Remarkably Active Non-Metallocene Ethylene Polymerization Catalysts

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Summary: The bis(tri-tert-butylphosphinimide) complexes $(t\text{-}Bu_3PN)_2TiCl_2$ (**1**) *and* $(t\text{-}Bu_3PN)_2TiMe_2$ (**2**) *were prepared and characterized crystallographically. Stoichiometric reactions of* **2** *with* $PhNMe_2H[B(C_6F_5)_4]$ *in the presence of* PMe_3 *afforded* $[(t\text{-}Bu_3PN)_2TiMe(PMe_3)][B(C_6F_5)_4]$ (**3**)*, while reaction of* **2** *with* $B(C_6F_5)_3$ *affords* $(t\text{-}Bu_3PN)_2TiMe(\mu\text{-}Me)B(C_6F_5)_3$ (**4**)*. Under laboratory conditions these compounds are effective ethylene polymerization catalysts. Under commercially relevant solution polymerization conditions, these catalysts are exceptionally active. Complex* **2***, when activated with* $Ph_3C[B(C_6F_5)_4]$*, produces high molecular weight polyethylene with a narrow polydispersity at a rate approximately 4 times faster than the constrained geometry catalyst* $((C_5Me_4SiMe_2N\text{-}t\text{-}Bu)TiX_2)$*. As such, these catalysts represent the first non-cyclopentadienyl, single-site catalysts competitive with derivatives of metallocenes under commercially relevant polymerization conditions.*

The polymerization of olefins is the basis of the immense plastics industry. While Ziegler and Natta discovered the first commercially useful examples of metal-catalyzed production of polyolefins some 45 years ago, the relatively recent advance of single-site catalyst technology is revolutionizing the polyolefin business.[1] The chemistry of metallocenes (Cp_2MX_2)[2−9] and more recently the "constrained geometry catalysts (CGC)" $(CpSiR_2NR)MX_2)$[10−13] have been the subject of intense experimental[6,14−19] and theoretical study.[20−25] While these systems are being used commercially, efforts to uncover alternative systems that better the extensively patented cyclopentadienyl compounds have drawn considerable attention.[26−41] In our efforts to this end, we have prepared and studied a large series of transition

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metal complexes of phosphinimide ligands. Herein, we describe bis(tri-*tert*-butylphosphinimide) compounds of titanium. The catalytic activity of these systems is unprecedented for ethylene polymerization under commercially relevant conditions, and as such, these catalysts represent the first non-cyclopentadienyl, single-site catalysts competitive with metallocenes.

The bis(tri-*tert*-butylphosphinimide) complex (t-Bu$_3$PN)$_2$TiCl$_2$ (**1**)[42] is readily prepared via heating 2 equiv of the trimethylsilylphosphinimine,[43] t-Bu$_3$PNSiMe$_3$, and TiCl$_4$ to 110 °C in toluene for 12 h. Subsequent removal of the toluene and the volatile byproduct Me$_3$SiCl under vacuum afforded the desired complex in quantitative yield. This species is converted to the corresponding dimethyl species (t-Bu$_3$PN)$_2$TiMe$_2$ (**2**)[42] in high yield by treatment of **1** with methylmagnesium bromide. ^{1}H,^{13}C, and ^{31}P NMR spectroscopic data as well as X-ray crystallographic data confirmed these formulations of **1** and **2** (Figure 1).[44] Both complexes exhibit the expected pseudo-tetrahedral geometries about titanium. The Ti−Cl (2.290(2) Å) and Ti−C (2.125(2) Å) bond distances in **1** and **2**, respectively, are typical. The geometry about nitrogen in **1** and **2** supports the notion of Ti−N multiple bonding. The Ti−N$_{av}$ bond distances (**1**, 1.791(4) Å; **2**, 1.827(3) Å) are relatively short although slightly longer than the Ti−N distances in the Ti−imido complex Cp$_2$Ti(N-t-Bu)(NC$_5$H$_5$) (1.73(1) Å).[45] Also, the Ti−N−P angles approach linearity (**1**, 175.5(2)°; **2**, 167.8(3)°). The concept of Ti−N π-bonding is also supported by the lengthening of the P−N bonds (**1**, 1.579(4) Å; **2**, 1.561(3) Å) compared to those seen in free phosphinimines (1.487 Å).[46]

