Altering molecular weight distributions: Benzyl–phosphinimide titanium complexes as ethylene polymerization catalysts

Emily Hollink, Pingrong Wei, and Douglas W. Stephan

Abstract: The phosphines and corresponding phosphinimines $R_2BnPNSiMe_3$ (R = *t*-Bu, Cy), *p*-$C_6H_4(CH_2PR_2)_2$ (R = *t*-Bu (**1**), Cy (**2**)), and *p*-$C_6H_4(CH_2PR_2NSiMe_3)_2$ (R = *t*-Bu (**3**), Cy (**4**)) were prepared in high yields. Subsequent reaction with Ti precursors afforded $(R_2BnPN)TiCp^*Cl_2$ (Cp* = η-C_5Me_5; R = *t*-Bu (**5**), Cy (**6**)), $(R_2BnPN)TiCpCl_2$ (Cp = η-C_5H_5; R = *t*-Bu (**7**), Cy (**8**)), *p*-$C_6H_4(CH_2PR_2NTiCp^*Cl_2)_2$ (R = *t*-Bu (**9**), Cy (**10**)), and *p*-$C_6H_4(CH_2PR_2NTiCpCl_2)_2$ (R = *t*-Bu (**11**), Cy (**12**)). Methylation of the above complexes gave $(R_2BnPN)TiCp^*Me_2$ (R = *t*-Bu (**13**), Cy (**14**)), $(R_2BnPN)TiCpMe_2$ (R = *t*-Bu (**15**), Cy (**16**)), *p*-$C_6H_4(CH_2PR_2NTiCp^*Me_2)_2$ (R = *t*-Bu (**17**), Cy (**18**)), and *p*-$C_6H_4(CH_2PR_2NTiCpMe_2)_2$ (R = *t*-Bu (**19**), Cy (**20**)). The activity of these species as catalyst precursors in ethylene polymerization catalysis was evaluated using Schlenk line and Buchi reactor techniques using activation by methylaluminoxane (MAO) or $[Ph_3C][B(C_6F_5)_4]$. All these catalysts showed good activities and yield polymers with relatively broad molecular weight distributions. The bimodal polymers derived from catalysts generated using MAO are proposed to result from additional active species, possibly as a result of reaction of MAO with the benzylic fragments. X-ray data are reported for **1**, **4–8**, **10**, **12–14**, **16**, and **18–20**.

Key words: phosphinimides, polymerization, catalysis, polyethylene, titanium, polymer molecular weight distributions.

Résumé : On a préparé les phosphines et les phosphinimines correspondantes $R_2BnPNSMe_3$ (R = *t*-Bu, Cy), *p*-$C_6H_4(CH_2PR_2)_2$ (R = *t*-Bu (**1**), Cy (**2**)), et *p*-$C_6H_4(CH_2PR_2NSiMe_3)_2$ (R = *t*-Bu (**3**), Cy (**4**)) avec d'excellents rendements. Les réactions subséquentes avec des précurseurs de Ti ont conduit à la formation des composés $(R_2BnPN)TiCp^*Cl_2$ (Cp* = η-C_5Me_5; R = *t*-Bu (**5**), Cy (**6**)), $(R_2BnPN)TiCpCl_2$ (Cp = η-C_5H_5; R = *t*-Bu (**7**), Cy (**8**)), *p*-$C_6H_4(CH_2PR_2NTiCp^*Cl_2)_2$ (R = *t*-Bu (**9**), Cy (**10**)), et *p*-$C_6H_4(CH_2PR_2NTiCpCl_2)_2$ (R = *t*-Bu (**11**), Cy (**12**)). Une méthylation subséquente de ces complexes conduit à la formation des composés $(R_2BnPN)TiCp^*Me_2$, (R = *t*-Bu (**13**), Cy (**14**)), $(R_2BnPN)TiCpMe_2$ (R = *t*-Bu (**15**), Cy (**16**)), *p*-$C_6H_4(CH_2PR_2NTiCp^*Me_2)_2$ (R = *t*-Bu (**17**), Cy (**18**)), et *p*-$C_6H_4(CH_2PR_2NTiCpMe_2)_2$ (R = *t*-Bu (**19**), Cy (**20**)). On a évalué l'activité de ces espèces comme précurseurs de catalyseurs pour la polymérisation de l'éthylène à l'aide d'une ligne de Schlenk et un réacteur de Büchi et d'une activation par méthylaluminoxane (MAO) ou du $[Ph_3C][B(C_6F_5)_4]$. Tous ces catalyseurs présentent de bonnes activités et ils conduisent à la formation de polymères ayant des distributions de poids moléculaires relativement larges. Il est suggéré que les polymères à deux modes obtenus à l'aide de catalyseurs résultant d'une génération au MAO pourraient provenir d'espèces actives additionnelles résultant possiblement d'une réaction du MAO avec les fragments benzyliques. On rapporte les données cristallographiques pour les composés **1**, **4–8**, **10**, **12–14**, **16** et **18–20**.

Mots clés : phosphinimides, polymérisation, catalyse, polyéthylène, titane, distributions des poids moléculaires des polymères.

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Introduction

Many of the developments in early-transition-metal chemistry in recent years have been prompted by attempts to uncover effective new homogeneous olefin polymerization catalysts. A number of studies have described non-metallocene systems based on a variety of novel ancillary ligands (1–3). Among such systems, we have described titanium catalysts that contain bulky phosphinimide ligands. The family of compounds of the form $CpTi(NPR_3)Cl_2$ (Cp = η-C_5H_5) yield active ethylene polymerization catalysts upon activation by methylaluminoxane (MAO) (4–8). Similarly, upon activation by $B(C_6F_5)_3$ or $Ph_3C[B(C_6F_5)_4]$, the species $(t\text{-}Bu_3PN)_2TiMe_2$ provides a remarkably active catalyst, producing polyethylene of narrow polydispersity and relatively high molecular weight (9).

Narrow polydispersities are typically observed for single-site or living polymerization catalysts; however, practical applications often require resins of broader molecular weight distribution for effective processing and manipulation (10, 11). There are a variety of methods employed to alter both the molecular weight and the molecular weight distributions of resins derived from single-site catalysts. These include controlled hydrogenolysis or hydrolysis of the polymeriza-

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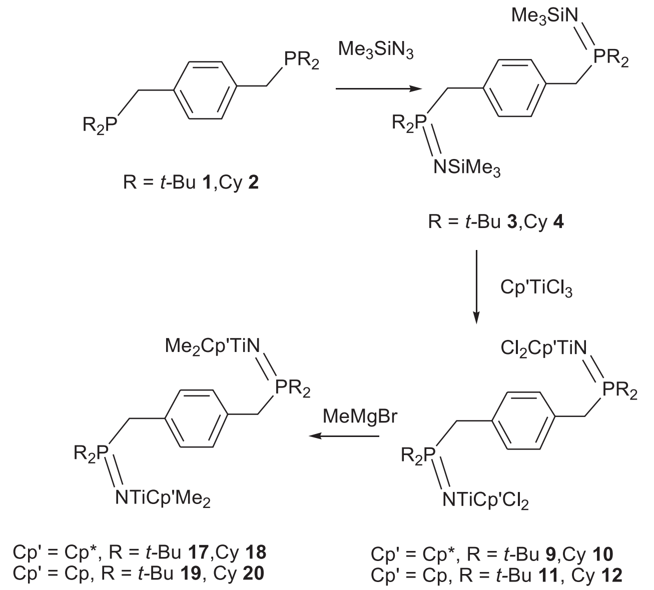
Scheme 1.

