47 (t, 8F, $^3J_{FF}$ = 17 Hz, *m*-$C_6F_5$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$): 55.9 (s).

### Generation of $[CpTiMe(NPtBu_3)][R_2P(C_6F_4)BMe(C_6F_5)_2]$ (R = Mes 16, *t*Bu 17)

These compounds were prepared in a fashion similar to that described for **15** employing the appropriate activator. **16**: Yield 115 mg (78%). $^1H$ NMR ($C_6D_5Br$): 6.71 (s, 4H, $C_6H_2$), 6.12 (s, 5H, Cp), 2.32 (s, 12H, $C_6H_2Me$-2,6), 2.16 (s, 6H, $C_6H_2Me$-4), 1.18 (s, 3H, BMe), 1.14 (br s, 27H, *t*Bu), 0.85 (s, 3H, TiMe). $^{11}B$ NMR ($C_6D_5Br$): −14.6 (br s). $^{13}C\{^1H\}$ NMR ($C_6D_5Br$) partial: 148.54 (dm, $^1J_{CF}$ = 250 Hz, CF), 147.15 (dm, $^1J_{CF}$ = 250 Hz, CF), 142.61 (d, $^2J_{CP}$ = 12 Hz, quat, Mes), 138.02 (s, quat, Mes), 137.76 (dm, $^1J_{CF}$ = 245 Hz, CF), 136.67 (dm, $^1J_{CF}$ = 240 Hz, CF), 130.13 (s, CH, Mes), 114.13 (s, Cp), 52.80 (br s, TiMe), 41.24 (br, *t*Bu), 28.71 (br, *t*Bu), 22.64 (d, $^3J_{CP}$ = 18 Hz, $C_6H_2Me$-2,6), 20.92 (s, $C_6H_2Me$-4), 10.50 (br s, BMe). $^{19}F$ NMR ($C_6D_5Br$): −132.24 (br, 6F, *o*-$C_6F_5$, $C_6F_4$), −135.37 (br, 2F, $C_6F_4$), −164.08 (br, 2F, *p*-$C_6F_5$), −166.47 (br, 4F, *m*-$C_6F_5$). $^{19}F$ NMR ($C_6D_5Br$, 243K): −132.57 (m, 5F, *o*-$C_6F_5$, $C_6F_4$), −133.52 (s, 1F, $C_6F_4$), −133.73 (s, 1F, $C_6F_4$), −136.10 (s, 1F, $C_6F_4$), −164.06 (m, 2F, *p*-$C_6F_5$), −166.66 (m, 4F, *m*-$C_6F_5$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$): 50.6 (br, P*t*Bu$_3$), −50.3 (br, $PMes_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$, 243K): 49.0 (br, P*t*Bu$_3$), −52.0 (t, $^3J_{PF}$ = 37 Hz, $PMes_2$).

### 17

Yield 115 mg (92%). $^1H$ NMR ($C_6D_5Br$): 6.12 (s, 5H, Cp), 1.23 (d, 18H, $^3J_{HP}$ = 13 Hz, P*t*Bu$_2$), 1.12 (s, 3H, BMe), 1.12 (d, 27H, $^3J_{HP}$ = 14 Hz, P*t*Bu$_3$), 0.85 (s, 3H, TiMe). $^{11}B$ NMR ($C_6D_5Br$): −14.5 (br s). $^{13}C\{^1H\}$ NMR ($C_6D_5Br$): 148.78 (dm, $^1J_{CF}$ = 250 Hz, CF), 138.46 (dm, $^1J_{CF}$ = 250 Hz, CF), 137.61 (dm, $^1J_{C\text{-}F}$ = 245 Hz, CF), 114.19 (s, Cp), 53.04 (s, TiMe), 41.14 (d, $^1J_{CP}$ = 42 Hz, P*t*Bu$_3$), 32.61 (d, $^1J_{CP}$ = 27 Hz, P*t*Bu$_2$), 30.46 (d, $^2J_{CP}$ = 14 Hz, P*t*Bu$_2$), 29.19 (s, P*t*Bu$_3$), 11.20 (s, BMe). $^{19}F$ NMR ($C_6D_5Br$): −124.58 (br, 1F, $C_6F_4$), −131.09 (br, 1F, $C_6F_4$), −132.38 (br, 4F, *o*-$C_6F_5$), −132.76 (br, 2F, $C_6F_4$), −160.99 (br, 2F, *p*-$C_6F_5$), −166.06 (br, 4F, *m*-$C_6F_5$). $^{19}F$ NMR ($C_6D_5Br$, 243K): −123.66 (s, 1F, $C_6F_4$), −132.20 (m, 4F, *o*-$C_6F_5$), −132.60 (m, 1F, $C_6F_4$), −133.13 (m, 1F, $C_6F_4$), −133.56 (m, 1F, $C_6F_4$), −160.76 (br, 2F, *p*-$C_6F_5$), −164.26 (m, 4F, *m*-$C_6F_5$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$): 50.8 (P*t*Bu$_3$), 21.2 (br d, $^3J_{PF}$ = 90 Hz, P*t*Bu$_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$, 243K): 50.1 (P*t*Bu$_3$), 17.6 (d, $^3J_{PF}$ = 95 Hz, P*t*Bu$_2$).