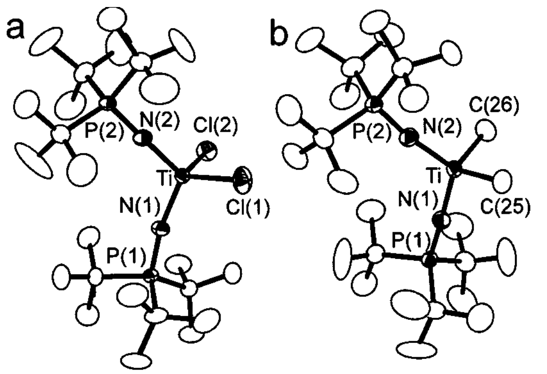

Figure 1. ORTEP drawing of (a) **1**; (b) **2**, 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. **1**: Ti−N(1) 1.789(4) Å, Ti−N(2) 1.792(4) Å, Ti−Cl(1) 2.288(2) Å, Ti−Cl(2) 2.292(2) Å, N(1)−Ti−N(2) 112.9(2)°, N(1)−Ti−Cl(1) 109.34(14)°, N(2)−Ti−Cl(1) 109.43(13)°, N(1)−Ti−Cl(2) 109.51(13)°, N(2)−Ti−Cl(2) 108.54(13)°, Cl(1)−Ti−Cl(2) 106.93(7)°. **2**: Ti−N(2) 1.824(2) Å, Ti−N(1) 1.830(2) Å, Ti−C(25) 2.121(3) Å, Ti−C(26) 2.129(3) Å, N(2)−Ti−N(1) 117.24(11)°, N(2)−Ti−C(25) 109.99(13)°, N(1)−Ti−C(25) 108.01(13)°, N(2)−Ti−C(26) 108.59(14)°, N(1)−Ti−C(26) 109.25(15)°, C(25)−Ti−C(26) 102.79(15)°.

The complexes **1** and **2** were shown in initial laboratory experiments to act as catalyst precursors for ethylene polymerization. The combination of **1** with methylalumoxane showed limited activity; however, the activity of **2** in the presence of single-component activators B(C$_6$F$_5$)$_3$, PhNMe$_2$H[B(C$_6$F$_5$)$_4$], or Ph$_3$C[B(C$_6$F$_5$)$_4$] was significant (Table 1). In the latter case, addition of **2** at 25 °C to a solution of trityl borate in toluene under 1 atm of ethylene resulted in rapid polymerization (1166 g mmol^{-1} h^{-1}) and the concurrent exotherm. This remarkably high activity was viewed as promising from a commercial perspective.

Further testing was carried out in a stainless steel reactor under conditions relevant to the commercial solution production of high- and low-density polyethylene (160 °C). Under these demanding conditions, very few single-site or Ziegler−Natta catalysts produce acceptable polymer molecular weight or exhibit high activity. In these experiments, the ethylene, solvent, and catalyst were pumped into the reactor, and the resulting polyethylene was removed continuously. In each case the catalyst and activator solutions were pumped separately and the active catalyst species was formed in the reactor itself. On exiting the reactor, further polymerization was prevented by the addition of a large excess of isopropyl alcohol and the polymer was recovered. The catalyst precursor/activator combinations (C$_5$Me$_4$SiMe$_2$N-t-Bu)TiMe$_2$/B(C$_6$F$_5$)$_3$ and **2**/B(C$_6$F$_5$)$_3$ produced polyethylene at similar rates of approximately 3000 g of PE mmol^{-1} h^{-1} at a reactor catalyst concentration of 13.9 × 10^{-6} M. Use of the trityl borate as the activator resulted in significantly enhanced activity. The catalyst derived from the commercially practiced constrained geometry precursor (C$_5$Me$_4$SiMe$_2$N-t-Bu)TiMe$_2$ produced polyethylene at a rate of 16 100 g of PE mmol^{-1} h^{-1}, converting 82% of the ethylene in the flow to polyethylene at the lower catalyst concentration of 2.3 × 10^{-6}