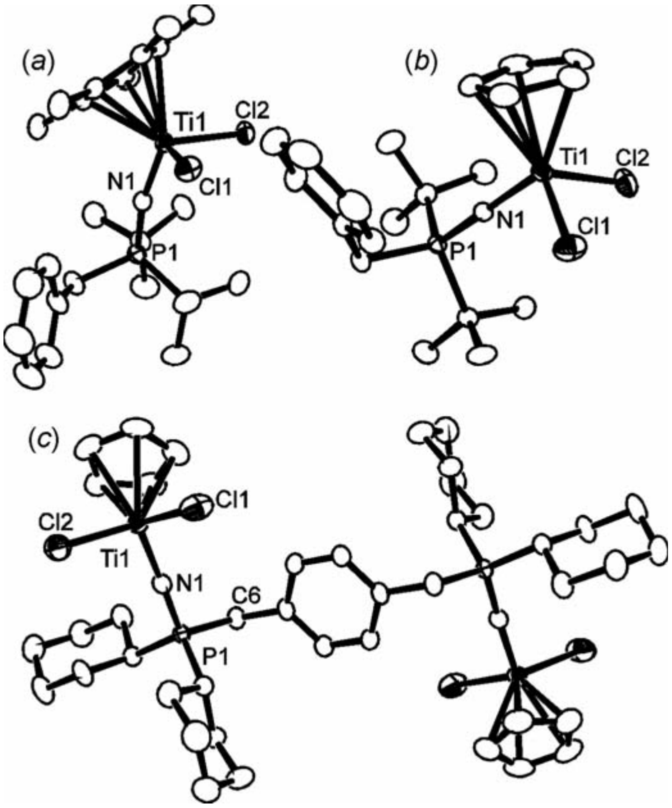


tion process (12, 13) or the use of sequential catalyst systems to produce the desired mixture of polymers (14–16). Academic studies and industrial developments continue in this area, with a particular emphasis on bimodal resins (7, 17–28). An alternative approach involves linking single-site catalysts together (16, 29–31), affording differing catalyst sites and thus broader molecular weight distributions (32). Synthetic routes to bimetallic catalyst precursors such as $C_6H_4((Me_3SiN)Zr(NMe_2)_2)_2$ (33), $C_6H_4(OMCpX_2)_2$ (M = Ti, Zr; X = Cl, Me), and $(CH_2PPh_2NCp^*TiX_2)_2$ and 2,6-$(C_5H_3N)(CH_2PPh_2NCp^*TiX_2)_2$ (Cp* = η-C_5Me_5; X = Cl, Me) (34) have recently appeared, and some of these compounds were tested for their catalytic activity upon activation with MAO. However, very poor catalytic activity was observed, and thus the nature of the resulting polymers has not been explored. In this paper, we describe the facile synthesis of a series of bimetallic phosphinimide-based titanium precatalysts and show that these systems provide effective ethylene polymerization catalysts upon activation by MAO. Moreover, the influence of the nature of the precatalysts on the resulting polymer molecular weight distributions is probed. The implications and ramifications of these data are discussed.

Results and discussion

The phosphines and corresponding phosphinimines $R_2BnPNSiMe_3$ (R = *t*-Bu, Cy) were prepared via a modification of a literature procedure (35). The related diphosphines *p*-$C_6H_4(CH_2PR_2)_2$ (R = *t*-Bu (**1**) or Cy (**2**)) were prepared by a method analogous to that used for the related meta-substituted isomers (36). Thus, treatment of *p*-$C_6H_4(CH_2Br)_2$ with HPR_2 (R = *t*-Bu or Cy) followed by addition of the base NEt_3 afforded **1** and **2** in yields of 88% and 85%, respectively. X-ray data for **1** confirmed the formulation. These phosphines were oxidized in a conventional manner with Me_3SiN_3 to give the species *p*-$C_6H_4(CH_2PR_2NSiMe_3)_2$ (R = *t*-Bu (**3**), Cy (**4**)), also in high yields. Spectroscopic data, as well as X-ray data for compound **4**, were consistent with these formulations. The X-ray data revealed that in the solid state, **4** is centrosymmetric with typical P–N and Si–N bond lengths averaging 1.542(2) and 1.663(3) Å, respectively. The P–N–Si angle was found to range from 153.4(1)° to 163.5(1)°, which falls within the range of P–N–Si angles reported in a number of monodentate phosphinimines (37).

Fig. 1. ORTEP drawings of (*a*) **5**, (*b*) **8,** and (*c*) **12.** 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.



Subsequent thermal reaction of the above phosphinimines with 1 or 2 equiv. of Cp^*TiCl_3 or $CpTiCl_3$ resulted in the high-yield formation of $(R_2BnPN)TiCp^*Cl_2$ (R = *t*-Bu (**5**), Cy (**6**)), $(R_2BnPN)TiCpCl_2$ (R = *t*-Bu (**7**), Cy (**8**)), *p*-$C_6H_4(CH_2PR_2NTiCp^*Cl_2)_2$ (R = *t*-Bu (**9**), Cy (**10**)), and *p*-$C_6H_4(CH_2PR_2NTiCpCl_2)_2$ (R = *t*-Bu (**11**) or Cy (**12**)) upon liberation of Me_3SiCl (Scheme 1). While the compounds **9** and **11** were less soluble in benzene than the others, spectroscopic data in all cases were consistent with the formulations. X-ray data (Table 1, Fig. 1) were also acquired for **5**–**8**, **10,** and **12**. Key metric parameters are tabulated in Table 2. In all cases, the Ti–N distances fall within the range of 1.764(3)–1.786(2) Å. The P–N–Ti angles in these compounds are approximately linear, ranging from 157.1(3)° to 175.2(1)°. These values are similar to those of 155.4(2)° and 165.7(1)° reported for 2,6-$(C_5H_3N)(CH_2PPh_2NTiCp^*Cl_2)_2$ and are typical of titanium complexes of phosphinimide derivatives (5, 37). Variations in the metric parameters among these species are consistent with the steric and electronic differences between the Cp* and Cp ligands.

Methylation of the above complexes proceeded in a facile manner to give $(R_2BnPN)TiCp^*Me_2$ (R = *t*-Bu (**13**), Cy (**14**)), $(R_2BnPN)TiCpMe_2$ (R = *t*-Bu (**15**), Cy (**16**)), *p*-$C_6H_4(CH_2PR_2NTiCp^*Me_2)_2$ (R = *t*-Bu (**17**), Cy (**18**)), and

Table 1 Crystallographic data.

	1	**4**	**5**	**6**	**7**	**8**	**10**
Formula	$C_{24}H_{44}P_2$	$C_{38}H_{70}N_2P_2Si_2$	$C_{25}H_{40}NCl_2PTi$	$C_{29}H_{44}Cl_2NPTi$	$C_{26}H_{36}C_{l2}NPTi$	$C_{24}H_{34}Cl_2NPTi$	$C_{52}H_{82}N_2Cl_2P_2Ti_2$
Formula wt.	394.53	673.08	504.35	556.42	512.33	486.29	1034.74
a (Å)	6.1600(2)	9.453(6)	9.743(6)	11.359(7)	12.3260(18)	11.660(6)	15.218(9)
b (Å)	8.2564(3)	14.566(8)	17.528(11)	16.383(10)	11.6587(17)	13.481(7)	24.238(14)
c (Å)	13.5269(6)	17.616(10)	16.130(10)	16.443(10)	19.500(5)	15.984(8)	15.996(9)
α (°)	80.1900(10)	106.248(11)					
β (°)	79.0530(10)	104.112(9)	98.567(12)	102.672(12)	101.975(11)		110.387(10)
γ (°))	71.0740(10)	103.764(11)					
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
V (Å^3)	634.54(4)	2133(2)	2724(3)	2985(3)	2741.3(9)	2512(2)	5530(5)
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
δ(calcd.) (g cm^{-1})	1.032	1.048	1.230	1.238	1.241	1.286	1.243
Z	1	2	4	4	4	4	4
μ(Mo Kα) (cm^{-1})	0.177	0.184	0.581	0.537	0.579	0.628	0.574
Data collected	3184	9172	11 282	12 502	13 075	10 691	22 618
Data $F_o^2 > 3\sigma(F_o^2)$	2131	6063	3860	4275	4767	3567	7876
Variables	124	397	271	307	280	262	559
R^a	0.0674	0.0372	0.0394	0.0330	0.0361	0.0233	0.0546
R_w^b	0.2067	0.0981	0.1213	0.0889	0.0711	0.0555	0.1515
GOF	0.913	0.903	1.114	0.965	0.840	0.981	0.859

Note: All data collected at 24 °C with Mo Kα radiation (λ = 0.71069 Å).

[a] $R = \Sigma (||F_o| - |F_c||)/ \Sigma|F_o|$.

[b] $R_w = [\Sigma (\omega(F_o^2 - F_c^2)^2)/\Sigma (\omega(F_o^2)^2)]^{1/2}$.

p-$C_6H_4(CH_2PR_2NTiCpMe_2)_2$ (R = t-Bu (**19**), Cy (**20**)) in isolated yields ranging from 46% to 83%. Each of these dimethyl derivatives was characterized spectroscopically. All of these species with the exception of compounds **15** and **17** were also characterized by crystallography (Table 2). In these structures, the Ti–N distances are slightly elongated in comparison to those in the corresponding dichloride derivatives. This is consistent with the increased electron density at the metal center as a result of methylation. The Ti–C bond lengths are typical, ranging from 2.119(7) to 2.228(3) Å. The remaining metric parameters of these compounds are unexceptional.