### Generation of $[CpTiMe(THF)(NPtBu_3)][R_2P(C_6F_4)BMe(C_6F_5)_2]$ (R = Mes 18, *t*Bu 19)

The species **16** or **17** were dissolved in THF (5 mL) at 25 °C, filtered and characterized by NMR spectroscopy. The solution was stirred for 5 min, the volatiles removed *in vacuo*, and the residue redissolved for NMR characterization. **18**: $^1H$ NMR ($C_6D_5Br$):

 

6.69 (s, 4H, $C_6H_2$), 6.09 (s, 5H, Cp), 3.61 (br s, 4H, THF), 2.25 (s, 12H, $C_6H_2$Me-2,6), 2.16 (s, 6H, $C_6H_2$Me-4), 1.59 (br s, 4H, THF), 1.22 (s, BMe), 1.11 (d, $^3J_{HP} = 14$ Hz, *t*Bu), 0.88 (s, TiMe). $^{11}$B NMR ($C_6D_5Br$): −14.9 (br s). $^{13}C\{^1H\}$ NMR ($C_6D_5Br$): 149.28 (dm, $^1J_{CF}$ = 240 Hz, CF), 148.80 (dm, $^1J_{CF}$ = 240 Hz, CF), 147.22 (dm, $^1J_{CF}$ = 245 Hz, CF), 142.71 (d, $^2J_{CP}$ = 16 Hz, quat, Mes), 137.90 (s, quat, Mes), 137.32 (dm, $^1J_{CF}$ = 245 Hz, CF), 136.68 (dm, $^1J_{CF}$ = 250 Hz, CF), 130.21 (s, CH Mes), 114.17 (s, Cp), 112.86 (d, $^1J_{CP} = 70$ Hz, quat, Mes), 76.11 (br s, THF), 52.19 (s, TiMe), 40.96 (d, $^1J_{CP} = 41$ Hz, *t*Bu), 28.97 (s, tBu), 22.88 (s, THF), 22.78 (d, $^3J_{CP} = 16$ Hz, $C_6H_2$Me-2,6), 21.08 (s, $C_6H_2$Me-4), 10.86 (br s, BMe). $^{19}$F NMR ($C_6D_5Br$): −131.31 (d, $^3J_{FF} = 24$ Hz, 4F, *o*-$C_6F_5$), −131.60 (m, 2F, $C_6F_4$), −134.86 (m, 2F, $C_6F_4$), −163.62 (m, 2F, *p*-$C_6F_5$), −166.15 (m, 4F, *m*-$C_6F_5$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$): 51.1 (P*t*Bu$_3$), −50.0 (t, $^3J_{PF} = 37$ Hz, $PMes_2$).