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[42] Syntheses: **1**: A toluene solution (10 mL) of TiCl$_4$ (0.500 g; 2.636 mmol) was added to a toluene solution (50 mL) of t-Bu$_3$P═NSiMe$_3$ (1.600 g; 5.526 mmol). The solution was heated to 110 °C for 12 h. The volatile products were removed under vacuum to give a white solid. The solid was washed with hexane (3 × 20 mL), isolated by filtration, and dried under vacuum (1.325 g; 2.403 mmol; 91%). ^{1}H NMR: δ 1.36 (d, $|J^3{}_{PH}| = 13.1$ Hz, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: δ 32.17. **2**: To a diethyl ether solution (10 mL) of **1** (0.500 g; 0.907 mmol) was added an excess of MeMgBr (0.9 mL; 3.0 M.; 2.7 mmol). The solution was stirred at 25 °C for 12 h. The solvent was removed under vacuum to give a gray solid. The solid was extracted with hexane (3 × 20 mL). The volume of the solution was reduced to 5 mL and left to crystallize at 25 °C for 12 h. White crystalline **2** was isolated by filtration and dried under vacuum (0.380 g; 0.744 mmol; 82%). ^{1}H NMR: δ 1.39 (d, $|J^3{}_{PH}| = 12.6$ Hz, 54H, PC*Me*$_3$), 0.90 (s, 6H, Ti*Me*$_2$). ^{31}P{^{1}H} NMR: δ 25.72. **3**: A CH$_2$Cl$_2$ solution (5 mL) of [PhNMe$_2$H]$^-$[B(C$_6$F$_5$)$_4$]$^-$ (0.080 g; 0.100 mmol) was added to a CH$_2$Cl$_2$ solution of complex **2** (0.050 g; 0.098 mmol) and PMe$_3$ (0.050 g; 0.657 mmol). The solution was stirred at 25 °C for 30 min. The solvent was removed under vacuum, and the residual solid was washed with hexane (3 × 10 mL). The solid is highly sensitive and was characterized spectroscopically without further purification. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 1.55 (d, $|J^3{}_{PH}| = 12.4$ Hz, 9H, P*Me*$_3$), 1.51 (d, $|J^3{}_{PH}| = 13.2$ Hz, 54H, PC*Me*$_3$), 0.80 (s, 3H, Ti*Me*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 42.75, −22.78. ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ −55.63 (s), −86.36 (t, $|J_{FF}| = 20.6$ Hz), −90.19 (t, $|J_{FF}| = 16.9$ Hz). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ −16.98. **4**: To a benzene solution of complex **2** (0.050 g; 0.098 mmol) was added a benzene solution of B(C$_6$F$_5$)$_3$ (0.051 g; 0.100 mmol). The solution was stirred for 30 min at 25 °C. The solvent was removed under vacuum. The resulting solid was washed with hexane to remove any starting materials. The solid is highly sensitive and was characterized spectroscopically without further purification. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 1.44 (d, $|J^3{}_{PH}| = 13.1$ Hz, 54H, PC*Me*$_3$), 0.54 (s, 3H, Ti*Me*), 0.47 (broad singlet, 3H *Me*B). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 49.75. ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ −55.78 (d, $|J_{FF}| = 21.5$ Hz), −88.07 (t, $|J_{FF}| = 19.9$ Hz), −90.58 (t, $|J_{FF}| = 18.7$ Hz). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ −15.27.

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[44] Crystallographic data: **1**: space group $P2_1/n$, $a = 13.091(2)$ Å, $b = 16.233(3)$ Å, $c = 15.413(4)$ Å, $\beta = 107.04(2)°$, $V = 3131.4(10)$ Å^3, $Z = 4$; $R = 0.0606$, $R_w = 0.1466$, GOF = 0.851. **2**: $a = 13.1885(3)$ Å, $b = 16.4592(4)$ Å, $c = 15.5549(3)$ Å, $\beta = 106.5890(10)°$, $V = 3235.99(12)$ Å^3, $Z = 4$; $R = 0.0512$, $R_w = 0.1438$, GOF = 1.119.

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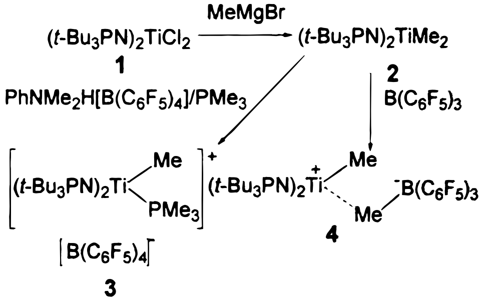
Table 1. Polymerization Data

catalyst precursor[a]	catalyst (μmol/L)	activator[a]	cat./act. ratio	C_2H_4 conv. (%)	activity (g $mmol^{-1}$ h^{-1})	M_w[c]	Pd
2[b]	12100	TB	2		1166		
2[b]	21500	B	0.9		167		
2[b]	21500	AB	2		265		
2[d]	13.89	B	2	93.7	3060	98900	2.2
2[d]	13.89	TB	1	99.5	3250		
2[d]	2.31	TB	1	96.5	18950		
2[d]	0.58	TB	1	79.5	62310	77500	1.9
CGC[d]	13.89	B	2	89.6	2920	159800	2.1
CGC[d]	13.89	TB	1	96.7	3160		
CGC[d]	2.31	TB	1	82.4	16130	134500	2.5
Cp_2ZrMe_2[d,e]	13.89	TB	1	98.6	3220		
Cp_2ZrMe_2[d,e]	4.63	TB	1	93.4	8850	12300	3.8