Olefin polymerization studies

Preliminary evaluation of these compounds as ethylene polymerization catalysts was performed in 50 mL of toluene in a Schlenk flask at 25 °C under 1 atm of ethylene and employing 1000 equiv. of MAO as co-catalyst. These experiments were allowed to run 30 min prior to quenching. The preliminary Schlenk screenings provided an indication of the relative polymerization activity (Table 3), revealing that among the bimetallic systems, precatalyst **19** afforded the best polymerization activity. While the activities were reproducible, the characteristics of the resulting polyethylene (MW and polydispersity index (PDI)) differed from those obtained subsequently, under the more controlled conditions in the Buchi reactor. Such inconsistencies were attributed to the effects of the heat of polymerization within the small volume of the Schlenk flask.

Subsequently, catalysts were tested in a 1-L Buchi reactor equipped with a temperature control bath and a stirring mechanism. The conditions in this case included 500 mL of toluene, 30 °C (±2 °C) and a much lower concentration of precatalyst (50 µmol/L). In initial screening experiments, low pressures of ethylene (1 atm or less) were used; nonetheless, the data was reproducible within acceptable experimental errors. The activities reported (Table 3) are averages of (at least) duplicate runs; however, insufficient saturation of the catalyst with ethylene may have resulted in an underestimation of the activity. Nonetheless, in general, the monometallic catalysts show higher activities, ranging from 200 to 280 g mmol^{-1} h^{-1} atm^{-1}. These activities fall within the range of those reported previously for a series of Ti–phosphinimide complexes (5). These values were significantly higher than those seen for catalysts derived from the previously reported bimetallic systems, where the activities ranged from 20 to 150 g mmol^{-1} h^{-1} atm^{-1}. In particular, these systems stand in contrast to those derived from the related species $(CH_2PPh_2NTiCp^*Cl_2)_2$, which was reported to exhibit extremely low activities for polymerization (34). The cause of such differences is not clear; however, the bimetallic systems are much less soluble than the corresponding monometallic systems. Similarly, this is true for systems incorporating Cp rather than Cp* ligands. It is also noteworthy that in all pairs of analogs, incorporation of the more sterically demanding substituents (Cp* in place of Cp or t-Bu in place of Cy) afforded higher catalyst activity. This observation is consistent with the previously suggested notion that steric protection of the phosphinimide N atom enhances activity (4, 38–40).

The monometallic catalysts derived from **5**, **7,** and **13** described herein yield polyethylene of molecular weights ranging from 239 800 to 628 400 g mmol^{-1} h^{-1} atm^{-1} with PDIs of 2.8–3.2 in the Buchi reactor. The corresponding bimetallic catalysts, in contrast, provided PE of molecular weights ranging from 143 300 to 1 416 000 g mmol^{-1} h^{-1} atm^{-1} depending on the precatalyst. These polymers showed broader bimodal molecular weight distributions (Fig. 2). The

12	**13**	**14**	**16**	**18**	**19**	**20**
$C_{42}H_{62}N_2Cl_4P_2Ti_2$ ($2CH_2Cl_2$)	$C_{27}H_{46}NPTi$	$C_{31}H_{50}NPTi$	$C_{26}H_{40}NPTi$	$C_{56}H_{94}N_2P_2Ti_2 \cdot 2C_6H_6$	$C_{38}H_{66}N_2P_2Ti_2$	$C_{52}H_{80}N_2P_2Ti_2$
1064.32	463.52	515.59	445.46	1109.29	708.67	890.92
8.974(5)	10.037(5)	11.613(6)	11.729(7)	16.526(10)	16.290(9)	8.794(5)
11.490(6)	19.055(10)	16.468(8)	13.616(8)	17.114(10)	16.455(9)	9.772(5)
14.905(8)	15.059(8)	16.287(8)	16.206(9)	24.453(14)	15.594(8)	16.678(9)
96.092(10)						77.211(10)
105.085(9)	104.047(10)	102.618(9)		106.280(10)	100.865(10)	79.909(10)
112.201(11)						68.500(9)
Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
1337.4(12)	2794(3)	3040(3)	2588(3)	6639(7)	4105(4)	1293.4(12)
$P1$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
1.322	1.102	1.127	1.143	1.110	1.147	1.144
1	4	4	4	4	4	1
0.789	0.376	0.352	0.404	0.327	0.493	0.404
5717	11 755	12 862	10 620	27 145	17 348	5554
3790	3986	4376	3656	9431	5861	3672
262	271	307	262	667	397	262
0.0461	0.0408	0.0414	0.0595	0.0510	0.0378	0.0379
0.1317	0.1209	0.1248	0.1196	0.1084	0.1081	0.1080
1.062	1.056	0.570	1.199	0.693	1.008	1.033

Table 2. Selected metric parameters from X-ray structures.

Compd.	Ti—X (X = Cl, Me) (Å)	Ti—N (Å)	N—P (Å)	Ti–N–P (°)
5	2.322(1), 2.324(1)	1.786(2)	1.598(2)	167.6(1)
6	2.317(1), 2.309(1)	1.776(2)	1.594(2)	157.3(1)
7	2.3072(9), 2.3091(8)	1.760(2)	1.599(2)	175.2(1)
8	2.313(1), 2.314(1)	1.765(2)	1.607(2)	168.4(1)
10	2.312(2), 2.328(2)	1.786(5)	1.589(5)	157.1(3)
	2.305(2), 2.317(2)	1.768(5)	1.602(5)	162.6(3)
12	2.303(2), 2.323(1)	1.764(3)	1.608(3)	172.7(2)
13	2.165(3), 2.228(3)	1.830(2)	1.580(2)	172.6(2)
14	2.136(3), 2.152(3)	1.811(2)	1.570(2)	162.8(2)
16	2.131(6), 2.130(6)	1.804(4)	1.579(4)	168.1(3)
18	2.119(7), 2.145(6)	1.829(5)	1.573(5)	163.4(4)
	2.160(6), 2.155(6)	1.813(5)	1.582(5)	161.5(4)
19	2.137(3), 2.143(3)	1.806(2)	1.582(2)	171.0(1)
	2.124(3), 2.130(4)	1.802(2)	1.581(2)	173.9(2)
20	2.160(3), 2.191(3)	1.806(2)	1.580(2)	167.9(1)

separation of the peak molecular weights and the relative intensities of the two modes were catalyst and condition dependent. For example, the polymer derived from the precatalyst **9** (Fig. 2*a*) exhibited a bimodal distribution that was fit with two Gaussian curves of peak molecular weights 98 600 and 447 700 g mmol^{-1}. In contrast, the catalyst derived from **19** (Fig. 2*b*) gave rise to a polymer with clearly separated peaks at 19 700 and 537 000 g mmol^{-1}. These results stand in marked contrast to previous reports regarding compounds of the form (R_3PN)TiCpCl_2, which upon activation by MAO, behave as single-site catalysts providing polyethylene of high molecular weight with narrow polydispersities (5).

Related tests done using the monometallic catalyst precursor **5** showed that under 2 atm of constant ethylene pressure (Table 4), polymer with a broaden molecular weight distribution in which a lower molecular weight polymer fraction is similar to that derived from **9** (Fig. 3) was produced. This observation seemed to counter the notion that a bimodal polymer was a direct result of the bimetallic catalysts. Monitoring the polymerizations using **5** and **13** over 10-min intervals revealed the initial appearance of a higher molecular weight fraction that accumulated over time (Fig. 4). This suggests that the active catalyst undergoes some sort of transformation during the course of the polymerization, possibly via reaction of the benzylic protons. It is noteworthy that Bochmann and co-workers have observed metallation of the methylene protons of $(CH_2PPh_2NTiCp^*Cl_2)_2$ (34).

Using similar increased pressure conditions, activation of the bimetallic catalyst precursors **18** and **20** with 1, 2, or

Table 3. Ethylene polymerization data.