**19**

$^1$H NMR ($C_6D_5Br$): 6.09 (s, 5H, Cp), 3.64 (br s, 4H, THF), 1.63 (br s, 4H, THF), 1.23 (d, 18H, $^3J_{HP} = 12$ Hz, P*t*Bu$_2$), 1.21 (s, 3H, BMe), 1.15 (d, 27H, $^3J_{HP} = 14$ Hz, P*t*Bu$_3$), 0.93 (s, 3H, TiMe). $^{11}$B NMR ($C_6D_5Br$): −15.0 (br s). $^{13}C\{^1H\}$ NMR ($C_6D_5Br$): 149.13 (dm, $^1J_{CF}$ = 250 Hz, CF), 137.57 (dm, $^1J_{CF}$ = 245 Hz, CF), 137.61 (dm, $^1J_{CF}$ = 250 Hz, CF), 113.28 (s, Cp), 68.40 (s, THF), 52.25 (s, TiMe), 41.19 (d, $^1J_{CP} = 44$ Hz, P*t*Bu$_3$), 32.53 (d, $^1J_{CP} = 28$ Hz, P*t*Bu$_2$), 29.37 (d, $^2J_{CP} = 16$ Hz, P*t*Bu$_2$), 29.01 (s, P*t*Bu$_3$), 10.83 (s, BMe). $^{19}$F NMR ($C_6D_5Br$): −124.97 (m, 1F, $C_6F_4$), −131.89 (m, 1F, $C_6F_4$), −132.03 (d, 4F, $^3J_{FF} = 22$ Hz, *o*-$C_6F_5$), −132.22 (s, 1F, $C_6F_4$), −132.43 (dd, 1F, $^3J_{FP} = 113$ Hz, $^3J_{FF} = 23$ Hz, $C_6F_4$), −160.99 (t, 2F, $^3J_{FF} = 23$ Hz, *p*-$C_6F_5$), −166.06 (t, 4F, $^3J_{FF} = 24$ Hz, *m*-$C_6F_5$). $^{31}P\{^1H\}$ NMR ($C_6D_5Br$): 50.9 (P*t*Bu$_3$), 19.6 (dd, $^3J_{PF} = 120$ Hz, $^3J_{PF} = 20$ Hz P*t*Bu$_2$).

### Polymerization protocol

For comparable results, routine standards were run regularly to ensure reproducibility. The polymerizations were performed in a 1 L Buchi reactor system. All polymerizations were performed in duplicate to ensure reproducibility. The average activities of at least duplicate runs are reported. Following assembly, the reactor vessel and solvent storage unit were refilled with nitrogen *via* 4 refill/evacuation cycles over at least 90 min. Approximately 600 mL of toluene was transferred to the solvent storage container from the purification column. The solvent was purged with dry nitrogen for 20 min and then transferred to the reactor vessel by differential pressure. The solvent was stirred at 1500 ± 5 rpm and the temperature was kept constant at 30 ± 2 °C. The system was then exposed to ethylene *via* five vent/refill cycles. The pre-catalyst,[48] cocatalysts[40-42] and scrubber stock solutions were freshly prepared as previously reported and loaded into syringes in a glove box, then transferred to the reactor immediately before injection to limit the possibility of catalyst decomposition.

### Sample injection sequence procedure

The sequence was the same for all polymerizations with the appropriate substitution of the activator; thus only one example is detailed. A prepared solution of triisobutylaluminium (TiBAl) (3.0 mL) was injected into the reaction vessel through the catalyst injection inlet and allowed to stir for 5 min. The prepared CpTiMe$_2$(NP*t*Bu$_3$) solution (1.0 mL) was injected followed immediately with the injection of the B($C_6F_5$)$_3$ solution (1.5 mL) into the reactor vessel. The mixture was stirred at 1500 ± 5 rpm at 30 °C under 2 atm of dynamic ethylene flow for 10 min. The temperature and ethylene flow rate were recorded manually at regular intervals. After 10 min, the polymerization was stopped by closing the ethylene inlet valve and venting the reactor, the stirring was stopped, and the reactor was disassembled. The contents of the reactor were emptied into a 4 L beaker containing approximately 100 mL of 10% HCl (v/v) in MeOH. The precipitated polymer was collected by filtration, washed with toluene and acetone, and dried under vacuum overnight at 25 °C. The resulting polymer was weighed and polymerization activity calculated.