[a] CGC: $[(C_5Me_4SiMe_2N\text{-}t\text{-}Bu)TiMe_2$. TB: trityl tetrakis(pentafluorophenylborate). B: tris(pentafluorophenylborane). AB: *N*,*N*-dimethylanilinium tetrakis(pentafluorophenylborate). [b] Polymerizations were initiated at 1 atm pressure of ethylene and 25 °C. A rapid exotherm was observed. The duration of the experiments was limited to 1−3 min to ensure that the rate was not limited by mass transport. [c] Molecular weight data were recorded against polyethylene standards. [d] Experiments were performed under commercially relevant solution polymerization conditions (160 °C and 1500 psi). Cyclohexane, catalyst in toluene (1 mM), and ethylene were continuously added to the reactor, and the product was continuously removed. The total flow was 27 mL/min. [e] Present for comparative purposes.

Scheme 1



M. Employing the catalyst precursor **2** at the same concentration resulted in almost 97% ethylene conversion. Under such conditions the activity of the catalyst cannot be reliably determined. To overcome this, the catalyst concentration in the reactor was further reduced to 0.58×10^{-6} M. At this concentration, conversion of ethylene to polyethylene was 80%. Putting this in activity terms, the catalyst derived from the bis(phosphinimide) complex **2** via activation by $Ph_3C[B(C_6F_5)_4]$ produces polyethylene at the rate of 62 300 g $mmol^{-1}$ h^{-1}, or approximately 4 times faster than the constrained geometry catalyst under these conditions relevant to commercial production.

Molecular weights of the polymers produced employing **2** under these conditions range from 78 to 99 000. Polydispersities of 1.9−2.2 are consistent with the operation of a single-site catalyst. These data in combination with the observation of exceptionally high catalyst activity demonstrate that this non-cyclopentadienyl catalyst system has commercial promise.

The nature of the active species in the above polymerizations was probed via stoichiometric reactions. The reaction of **2** with $Ph_3C[B(C_6F_5)_4]$ in CD_2Cl_2 under a nitrogen atmosphere resulted in degradation. Nonetheless, reaction of **2** with $PhNMe_2H[B(C_6F_5)_4]$ in the presence of PMe_3 afforded $[(t\text{-}Bu_3PN)_2TiMe(PMe_3)][B(C_6F_5)_4]$ (**3**),[42] suggesting the cation is stable only in the presence of a donor, which presumably during catalysis is ethylene. Reaction of **2** with $B(C_6F_5)_3$ in hexane affords the yellow ion-paired complex $(t\text{-}Bu_3PN)_2TiMe(\mu\text{-}Me)B(C_6F_5)_3$ (**4**)[42] (Scheme 1). While both **3** and **4** were oily, extremely air-sensitive materials that were not isolable, spectroscopic characterization in solution by ^{11}B, ^{19}F, ^{31}P, and ^{1}H NMR spectroscopy confirmed the above formulations. ^{1}H NMR data for **4** reveal two resonances attributable to the Ti- and B-bound methyl groups, inferring the absence of a rapid exchange process as observed for analogous metallocene systems.[47] No evidence of exchange was observed upon warming to 40 °C.

Comparison of the structures of the molecular fragments $(t\text{-}Bu_3PN)_2Ti$ and Cp_2Ti reveals that the N−Ti−N angles in **1** (112.9(2)°) and **2** (117.24(11)°) are significantly less than the Cp−Ti−Cp angle (130.96°) in Cp_2TiCl_2.[48] While the Cp−M−N angles (102.0−107.9°) in the CGC are smaller still,[10−13] the steric bulk of the phosphinimide substituents in $(t\text{-}Bu_3PN)_2Ti$ is further removed from the metal center. This is illustrated by the Ti−P (3.30 Å) distances, which are significantly greater than the typical Cp−Ti distances of 2.1 Å. These data suggest the metal center in the bis(phosphimide) complexes is very accessible, and this may in part account for the high activity.

In summary, the bis(phosphinimide) complexes $(t\text{-}Bu_3PN)_2TiX_2$ afford a new class of ethylene polymerization catalyst precursors. While the activation strategy clearly has an effect on the levels of activity, activation of **2** with trityl borate results in high molecular weight polyethylene and catalyst activity that is unprecedented. Consequently these systems are the first non-cyclopentadienyl catalysts competitive with metallocenes under conditions relevant to commercial, high-temperature solution polymerization. The discovery of this new class of highly active catalysts presents a variety of opportunities for systematic modification and catalyst design. It is these issues that are the subject of current study.

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Supporting Information Available: NMR spectra for **3** and **4** and spectroscopic and crystallographic information tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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