Precatalyst	T (°C)	Catalyst concn. (µmol L^{-1})	Activity	M_w[a] (g mol^{-1})	PDI[a,b]	MW[c] (g mol^{-1})
9	25	350	36	131 100	5.4	—
10	25	350	<1	—[d]	—[d]	—
11	25	350	20	15 200	4.8	—
12	25	350	<1	—[d]	—[d]	—
5	25	350	42	234 100	4.35	—
17	25	350	93	138 700	1.6	—
18	25	350	55	—[e]	—[e]	—
19	25	350	100	38 100	2.2	—
20	25	350	11	536 500	2.0	—
13	25	350	170	117 400	2.02	—
$ZrCp_2Cl_2$	25	350	200	35 600	2.5	—
9	30	50	150	319 200	3.2	98 600, 447 700
10	30	50	85	—[e]	—[e]	—
11	30	50	50	143 300	4.8	34 300, 653 100
12	30	50	25	1 104 000	1.9	684 200, 1 407 700
5	30	50	200	239 800	2.8	—
17	30	50	100	468 600	1.9	299 200, 1 425 600
18	30	50	92	—[e]	—[e]	—
19	30	50	60	195 200	10.0	19 700, 537 000
20	30	50	20	1 416 000	3.4	522 400, 1 710 000
13	30	50	280	628 400	3.2	—
$ZrCp_2Cl_2$	30	50	610	340 800	2.1	—

Note: Ti:Al ratio of 1:500, toluene solvent, 30 min, 1 atm ethylene Activities are in units of g $mmol^{-1}$ h^{-1} atm^{-1}. Limited ethylene supply may result in an underestimation of the activity.

[a] Values are overall averages observed.

[b] PDI, polydispersity index.

[c] Peak molecular weight from nonlinear Gaussian fit.

[d] Too little polymer to analyze.

[e] Polymer would not dissolve in solvent.

Table 4. Ethylene polymerization data.

Precatalyst	T (°C)	Co-catalyst[a]	Activity	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI[b]
5	10	MAO	1510			
5	15	MAO	1190			
5	20	MAO	1050			
13	10	MAO	1580			
13	15	MAO	1260			
13	20	MAO	1140			
13	30	MAO	780			
$ZrCp_2Me_2$	10	MAO	1880			
$ZrCp_2Cl_2$	10	MAO	2030			
18	10	TB (1 equiv)	630	213 600	566 400	2.7
18	10	TB (2 equiv)	895	126 300	382 300	3.0
18	10	TB (4 equiv)	525	252 200	718 000	2.9
20	10	TB (1 equiv)	10	50 300	206 700	4.1
20	10	TB (2 equiv)	95	628 900	1 270 000	2.0
20	10	TB (4 equiv)	126	157 500	491 000	3.1
$ZrCp_2Me_2$[c]	10	TB (2 equiv)	1030	171 000	334 800	1.9

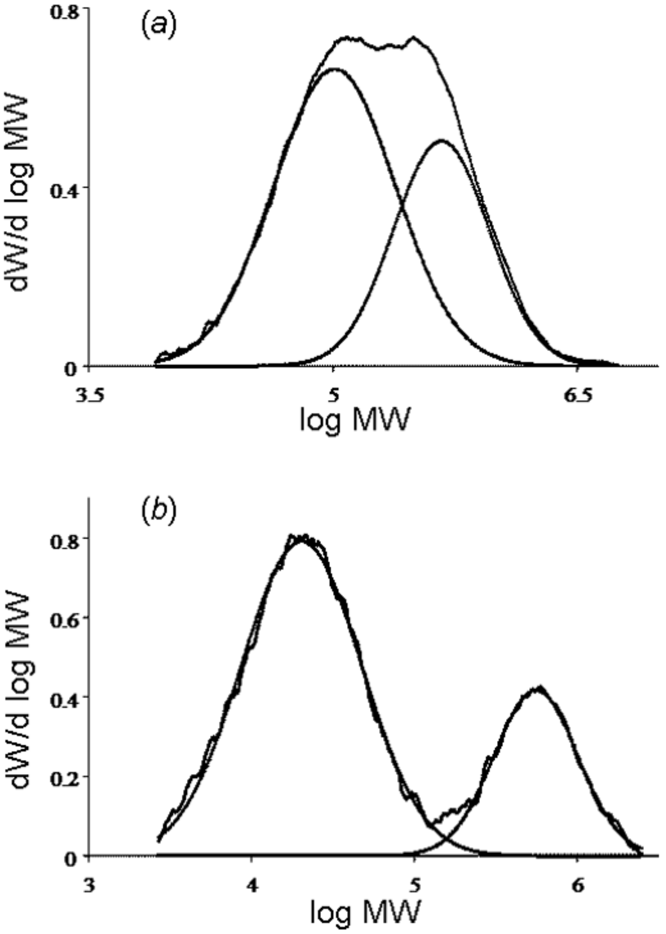
Note: Toluene solvent, 30 °C, 1.82 atm ethylene (constant). Activities are in units of g $mmol^{-1}$ h^{-1} atm^{-1}.

[a] For MAO activation, Ti:Al or Zr:Al ratio of 1:500; for TB ($[Ph_3C][B(C_6F_5)_4]$), Al(*i*-Pr)$_3$ scrubber, Ti:Al ratio of 1:5.

[b] PDI, polydispersity index.

[c] Zr:Al ratio of 1:20.

Fig. 2. Observed and two-Gaussian fit of GPC of polyethylene derived from the precatalysts (*a*) **9** and (*b*) **19**.



4 equiv. of $[Ph_3C][B(C_6F_5)_4]$ resulted in the efficient polymerization of ethylene (Table 4). In general, with an increase in the amount of activator from 1 to 2 equiv., polymerization activities also increased. The bulkier Cp* derivative showed 4 times the activity of the Cp analog when 4 equiv. of $[Ph_3C][B(C_6F_5)_4]$ were used, and ca. 60 times the activity when only 1 equiv. of activator was employed. The resulting polymers showed monodisperse GPC traces with PDI values less than 4. This is in contrast to the results obtained when MAO was used as an activator.

Fig. 3. GPC of polyethylene from catalysts derived from **9** (——) and derivative **5** (– – –).

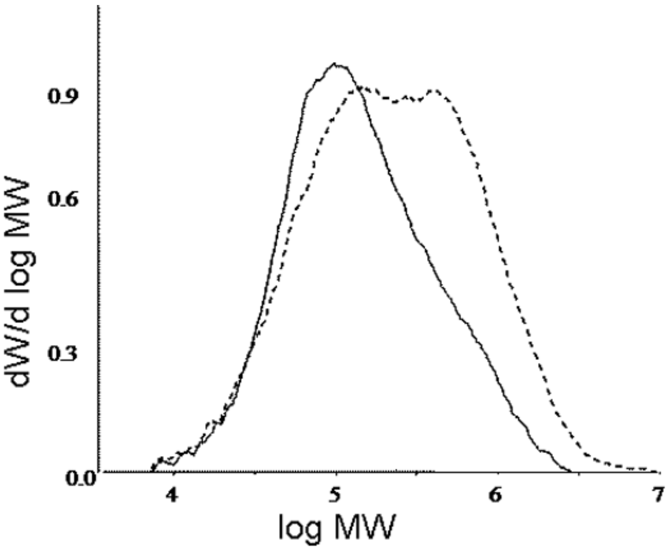
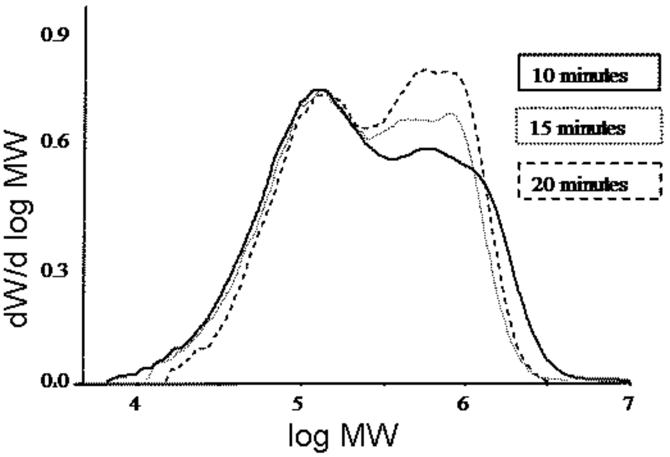


Fig. 4. GPC of polyethylene from catalysts derived from **5** as a function of time.



In conclusion, MAO or $[Ph_3C][B(C_6F_5)_4]$ activation of the monometallic and bimetallic benzyl-phosphinimide catalysts produced polyethylene with good activities. While all these catalyst systems gave relatively broad molecular weight distributions, catalysts generated using MAO gave bimodal polymers. Given that previous studies have shown that other phosphinimide catalysts give single-site activity, the present observations infer that MAO reacts with the present catalysts, probably at the benzylic fragment, to modify the active species, resulting in two (or more) catalyst sites. While this postulate remains unconfirmed, it is noteworthy that in related systems, Bochmann and co-workers (34) have observed metallation of methylene groups in phosphinimide ligands. While the precise cause remains a subject of investigation, it is clear that modification of the catalyst structure alters the nature of the resulting polymer. We are currently investigating strategies to other modified catalyst systems in an effort to understand the relationship between catalyst structure and polymer properties in more detail.