### Molecular modeling calculations[49]

Energy minimization calculations were performed by employing the MMX and MM2 options of the Cache Software system. Initial coordinates and geometric parameters were taken from X-ray data.

## Results and discussion

It is well established that early metal alkyl cations which act as polymerization catalysts can be generated by protonolysis of a methyl group from a dialkyl-catalyst precursor.[1-6,19] In probing the viability of the phosphonium-borates [$R_3$PH][B($C_6F_5$)$_4$] (R = Cy **1**, Mes **2**, *t*Bu **3**) and $R_2$PH$C_6F_4$B$F$($C_6F_5$)$_2$ (R = Cy **4**, Mes **5**, *t*Bu **7**; $R_2$ = *t*BuMes **6**) to effect protonolysis to generate such a polymerization catalyst, 1:1 stoichiometric combinations of these species and CpTiMe$_2$(NP*t*Bu$_3$) were monitored by NMR spectroscopy. In the case of **1**/CpTiMe$_2$(NP*t*Bu$_3$) or **2**/CpTiMe$_2$(NP*t*Bu$_3$), gas evolution was apparent upon mixing, while $^{31}$P NMR data revealed complete generation of the free phosphine as evidenced by the signals at 11.1 and 35.5 ppm for $Cy_3$P and $Mes_3$P, respectively.$^{31}$P and $^1$H NMR spectroscopy were consistent with the generation of the species, [CpTiMe(NP*t*Bu$_3$)][B($C_6F_5$)$_4$] **15**.[7] The inability of the liberated sterically bulky phosphines to coordinate to the Ti-cations is noteworthy and is considered (*vide infra*). Although the species **15** was previously reported to be unstable,[7] it proved to be stable in bromobenzene, permitting spectroscopic characterization. Not surprisingly, attempts to isolate this species were unsuccessful as a result of the extreme air and moisture sensitivity of this coordinatively unsaturated cation. Similar sensitivities of related cations have been previously noted.[7,9,10,47]

The analogous experiment employing **3**/CpTiMe$_2$(NP*t*Bu$_3$) showed $^{31}$P NMR signals attributable to 1:1 ratio of *t*Bu$_3$P and [*t*Bu$_3$PH]$^+$, as well as resonance attributable to the phosphinimide ligand in the previously reported methyl-bridged dimer, [{Cp(NP*t*Bu$_3$)TiMe}$_2$(μ-Me)][B($C_6F_5$)$_4$] (Fig. 3).[47] These data suggest that **3** is less efficient at activation, allowing CpTiMe$_2$(NP*t*Bu$_3$) to intercept the generated cation. This is attributed to the greater basicity of the phosphine.

In a similar fashion, the stoichiometric reaction of CpTiMe$_2$(NP*t*Bu$_3$) with the phosphonium-fluoroborate **5** was monitored by NMR spectroscopy. This reaction gave rise to a complex mixture of products. However, NMR data suggested incomplete deprotonation of the PH moiety, as well as some B–F for B–Me exchange. In related experiments, combination

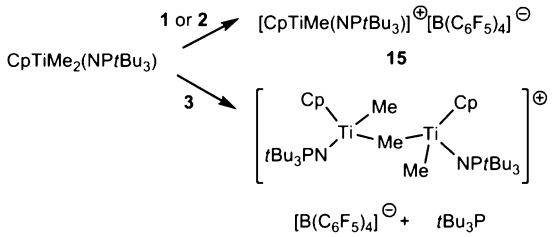


**Fig. 3** Activation of $CpTiMe_2(NPtBu_3)$ by phosphonium borates **1–3**.

of the $Cy_3PC_6F_4BF(C_6F_5)_2$ **9** and $CpTiMe_2(NPtBu_3)$ showed no reaction whereas addition of **9** to independently generated $[CpTiMe(NPtBu_3)][B(C_6F_5)_4]$ showed evidence of immediate B–F/Me exchange. This confirms that such exchange requires the presence of the highly Lewis acidic Ti-cation. It is noteworthy that this reactivity does not preclude the use of these phosphonium-fluoroborate as activators. Marks and coworkers[50-51] have recently reported the use of $[Ph_3C][FM(C_6F_5)_3]$, where M = B and Al, as co-catalysts for olefin polymerization, despite the formation of species containing bridging Zr–F–Zr fragments in stoichiometric reactions of these activators with $Me_2C(Cp)(Flu)ZrMe_2$ in the absence of olefin.

An alternative strategy to activate dialkyl-catalyst precursors is methyl abstraction. Thus the stoichiometric reactivity of the phosphine-boranes of the form $R_2PC_6F_4B(C_6F_5)_2$ were also probed. In the case of the reactions of **10** (R = Mes) and **12** (R = *t*Bu) with $CpTiMe_2(NPtBu_3)$, clean formation of the salts $[CpTiMe(NPtBu_3)][R_2P(C_6F_4)BMe(C_6F_5)_2]$ (R = Mes **16**, *t*Bu **17**) was observed. For compound **17**, the $^1H$ NMR showed signals at 1.22 and 0.88 ppm, corresponding to the B–Me and Ti–Me groups, respectively. The assignment of these resonances was confirmed by $^1H$–$^{13}C$ HSQC experiments which correlated the $^1H$ NMR signals of the B–Me and Ti–Me groups to $^{13}C$ NMR resonances at 10.7 and 50.4, respectively. A $^1H$–$^1H$ EXSY experiment showed these methyl groups do not exchange. The $^{31}P$ NMR spectrum of **17** showed a slight broadening of the doublet at 21.2 ppm (P–F coupling) attributed to the P of the phosphine-borate. Upon addition of excess THF to the above reaction mixtures the species $[CpTiMe(THF)(NPtBu_3)]$ $[R_2P(C_6F_4)BMe(C_6F_5)_2]$ (R = Mes **18**, *t*Bu **19**) are immediately formed (Fig. 4). The $^{31}P$ NMR peaks sharpen and are better resolved. For example, the $^{31}P$ resonance for the anion of **19** was resolved to a doublet of doublets, characteristic of the independently generated anionic phosphino-borate where coupling to the *o*-fluorines of the $C_6F_4$ bridge is observed. These results suggest that no significant interaction between the Ti center in **17** and the P on the borate anion.

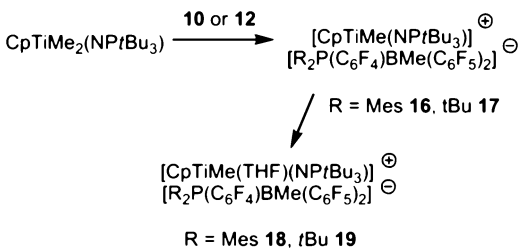


**Fig. 4** Activation of $CpTiMe_2(NPtBu_3)$ by phosphine-boranes **10**, **12**.

The above series of phosphonium borates and phosphine-boranes were also employed as coacatalysts to activate

**Table 1** Ethylene polymerization activity with varying activators[a]

| Activator | Activity | Activator | Activity |
|---|---|---|---|
| $B(C_6F_5)_3$ | 8800 | **6** | 5000 |
| $[Ph_3C][B(C_6F_5)_4]$ | 7500 | **7** | 2900 |
| $[Me_2PhNH][B(C_6F_5)_4]$ | 3000 | **8** | 600 |
| **1** | 6600 | **10** | 4800 |
| **2** | 6000 | **11** | 9200 |
| **3** | 330 | **12** | 17900 |
| **4** | 4500 | **13** | 14500 |
| **5** | 11600 | **14** | 100 |

[a] Polymerizations were performed using the catalyst/cocatalyst combination $CpTiMe_2(NPtBu_3)/B(C_6F_5)_3$ in 600 mL toluene (5 μmol/L), 30 °C, 20 equiv $iBu_3Al$, 1 equiv $B(C_6F_5)_3$, 2 atm $C_2H_4$, 10 min. Activity given in g PE/mmol/h/atm.