Experimental

General data

The syntheses were performed under an atmosphere of dry, oxygen-free nitrogen in a Vacuum Atmospheres (Hawthorne, Calif.) inert atmosphere glove box or by standard Schlenk techniques. Proton NMR data were acquired on a Bruker Avance 500-MHz spectrometer, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data on a Bruker Avance 300-MHz spectrometer. Proton and ^{13}C NMR chemical shifts are listed downfield from $SiMe_4$ in parts per million and were referenced to the residual proton or carbon peak of the solvent. Phosphorus-31 NMR data were referenced using an external standard relative to 85% H_3PO_4. All NMR spectra were recorded in C_6D_6 unless otherwise stated. Combustion analyses were performed by Galbraith Laboratories Inc. or inhouse elemental analysis services. In a very few cases, despite repeated analyses and the use of added oxidant, C analyses yielded deviations from calculated values. We attribute this to partial formation of Ti–C during combustion of the Ti-organometallic derivatives. Gel permeation chromatography (GPC) was performed employing a Waters 150C GPC using 1,2,4-trichlorobenzene as the mobile phase at 140 °C at NOVA Research and Technology Centre (Calgary, Alta.). The samples were prepared for GPC analyses by dissolving the polymer in the mobile-phase solvent in an external oven at 0.1% (*w*/*v*) and were filtered before injection. Molecular weights are expressed as polyethylene equivalents with a relative standard deviation of 2.9% and 5.0% for M_n and M_w, respectively. Reagent-grade solvents and NEt_3 were purchased from Aldrich Chemical Co. Benzene, toluene, and Et_2O were dried over Na, MeOH was dried over Mg, and NEt_3 was dried over KOH prior to distillation. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotopes Laboratories (Andover, Mass.) and degassed by at least 4 freeze/pump/thaw cycles before storing over 4Å molecular sieves. The compounds R_2BnP and $R_2BnPNSiMe_3$ (Bn = benzyl; R = *t*-Bu, Cy) (35) and $CpTiCl_3$ (41) were prepared according to literature methods, and the phosphines were prepared via a modification of a literature procedure (36). The reagents MeMgBr, Me_3SiN_3, and *p*-$C_6H_4(CH_2Br)_2$ were purchased from Aldrich Chemical Co., and HP(*t*-Bu)$_2$, $HPCy_2$, and Cp*$TiCl_3$ were purchased from Strem Chemical Co. (Newburyport, Mass.); all were used without further purification.

Synthesis of *p*-$C_6H_4(CH_2PR_2)_2$ (R = *t*-Bu, Cy)

Compounds **1** (R = *t*-Bu) and **2** (R = Cy) were prepared in a similar manner to a literature method for the related meta-substituted analogs (36). *p*-$C_6H_4(CH_2Br)_2$ (0.88 g, 3.3 mmol) was slurried in MeOH, and HP(*t*-Bu)$_2$ (1.08 g, 7.3 mmol) was added via syringe. The mixture was stirred at 25 °C for 16 h, during which time the mixture became a homogeneous solution. NEt_3 (0.74 g, 7.3 mmol) was added via syringe, and a fine white solid precipitated from solution. The solid was washed with MeOH (3 × 20 mL) and dried in vacuo for 5 h. A second crop was obtained by concentrating the mother liquor and precipitating the product with degassed water; no degradation in purity was evidenced by the ^1H NMR spectrum. Compound **1**: White solid. Yield 1.16 g (88%). ^1H NMR: 7.38 (s, 4H, C_6H_4), 2.73 (s, 4H, CH_2), 1.06 (d, 36H, $J_{P–H}$ = 10 Hz, *t*-Bu). $^{13}C\{^1H\}$ NMR: 138.4 (s, C_6H_4), 130.1 (s, C_6H_4), 32.1 (d, $J_{P–C}$ = 54 Hz, *t*-Bu), 30.1 (s, *t*-Bu), 29.0 (d, $J_{P–C}$ = 48 Hz, CH_2). $^{31}P\{^1H\}$ NMR: 33.4 (s). Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. Anal. Calcd. for $C_{24}H_{44}P_2$: C 73.06, H 11.24; found: C 72.36, H 11.05. Compound **2**: White solid. Yield 4.23 g, 85%. ^1H NMR: 7.33 (s, 4H, C_6H_4), 2.72 (s, 4H, CH_2P), 1.80–1.51 (m, 18H, Cy), 1.25–1.12 (m, 26H, Cy). $^{13}C\{^1H\}$ NMR: 137.9 (s, C_6H_4), 129.7 (s, C_6H_4), 34.0 (d, $J_{P–C}$ = 17 Hz, Cy), 30.3 (d, $J_{P–C}$ = 14 Hz, CH_2P), 29.7 (d, $J_{P–C}$ = 10 Hz, Cy), 27.6 (s, Cy), 26.9 (s, Cy). $^{31}P\{^1H\}$ NMR: 1.2 (s). Anal. Calcd. for $C_{32}H_{52}P_2$: C 77.07, H 10.51; found: C 76.42, H 10.68.

Synthesis of *p*-$C_6H_4(CH_2PR_2NSiMe_3)_2$ (R = *t*-Bu, Cy)

Compounds **3** (R = *t*-Bu) and **4** (R = Cy) were both prepared in a similar manner, and one sample preparation is detailed. Solid **1** (0.69 g, 1.7 mmol) and Me_3SiN_3 (1.00 g, 8.7 mmol) were combined to generate a slurry. The mixture was heated at reflux for 15 h, after which time the excess Me_3SiN_3 was removed in vacuo. The beige solid was crushed with a mortar and pestle into a fine powder, washed with hexanes (3 × 10 mL), and dried in vacuo for an additional 5 h. Compound **3**: Yield 0.88 g, 88%. Crystals suitable for X-ray diffraction were grown by slow evaporation from hexanes. ^1H NMR: 7.39 (s, 4H, C_6H_4), 2.73 (d, 4H, $J_{P–H}$ = 10 Hz, CH_2), 0.99 (d, 36H, $J_{P–H}$ = 13 Hz, *t*-Bu), 0.35 (s, 18H, Me). $^{13}C\{^1H\}$ NMR: 133.4 (s, C_6H_4), 130.4 (s, C_6H_4), 37.1 (d, $J_{P–C}$ = 60 Hz, CH_2), 30.1 (d, $J_{P–C}$ = 57 Hz, CH_2), 27.6 (s, *t*-Bu), 1.4 (s, Me_3). $^{31}P\{^1H\}$ NMR: 24.6 (s). Anal. Calcd. for $C_{30}H_{62}N_2P_2Si_2$: C 63.33, H 10.98, N 4.92; found: C 63.34, H 10.36, N 4.93. Compound **4**: Yield 2.77 g, 94%. ^1H NMR: 7.34 (s, 4H, C_6H_4), 2.67 (d, 4H, $J_{P–H}$ = 12 Hz, CH_2P), 1.78–1.58 (m, 18H, Cy), 1.45–1.07 (m, 26H, Cy), 0.41 (s, 18H, Me). $^{13}C\{^1H\}$ NMR: 132.9 (s, C_6H_4), 130.1 (s, C_6H_4), 37.6 (d, $J_{P–C}$ = 65 Hz, Cy), 33.7 (d, $J_{P–C}$ = 60 Hz, CH_2P), 27.2 (d, $J_{P–C}$ = 13 Hz, Cy), 26.5 (s, Cy), 26.2 (s, Cy), 5.2 (s, Me_3). $^{31}P\{^1H\}$ NMR: 13.5 (s). Anal. Calcd. for $C_{38}H_{70}N_2P_2Si_2$: C 67.81, H 10.48, N 4.16; found: C 68.08, H 10.85, N 3.89.