$CpMe_2Ti(NPtBu_3)$ to effect ethylene polymerization. These polymerizations were performed at 30 °C for 10 min using a catalyst concentration of 5 μmol/L in approximately 600 mL of toluene and an ethylene pressure of 2 atm. TiBAL (20 equiv) was used as a scavenger. The ratio of Ti:activator used was 1:1 unless otherwise noted. For a given activator the polymerization were performed in at least duplicate to ensure reproducibility within ±10% of the reported activity. Standard runs employing $CpTiMe_2(NPtBu_3)/B(C_6F_5)_3$ were performed regularly to ensure systematic and procedural reproducibility. It has been previously documented that activation of this catalyst as described herein, results in a single-site polymerization producing linear high molecular weight polyethylene with PDIs ranging from 1.2–2.6.[7-10] To ensure valid and reproducible activities, polymerizations were performed for 10 min. These conditions are known to result in high molecular weight PE (> 1,300,000 g/mol).[7-10] Indeed, attempts to obtain GPC data for the polymers from the present polymerizations were unsuccessful due to solubility and instrumental limitations. Nonetheless, the activity data provide a basis for comparison of the cocatalyst efficacy.

Initially, the phosphonium borates **1–3** were employed as activators in reaction with $CpTiMe_2(NPtBu_3)$ (Table 1). In the case of **1** and **2**, the activities observed were slightly less than that seen when $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ were used. Nonetheless, **1** and **2** gave rise to significantly higher activity than that derived from $[Me_2PhNH][B(C_6F_5)_4]$, inferring that the bulky phosphonium salts were protic enough to effect Ti–C bond cleavage and that the liberated phosphines were bulky enough to deter coordination to Ti.

In contrast, the catalyst generated using **3** as the co-catalyst gave rise to much lower activity. Considering that the liberated phosphine, $tBu_3P$, has a cone angle of 182°, which is between those of $Cy_3P$ (170°) and $Mes_3P$ (212°),[52] it seems unlikely that $tBu_3P$ coordinates to the Ti cation. Instead, a far more likely explanation is that **3** is less effective at protonation of a Ti–C bond as a result of the significantly lower acidity of the PH moiety.[53] This observation is consistent with the stoichiometric reactivity described above.

Similar trends were observed employing phosphonium-borates that incorporate a $C_6F_4$ linker between B and P; $R_2PHC_6F_4BX(C_6F_5)_2$ (X = F; R = Cy **4**, Mes **5**, *t*BuMes **6**, *t*Bu **7**, X = Cl, R = Mes **8**). The activator **5** gave rise to the highest activity while **7** like **3**, resulted in a much less active catalyst. Comparing **2** and **5**, the greater activity resulting from **5** can be ascribed to the increase in PH acidity as a result of the presence of the

 

electron-withdrawing $C_6F_4$ fragment. Indeed generally, it appears that the activity increases with the acidity of the PH moiety, consistent with the importance of efficient cation generation in the determination of activity. It is also noteworthy that the inclusion of B–F bonds in **4–7** does not have a deleterious effect on the catalyst activity, despite the complex reactivity observed in stoichiometric reactions. In these cases, clearly the Ti cation reacts much faster with ethylene than B–F affording an active polymerization catalyst. In contrast, incorporation of B–Cl in **9** results in a significant decrease in catalyst turnover. Presumably in the latter case the Ti cation can be deactivated by capture of chloride. This view is also consistent with the greater bond strength of B–F *versus* B–Cl.

The phosphonium alkoxy-borates $Mes_2PHC_4H_8OB(C_6F_5)_3$ **13** $tBu_2PHC_4H_8OB(C_6F_5)_3$ **14** were also evaluated as activators. The species **13** was highly effective while the latter species proved to be a very poor activator. Although the reduced acidity of the PH moiety in **14** may also account for ineffective activation, the high activity derived from use of **13** reflects the improved solubility of the resulting anion in hydrocarbon solvent. Moreover, the activity derived from **13** supports the view that the B–O bond are resistant to abstraction by the Ti cation, at least under the conditions employed herein. In related systems, alcohol adducts of $B(C_6F_5)_3$ have been employed as Brønsted acids and shown to be capable of cleaving metal–alkyl bonds of $Cp_2ZrMe_2$ to generate the active olefin polymerization catalyst, $[Cp_2ZrMe][ROB(C_6F_5)]$.[54-55]

In contrast to the salts above, the phosphine-borane activators, $Mes_2PC_6F_4B(C_6F_5)_2$ **10**, $t$BuMesP$C_6F_4B(C_6F_5)_2$ **11** and $tBu_2PC_6F_4B(C_6F_5)_2$ **12** act *via* methyl abstraction rather than protonation. The activities resulting from these activators correlate with increasing basicity of the P centers, thus following the order **10** < **11** < **12**. Although seemingly counter-intuitive, it appears that an electron rich P center in the methylborate anions $[R_2PC_6F_4B(Me)(C_6F_5)_2]$, facilitates polymerization of the Ti cation. This suggests that the presence of electrostatic approach of the sterically encumbered phosphine to the Ti cation crowds, but fails to bind to the Ti center. This crowding weakens the Ti–methyl–borate interaction, effecting an increase in the average cation–anion separation, facilitating polymerization activity.

### Additives

It is demonstrated above that phosphonium-borate and phosphine-borane activators are effective despite the liberation of phosphine donors. This was ascribed to the steric bulk of these systems. This prompted the examination of impact of added phosphine on catalytic activity. Polymerizations were performed employing the precatalyst–activator combination $CpTiMe_2(NPtBu_3)/B(C_6F_5)_3$. Immediately prior to the addition of cocatalyst 2, 10, 20 and 50 equivalents of $PEt_3$ were added to reaction mixtures. While the polymerization activity diminished with increasing concentration of phosphine, some activity did persist in the presence of up to 20 equivalents of phosphine (Table 2). Addition of 50 equivalents completely quenched the catalyst activity, and no polymer was isolable. These observations suggest that although ethylene appears to compete to some degree with phosphine donors, ultimately with increased phosphine concentration the catalytically active species is sequestered as the base-stabilized Ti cationic complex $[CpTi(NPtBu_3)Me(PR_3)][MeB(C_6F_5)_3]$. Such

**Table 2** Ethylene polymerization activity with added phosphine[a]

| Equiv. $PR_3$ | $PEt_3$ | $PCy_3$ | $PMes_3$ | $PtBu_3$ |
|---|---|---|---|---|
| 0 | 14000 | 14000 | 14000 | 14000 |
| 2 | 9700 | 11000 | 16900 | 26200 |
| 10 | 7400 | 22000 | 19200 | 48400 |
| 20 | 4900 | 24000 | 17200 | 31700 |
| 50 | 0 | 7300 | 13400 | 27800 |

[a] Polymerizations were performed using the catalyst/cocatalyst combination $CpTiMe_2(NPtBu_3)/B(C_6F_5)_3$ in 600 mL toluene (3 μmol/L), 30 °C, 20 equiv. $iBu_3Al$, 1 equiv. $B(C_6F_5)_3$, 2 atm $C_2H_4$, 10 min. Activity given in g PE/mmol/h/atm.

complexes have been previously prepared, isolated and fully characterized.[47]

The analogous experiments employing 2, 10, 20 and 50 equivalents of the much more sterically demanding phosphines $PCy_3$, $PMes_3$ and $PtBu_3$ resulted surprisingly in *increased* activity. Addition of 20 equivalents of $PCy_3$ or 10 equivalents of $PtBu_3$ resulted in significant increases in the activity to over $24.0 \times 10^3$ and $48.0 \times 10^3$ g PE/mmol of catalyst/atm/h, respectively. In subsequent polymerizations using increased equivalents of phosphine, the activity began to decline.

The above observations are initially surprising and appear counter-intuitive as the addition of a donor is expected to sequester Ti cations and preclude polymerization. However, it is noteworthy that previous efforts to isolate complexes of the form $[CpTi(NPtBu_3)Me(PR_3)][MeB(C_6F_5)_3]$ with sterically bulky phosphines (R = Mes, $t$Bu) were unsuccessful and indeed no evidence of Ti–P binding was observed.[47] Thus, it appears that despite the absence of a direct bonding interaction, the presence of phosphine alters the environment of the active site.