Synthesis of $(R_2BnPN)Cp'TiCl_2$ (Cp′ = Cp*, Cp; R = *t*-Bu, Cy)

Compounds **5** (Cp′ = Cp*; R = *t*-Bu), **6** (Cp′ = Cp*; R = Cy), **7** (Cp′ = Cp; R = *t*-Bu), and **8** (Cp′ = Cp; R = Cy) were all prepared in a similar manner, and thus only one preparation is detailed. Solid Cp*$TiCl_3$ (1.12 g, 3.8 mmol) was dissolved in toluene (100 mL) to give a clear, red solution. Liquid (*t*-Bu)$_2BnPNSiMe_3$ (1.24 g, 3.8 mmol) was added dropwise at 25 °C, and the mixture was stirred for 24 h. The volatile products were removed in vacuo, and the bright orange solid was washed with hexanes (3 × 10 mL) and dried. Compound **5**: Yield 1.73 g, 91%. ^1H NMR: 7.39 (d, 2H, $J_{H–H}$ = 8 Hz, C_6H_5), 7.19 (t, 2H, $J_{H–H}$ = 8 Hz, Ph), 7.08 (t, 1H, $J_{H–H}$ = 8 Hz, Ph), 2.92 (d, 2H, $J_{P–H}$ = 12 Hz, CH_2), 2.21 (s, 15H, Cp*), 1.10 (d, 18H, $J_{P–H}$ = 14 Hz, P*t*-Bu$_2$). $^{13}C\{^1H\}$ NMR: 140.8 (s, Ph), 131.2 (s, Ph), 128.7 (s, Ph), 127.1 (s, Ph), 125.9 (s, Cp*), 39.6 (d, $J_{P–C}$ = 52 Hz, *t*-Bu), 30.9 (d, $J_{P–C}$ = 48 Hz, CH_2), 27.8 (s, *t*-Bu), 13.1 (s, Cp*). $^{31}P\{^1H\}$ NMR: 35.3 (s). Anal. Calcd. for $C_{25}H_{40}Cl_2NPTi$: C 59.54, H 7.99, N 2.78; found: C 59.74, H 7.88, N 2.95. Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. Compound **6**: Bright orange solid. Yield 580 mg, 93%. ^1H NMR δ: 7.20 (d, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*o*-H)), 7.15 (dd, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*m*-H)), 7.04 (t, 1H, $^3J_{H–H}$ = 8 Hz, Ph (*p*-H)), 3.01 (d, 2H, $^2J_{P–H}$ = 14 Hz, CH_2P), 2.20 (s, 15H, Cp*), 1.71–0.96 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR δ: 132.6 (d, $^2J_{P–C}$ = 7 Hz, Ph (*ipso*-C)), 130.5 (d, $^3J_{P–C}$ = 5 Hz, Ph (*o*-C)), 128.9 (s, Ph (*m*-C)), 127.2 (s, Ph (*p*-C)), 125.9 (s, Cp*), 37.2 (d, $^1J_{P–C}$ = 59 Hz, Cy (*ipso*-C)), 32.2 (d, $^1J_{P–C}$ = 52 Hz, CH_2P), 26.8 (d, $^2J_{P–C}$ = 12 Hz, Cy (*o*-C)), 26.7 (d, $^2J_{P–C}$ = 12 Hz, Cy (*o*-C)), 26.1 (s, Cy (*m*-C)), 26.0 (s, Cy (*p*-C)), 13.2 (s, Cp*). $^{31}P\{^1H\}$ NMR δ: 23.0 (s). Anal. Calcd. for $C_{29}H_{44}Cl_2NPTi$: C 62.60, H 7.97, N 2.52; found: C 62.29, H 8.27, N 2.45. Orange crystals suitable for X-ray diffraction were grown by slow diffusion of pentanes/hexanes into benzene. Compound **7**: Bright yellow solid. Yield

0.390 g, 77%. ^{1}H NMR δ: 7.26 (d, 2H, $^3J_{H–H}$ = 8 Hz, Ph), 7.20 (t, 2H, $^3J_{H–H}$ = 8 Hz, Ph), 7.07 (t, 1H, $^3J_{H–H}$ = 8 Hz, Ph), 6.22 (s, 5H, Cp), 2.61 (d, 2H, $^2J_{P–H}$ = 10 Hz, CH$_2$), 1.04 (d, 18H, $^3J_{P–H}$ = 15 Hz, *t*-Bu). ^{13}C{^{1}H} NMR δ: 131.5 (d, $^2J_{P–C}$ = 5 Hz, (*ipso*-C)), 128.7 (d, $^3J_{P–C}$ = 5 Hz, (*o*-C)), 128.6 (s, Ph), 128.3 (s, Ph), 115.5 (s, Cp), 39.3 (d, $^1J_{P–C}$ = 51 Hz, *t*-Bu), 28.9 (d, $^1J_{P–C}$ = 47 Hz, CH$_2$), 27.2 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 34.9 (s). Anal. Calcd. for $C_{20}H_{30}Cl_2NPTi$: C 55.32, H, 6.96, N 3.23; found: C 55.49, H, 7.14, N 3.19. Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. Compound **8**: Bright yellow solid. Yield 685 mg, 92%. ^{1}H NMR δ: 7.27 (d, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*o*-H)), 7.18 (dd, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*m*-H)), 7.06 (t, 1H, $^3J_{H–H}$ = 8 Hz, Ph (*p*-H)), 6.38 (s, 5H, Cp), 2.65 (d, 2H, $^2J_{P–H}$ = 13 Hz, CH$_2$P), 1.74–0.84 (m, 22H, Cy). ^{13}C{^{1}H} NMR δ: 131.6 (d, $^2J_{P–C}$ = 8 Hz, Ph (*ipso*-C)), 130.8 (d, $^3J_{P–C}$ = 5 Hz, Ph (*o*-C)), 128.9 (s, Ph (*m*-C)), 128.5 (s, Ph (*p*-C)), 115.2 (s, Cp), 36.6 (d, $^1J_{P–C}$ = 58 Hz, Cy (*ipso*-C)), 30.9 (d, $^1J_{P–C}$ = 52 Hz, CH$_2$P), 26.6 (d, $^2J_{P–C}$ = 13 Hz, Cy (*o*-C)), 25.9 (s, Cy (*m*-C)), 25.7 (s, Cy (*p*-C)). ^{31}P{^{1}H} NMR δ: 24.3 (s). Anal. Calcd. for $C_{24}H_{34}Cl_2NPTi$: C 59.27, H 7.05, N 2.88; found: C 59.68, H 7.28, N 2.82. Yellow crystals suitable for X-ray diffraction were grown by slow diffusion of pentanes/hexanes into benzene.

Synthesis of *p*-$C_6H_4(CH_2PR_2NTiCp'Cl_2)_2$ (Cp′ = Cp*, Cp; R = *t*-Bu, Cy)

Compounds **9** (Cp′ = Cp*; R = *t*-Bu), **10** (Cp′ = Cp*; R = Cy), **11** (Cp′ = Cp; R = *t*-Bu), and **12** (Cp′ = Cp; R = Cy) were all prepared in a similar manner, and only one sample preparation is detailed. Compound **3** (0.81 g, 1.2 mmol) and Cp*TiCl$_3$ (0.70 g, 2.4 mmol) were slurried in toluene (80 mL) to afford a bright orange, foggy solution. The mixture was heated at reflux for 15 h, after which time it was filtered. The filtrate was concentrated to ca. 20 mL, and the bright orange powder that precipitated was filtered, washed with benzene (3 × 15 mL), and dried in vacuo. Compound **10**: Yield 2.34 g, 95%. ^{1}H NMR (CD$_2$Cl$_2$): 7.48 (s, 4H, C$_6$H$_4$), 3.38 (d, 4H, $J_{P–H}$ = 12 Hz, CH$_2$), 2.14 (s, 30H, Cp*), 1.34 (d, 36H, $J_{P–H}$ = 15 Hz, *t*-Bu). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 133.4 (s, C$_6$H$_4$), 131.5 (s, C$_6$H$_4$), 123.2 (s, Cp*), 40.6 (s, CH$_2$), 39.8 (d, $J_{P–C}$ = 55 Hz, *t*-Bu), 28.3 (s, *t*-Bu), 8.9 (s, Cp*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 37.2 (s). Anal. Calcd. for $C_{44}H_{74}Cl_4N_2P_2Ti_2$: C 56.79, H 8.02, N 3.01; found: C 54.92, H 8.16, N 3.35. Compound **10**: Bright orange solid. Yield 0.98 g, 79%. ^{1}H NMR: 7.36 (s, 4H, C$_6$H$_4$), 3.01 (d, 4H, $J_{P–H}$ = 13 Hz, CH$_2$P), 2.24 (s, 30H, Cp*), 1.71–1.45 (m, 18H, Cy), 1.18–1.03 (m, 26H, Cy). ^{13}C{^{1}H} NMR: 137.4 (s, C$_6$H$_4$), 131.0 (s, C$_6$H$_4$), 125.8 (s, Cp*), 37.2 (d, $J_{P–C}$ = 59 Hz, Cy), 31.9 (d, $J_{P–C}$ = 52 Hz, CH$_2$P), 26.8 (d, $J_{P–C}$ = 12 Hz, Cy), 26.1 (s, Cy (*m*-C)), 26.1 (s, Cy), 13.2 (s, Cp*). ^{31}P{^{1}H} NMR: 22.4 (s). Anal. Calcd. for $C_{52}H_{82}Cl_4N_2P_2Ti_2$: C 60.36, H 7.99, N 2.71; found: C 60.20, H 8.19, N 2.76. Crystals suitable for X-ray diffraction were grown by slow evaporation from toluene. Compound **11**: Yellow solid. Yield 2.34 g, 95%. ^{1}H NMR (CD$_2$Cl$_2$): 7.54 (s, 4H, C$_6$H$_4$), 6.29 (s, 10H, C$_5$H$_5$), 3.31 (d, 4H, $J_{P–H}$ = 10 Hz, CH$_2$), 1.40 (d, 36H, $J_{P–H}$ = 13 Hz, *t*-Bu). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 132.7 (s, C$_6$H$_4$), 132.0 (s, C$_6$H$_4$), 116.0 (s, Cp), 46.4 (s, CH$_2$), 40.0 (d, $J_{P–C}$ = 51 Hz, *t*-Bu), 27.8 (s, *t*-Bu). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 38.7 (s). Anal. Calcd. for $C_{34}H_{54}Cl_4N_2P_2Ti_2$: C 51.67, H 6.89, N 3.54; found: C 52.65, H 7.64, N 3.45. Compound **12**: Light yellow solid. Yield 1.36 g, 95%. ^{1}H NMR: 7.46 (s, 4H, C$_6$H$_4$), 6.39 (s, 10H, Cp), 3.21 (d, 4H, $J_{P–H}$ = 12 Hz, CH$_2$P), 1.96–1.27 (m, 44H, Cy). ^{13}C{^{1}H} NMR: 131.8 (s, C$_6$H$_4$), 131.5 (s, C$_6$H$_4$), 115.7 (s, Cp), 37.1 (d, $J_{P–C}$ = 58 Hz, Cy), 31.1 (d, $J_{P–C}$ = 53 Hz, CH$_2$P), 27.0 (d, $J_{P–C}$ = 13 Hz, Cy), 26.3 (s, Cy), 26.3 (s, Cy). ^{31}P{^{1}H} NMR: 27.0 (s). Anal. Calcd. for $C_{42}H_{62}Cl_4N_2P_2Ti_2$: C 56.40, H 6.99, N 3.13; found: C 56.23, H 7.00, N 3.36. Crystals suitable for X-ray diffraction were grown by slow evaporation from CH$_2$Cl$_2$.

Synthesis of (R$_2$BnPN)TiCp′Me$_2$ (Cp′ = Cp*, Cp; R = *t*-Bu, Cy)

Compounds **13** (Cp′ = Cp*; R = *t*-Bu), **14** (Cp′ = Cp*; R = Cy), **15** (Cp′ = Cp; R = *t*-Bu), and **16** (Cp′ = Cp; R = Cy) were all prepared in a similar manner, and thus only the preparation of **13** is detailed. Compound **5** (160 mg, 0.32 mmol) was slurried in Et$_2$O (15 mL), and a 3.0 mol L^{-1} solution of MeMgBr in the same solvent (2.24 mL, 0.67 mmol) was added dropwise via syringe at 25 °C. The heterogeneous solution was stirred for 15 h, after which time the solvent was removed in vacuo. Extraction with hexanes (3 × 10 mL) and filtration through Hyflo Super Cel® (Beaver Chemicals, Burlington, Ont.) afforded a bright yellow solution. Subsequent removal of the solvent in vacuo generated bright yellow crystals of **13**. Yield 122 mg, 83%. ^{1}H NMR δ: 7.38 (d, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*o*-H)), 7.15 (dd, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*m*-H)), 7.08 (t, 1H, $^3J_{H–H}$ = 8 Hz, Ph (*p*-H)), 2.90 (d, 2H, $^2J_{P–H}$ = 12 Hz, CH$_2$), 2.03 (s, 15H, Cp*), 1.16 (d, 18H, $^3J_{P–H}$ = 14 Hz, *t*-Bu), 0.39 (s, 6H, TiMe). ^{13}C{^{1}H} NMR δ: 135.0 (d, $^2J_{P–C}$ = 7 Hz, Ph (*ipso*-C)), 130.9 (d, $^3J_{P–C}$ = 5 Hz, Ph (*o*-C)), 128.3 (s, Ph (*m*-C)), 126.7 (s, Ph (*p*-C)), 118.5 (s, Cp*), 44.4 (s, TiMe), 39.0 (d, $^1J_{P–C}$ = 54 Hz, *t*-Bu), 31.6 (d, $^1J_{P–C}$ = 48 Hz, CH$_2$), 28.0 (s, *t*-Bu), 12.2 (s, Cp*). ^{31}P{^{1}H} NMR δ: 21.4 (s). Anal. Calcd. for $C_{27}H_{46}NPTi$: C 69.96, H 10.00, N 3.02; found: C 69.59, H 10.03, N 3.02. Yellow crystals suitable for X-ray diffraction were grown by slow evaporation from hexanes. Compound **14**: Light yellow solid. Yield 100 mg, 47%. ^{1}H NMR δ: 7.28 (d, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*o*-H)), 7.17 (dd, 2H, $^3J_{H–H}$ = 8 Hz, Ph (*m*-H)), 7.06 (t, 1H, $^3J_{H–H}$ = 8 Hz, Ph (*p*-H)), 2.93 (d, 2H, $^2J_{P–H}$ = 13 Hz, CH$_2$P), 2.08 (s, 15H, Cp*), 1.91–1.03 (m, 22H, Cy), 0.45 (s, 6H, TiMe). ^{13}C{^{1}H} NMR δ: 134.2 (d, $^2J_{P–C}$ = 7 Hz, Ph (*ipso*-C)), 130.3 (d, $^3J_{P–C}$ = 5 Hz, Ph (*o*-C)), 128.6 (s, Ph (*m*-C)), 126.8 (s, Ph (*p*-C)), 118.5 (s, Cp*), 42.6 (s, TiMe), 38.1 (d, $^1J_{P–C}$ = 60 Hz, Cy), 34.4 (d, $^1J_{P–C}$ = 52 Hz, CH$_2$P), 27.0 (d, $^2J_{P–C}$ = 3 Hz, Cy), 26.8 (d, $^2J_{P–C}$ = 3 Hz, Cy), 26.4 (s, Cy), 26.3 (s, Cy), 12.3 (s, Cp*). ^{31}P{^{1}H} NMR δ: 8.4 (s). Anal. Calcd. for $C_{31}H_{50}NPTi$: C 72.22, H, 9.77, N 2.72; found: C 71.93, H, 10.10, N 2.52. Yellow–orange crystals suitable for X-ray diffraction were grown by slow evaporation from pentanes. Compound **15**: Beige solid. Yield 74 mg, 78%. ^{1}H NMR δ: 7.32 (d, 2H, $^3J_{H–H}$ = 7 Hz, Ph (*o*-H)), 7.16 (dd, 2H, $^3J_{H–H}$ = 7 Hz, Ph (*m*-H)), 7.05 (t, 1H, $^3J_{H–H}$ = 7 Hz, Ph (*p*-H)), 6.08 (s, 5H, Cp), 2.74 (d, 2H, $^2J_{P–H}$ = 11 Hz, CH$_2$), 1.06 (d, 18H, $^3J_{P–H}$ = 14 Hz, *t*-Bu), 0.70 (s, 6H, TiMe). ^{13}C{^{1}H} NMR δ: 134.0 (s, Ph (*ipso*-C)), 131.1 (d, $^3J_{P–C}$ = 4 Hz, Ph (*o*-C)), 128.4 (s, Ph (*m*-C)), 126.8 (s, Ph (*p*-C)), 111.1 (s, Cp), 41.4 (s, TiMe), 38.5 (d, $^1J_{P–C}$ = 54 Hz, *t*-Bu), 30.2 (d, $^1J_{P–C}$ = 48 Hz, CH$_2$), 27.5 (s, *t*-Bu).