It is reasonable to propose that an equilibrium involving the electrostatic attraction of the Ti-cation and the sterically demanding Lewis base results in some degree of association in solution. While the nature of the molecular orbitals of the cation is well understood,[48] we have probed the steric interactions of a sterically demanding phosphine approaching the cation employing molecular mechanics calculations.[49] Models based on crystallographic data for the two fragments $[CpTi(NPtBu_3)Me]^+$ and $PtBu_3$ were employed to calculate the total energy as a function of approach of $PtBu_3$ on a vector towards the vacant coordination site on Ti. (Fig. 5). These computations reveal that the minimum energy corresponds to a Ti/P separation of 4.2 Å and support the view that steric demands preclude Ti–P bonding for sterically encumbered $PtBu_3$. It is noteworthy that previous computational studies have shown the most significant energy barrier to insertion of ethylene into the growing polymer chain is cation–anion separation.[48] Thus it is proposed that the affiliation of the sterically demanding phosphine and the Ti-cation may crowd the anion, resulting in greater anion–cation separation, and thus increased activity. Although $PMes_3$ is even more sterically shielded, it is much less basic, and this appears to diminish the positive impact on activity.

Interestingly and in marked contrast, the corresponding polymerization employing $[Ph_3C][B(C_6F_5)_4]$ as the activator and 20 equivalents of $tBu_3P$ resulted in a slight decrease in activity to 8700 g PE/mmol of catalyst/atm/h compared to the case in

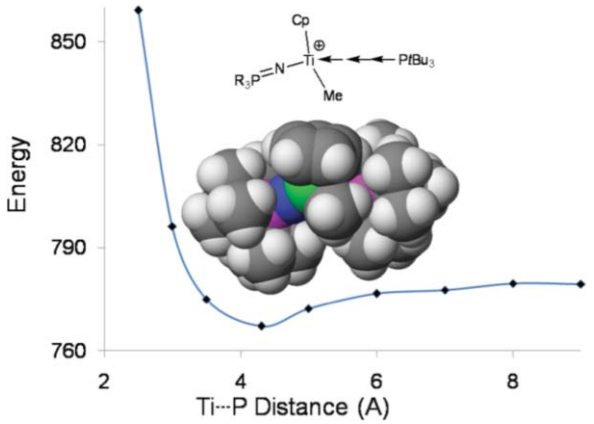


**Fig. 5** Plot of total energy *vs* Ti···P distance and space-filling diagram of the minimum energy conformation of $[CpTiMe(NPtBu_3)]^+$ and $PtBu_3$ with Ti/P separation: 4.2 Å. (P: pink, N: blue; Ti: green; C: gray; H: white).

which no phosphine was added. It must be noted that trityl cation has been shown to react with $PtBu_3$ to give the product of *para*-attack $[tBu_3P(C_6H_4)CHPh_2][B(C_6F_5)_4]$[56] whereas $PtBu_3$ does not react with $B(C_6F_5)_3$. The reduced activity with larger excesses of phosphine, presumably reflects the competitive formation of this product.

It is also instructive to note the analogy between the current polymerization experiments and main group FLPs, where the absence of a dative bond prompts reactivity. The present combination of Lewis acidic Ti-cations and sterically encumbered phosphines appears to provide metal-based FLPs which are active polymerization catalysts.

## Conclusions

Herein it has been demonstrated that phosphonium-borates and phosphine-boranes that incorporate sterically encumbered P centers can be utilized to effect the activation of an early metal ethylene polymerization pre-catalyst. The former activators operated *via* protonation of a metal–alkyl bond while the latter abstract methyl to form a methyl-borate anion. In general these activators give highly active catalysts despite the liberation or initial provision of a free phosphine. Furthermore, rather than having a detrimental effect on activity, excess equivalents of sterically encumbered phosphines enhance polymerization activity, although this effect is activator dependent. This observation points to the impact of steric congestion on electrostatic donor–acceptor attraction. These latter observations suggest that metal-based FLPs are uniquely reactive. The reactivity of such combinations continues to be the subject of study in our laboratories and will be reported in due course.

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