$^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ: 21.6 (s). Anal. Calcd. for $C_{22}H_{36}NPTi$: C 67.17, H 9.22, N 3.56; found: C 67.09, H 9.03, N 3.02. Compound **16**: Beige solid. Yield 230 mg, 46%. ^1H NMR δ: 7.33 (d, 2H, $^3J_{H-H}$ = 8 Hz, Ph (*o*-H)), 7.18 (dd, 2H, $^3J_{H-H}$ = 8 Hz, Ph (*m*-H)), 7.06 (t, 1H, $^3J_{H-H}$ = 8 Hz, Ph (*p*-H)), 6.18 (s, 5H, Cp), 2.71 (d, 2H, $^2J_{P-H}$ = 13 Hz, CH_2P), 1.62–0.98 (m, 22H, Cy), 0.73 (s, 6H, TiMe). $^{13}C\{^1H\}$ NMR δ: 133.5 (d, $^2J_{P-C}$ = 7 Hz, Ph (*ipso*-C)), 130.5 (d, $^3J_{P-C}$ = 5 Hz, Ph (*o*-C)), 128.5 (s, Ph (*m*-C)), 127.0 (s, Ph (*p*-C)), 110.8 (s, Cp), 40.7 (s, TiMe), 37.6 (d, $^1J_{P-C}$ = 60 Hz, Cy (*ipso*-C)), 32.9 (d, $^1J_{P-C}$ = 53 Hz, CH_2P), 26.8 (d, $^2J_{P-C}$ = 12 Hz, Cy (*o*-C)), 26.3 (s, Cy (*p*-C)), 26.0 (d, $^3J_{P-C}$ = 8 Hz, Cy (*m*-C)). $^{31}P\{^1H\}$ NMR δ: 10.2 (s). Anal. Calcd. for $C_{26}H_{40}NPTi$: C 70.11, H 9.05, N 3.14; found: C 69.03, H 9.20, N 3.08. Yellow crystals suitable for X-ray diffraction were grown by slow evaporation from pentanes.

Synthesis of *p*-$C_6H_4(CH_2PR_2NTiCp'Me_2)_2$ (Cp′ = Cp*, Cp; R = *t*-Bu, Cy)

Compounds **17** (Cp′ = Cp*; R = *t*-Bu), **18** (Cp′ = Cp*; R = Cy), **19** (Cp′ = Cp; R = *t*-Bu), and **20** (Cp′ = Cp; R = Cy) were all prepared in a similar manner and one sample preparation is detailed. Compound **5** (0.21 g, 0.27 mmol) was slurried in Et_2O (25 mL), and a solution of MeMgBr in the same solvent (1.4 mmol) was added dropwise via syringe at 25 °C. The heterogeneous solution was stirred for 15 h, after which time the solvent was removed in vacuo. Extraction with hexanes (3 × 10 mL) and filtration through Hyflo Super Cel® afforded a colorless liquid. Removal of the solvent in vacuo generated a white solid. The yield increased when extraction was performed with toluene. Compound **17**: Yield 0.23 g, 77%. ^1H NMR: 7.50 (s, 4H, C_6H_4), 2.96 (d, 4H, J_{P-H} = 11 Hz, CH_2), 2.12 (s, 30H, Cp*), 1.17 (d, 36H, J_{P-H} = 14 Hz, *t*-Bu), 0.46 (s, 12H, TiMe). $^{13}C\{^1H\}$ NMR: 133.4 (s, C_6H_4), 130.8 (s, C_6H_4), 118.4 (s, Cp*), 44.4 (s, TiMe), 38.9 (d, J_{P-C} = 54 Hz, *t*-Bu), 31.6 (d, J_{P-C} = 48 Hz, CH_2), 28.0 (s, *t*-Bu), 12.3 (s, Cp*). $^{31}P\{^1H\}$ NMR: 22.0 (s). Anal. Calcd. for $C_{48}H_{86}N_2P_2Ti_2$: C 67.91, H 10.21, N 3.30; found: 67.51, H 9.96, N. 2.95. Compound **18**: White solid. Yield 0.41 g, 73%. ^1H NMR: 7.35 (s, 4H, C_6H_4), 2.92 (d, 4H, J_{P-H} = 13 Hz, CH_2P), 2.10 (s, 30H, Cp*), 1.81–1.10 (m, 44H, Cy), 0.43 (s, 12H, TiMe). $^{13}C\{^1H\}$ NMR: 132.5 (s, C_6H_4), 130.5 (s, C_6H_4), 122.3 (s, Cp*), 42.7 (s, TiMe), 38.2 (d, J_{P-C} = 61 Hz, Cy), 34.0 (d, J_{P-C} = 52 Hz, CH_2P), 27.1 (d, J_{P-C} = 12 Hz, Cy), 26.5 (d, J_{P-C} = 6 Hz, Cy), 26.4 (s, Cy), 11.9 (s, Cp*). $^{31}P\{^1H\}$ NMR: 8.0 (s). Anal. Calcd. for $C_{54}H_{94}N_2P_2Ti_2$: C 69.81, H, 10.20, N 3.02; found: 69.56, H, 9.94, N 2.94. **19**: Colorless block crystals. Yield 0.16 g, 83%. ^1H NMR: 7.48 (s, 4H, C_6H_4), 6.18 (s, 10H, Cp), 2.80 (d, 4H, J_{P-H} = 10 Hz, CH_2P), 1.06 (d, 36H, J_{P-H} = 14 Hz, *t*-Bu), 0.72 (s, 12H, TiMe). $^{13}C\{^1H\}$ NMR: 132.5 (s, C_6H_4), 130.8 (s, C_6H_4), 110.9 (s, Cp), 41.3 (s, CH_2P), 38.4 (d, J_{P-C} = 54 Hz, *t*-Bu), 31.7 (s, TiMe), 27.4 (s, *t*-Bu). $^{31}P\{^1H\}$ NMR: 22.6 (s). Anal. Calcd. for $C_{38}H_{66}N_2P_2Ti_2$: C 64.41, H 9.39, N 3.95; found: C 64.15, H 9.39, N 3.47. Crystals suitable for X-ray diffraction were grown by slow evaporation from toluene. Compound **20**: White solid. Yield 0.45 g, 77%. ^1H NMR δ: 7.48 (s, 4H, C_6H_4), 6.22 (s, 10H, Cp), 2.70 (d, 4H, J_{P-H} = 12 Hz, CH_2P), 1.65–1.06 (m, 44H, Cy), 0.74 (s, 12H, TiMe). $^{13}C\{^1H\}$ NMR: 132.1 (s, C_6H_4), 130.6 (s, C_6H_4), 110.8 (s, Cp), 40.8 (s, TiMe), 37.6 (d, J_{P-C} = 60 Hz, Cy), 32.4 (d, J_{P-C} = 53 Hz, CH_2P), 26.9 (d, J_{P-C} = 12 Hz, Cy), 26.3 (s, Cy), 26.1 (s, Cy). $^{31}P\{^1H\}$ NMR: 10.1 (s). Anal. Calcd. for $C_{52}H_{80}N_2P_2Ti_2$: C 70.10, H 9.05, N 3.14; found: C 70.30, H 9.45, N 3.06. Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene.

Polymerization protocol

Two protocols were employed. In the first, a Schlenk flask was charged with toluene (50 mL) and MAO (1000 equiv., 10% in toluene), and the solution was presaturated with the monomer by briefly evacuating/backfilling (4×) and then stirring under an atmosphere of C_2H_4 for 5 min. A toluene, solution of the catalyst precursor (350 μmol) was injected, and the mixture was stirred at 25 °C for 30 min. The reaction was quenched with 1 mol/L HCl in MeOH, and the precipitated polymer was subsequently washed with HCl, HCl/MeOH, and toluene before drying at 50 °C for at least 48 h prior to weighing. In the second protocol, a 1-L Buchi reactor was dried in vacuo (10^{-2} mm Hg (1 mm Hg = 133.322 Pa)) for several hours. Toluene (500 mL) was transferred into the vessel under a positive pressure of N_2 and was heated to 30°C. The temperature was controlled (to ca. ±2 °C) with an external heating/cooling bath and was monitored by a thermocouple that extended into the polymerization vessel. The vessel was vented of N_2 and then pressurized with C_2H_4 (12 psig) while the solvent stirred at a rate of 150 rpm. A solution of MAO (1000 equiv., 10% in toluene) was injected and the mixture was stirred for 5 min. A toluene solution, of the precatalyst (50 μmol) was injected, the rate of stirring was increased to 1000 rpm, and the solution was stirred for 30 min. Any recorded exotherm was within the allowed temperature differential of the heating/cooling system. The quenching of the reaction and the collection/treatment of the polymer were as described above.

X-ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10-s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5° < 2θ < 45–50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages (Bruker AXS, Madison, Wis.). An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package (Bruker AXS, Madison, Wis.).

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations (42). The heavy-atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference

Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $\omega(|F_o| - |F_c|)^2$, where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$, and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C-H atom positions were calculated, and the hydrogens were allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which the hydrogens are bonded. The H-atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Details are provided in Table 1 and the supplementary data.

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Supplementary data

Supplementary data may be purchased form the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A OS2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on obtaining electronically). CCDC 223337–223350 contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; or deposit@ccdc.cam.ca.uk).

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