Titanium pyridyl-phosphinimide complexes — Synthesis, structure, and ethylene polymerization catalysis

Chad Beddie, Pingrong Wei, and Douglas W. Stephan

Abstract: A series of Ti–pyridyl-phosphinimide complexes of the form $Cp'TiX_2[NPR_2(2\text{-}CH_2Py)]$ (Cp' = Cp, Cp*, R = *i*-Pr, *t*-Bu, X = Cl, Me) have been prepared and characterized. These complexes generate ethylene polymerization catalysts upon activation with MAO or $B(C_6F_5)_3$. The resulting polymers exhibit broad molecular weight distributions. The role of the pyridyl group is discussed in light of stoichiometric reactions of $CpTiCl_2[NPR_2(2\text{-}CH_2Py)]$ with $B(C_6F_5)_3$.

Key words: phosphinimide complexes, pyridyl-phosphinimides, olefin polymerization.

Résumé : On a préparé et caractérisé une série de complexes Ti–pyridyl-phosphinimide de la forme $Cp'TiX_2[NPR_2(2\text{-}CH_2Py)]$ (Cp' = Cp, Cp*, R = *i*-Pr, *t*-Bu, X = Cl, Me). Par activation avec du MAO ou du $B(C_6F_5)_3$, ces complexes peuvent générer des catalyseurs pour la polymérisation de l'éthylène. Les polymères ainsi obtenus présentent de larges distributions de poids moléculaires. On discute du rôle du groupe pyridyle à la lumière des réactions stoechiométriques du $CpTiCl_2[NPR_2(2\text{-}CH_2Py)]$ avec le $B(C_6F_5)_3$.

Mots clés : complexe du phosphimide, pyridyl-phosphimides, polymérisation d'oléfines.

[Traduit par la Rédaction]

Introduction

The quest for new and effective homogeneous olefin polymerization catalysts have prompted much interest in early transition metal chemistry over the last two decades. Studies of non-metallocene systems have probed a wide variety of novel ancillary ligands (1–3). In our own work we have described titanium catalysts that contain bulky-phosphinimide ligands. This family of compounds of the form $CpTi(NPR_3)Cl_2$ yield active ethylene polymerization catalysts upon activation by MAO (4–10), while activation of the species $Ti(t\text{-}Bu_3PN)_2Me_2$ by $B(C_6F_5)_3$ or $Ph_3C[B(C_6F_5)_4]$ provides a remarkably active catalyst, producing polyethylene of narrow polydispersity and relatively high molecular weight (7). Single-site or living polymerization catalysts typically afford narrow polydispersities (1.0–2.0), however, in practical terms such resins prove difficult to process (11, 12). Thus, while single-site polymerization offers access to unique polymers, such materials prompt other problems. A number of methods can be employed to alter both the molecular weight and the molecular weight distributions of resulting polymers. In some cases, controlled hydrogenolysis (13, 14) can be utilitzed to broaden the molecular weight distributions. Alternatively, sequential catalysts can be employed to produce bimodal resins (15–29). In attempting to address this issue, we are examining potential single-site catalyst precursors that offer the possibility of generating several single-site catalysts upon activation. To this end, we report the synthesis and evaluation of Ti–phosphinimide complexes that incorporate pendant pyridyl substituents. The notion here is that these substituents may interact with the Lewis acid activators in a reversible manner and thus afford the possibility of two or more catalysts in solution. In this, our first report employing this strategy, we describe the synthesis and characterization of such compounds and evaluate such species in ethylene polymerization catalysis. The effect of the pyridyl group on the polymer molecular weight distributions is considered and discussed.

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Experimental

General data

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a MBraun inert atmosphere glovebox. Solvents were purified employing a Grubbs' type solvent purification system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C_6D_6 at 25 °C unless otherwise noted. All chemical shifts are reported in ppm. Trace amounts of protonated solvents were used as references and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Combustion analyses were done in-house employing a PerkinElmer CHN analyzer. The compounds $PR_2(2\text{-}CH_2Py)$ (R = *i*-Pr (**1**), *t*-Bu (**2**)) (30, 31), and $Me_3SiNP(i\text{-}Pr)_2(2\text{-}CH_2Py)$ (**3**) (32)) were prepared by literature methods. $CpTiCl_3$, Cp^*TiCl_3 ($Cp^* = Me_5Cp$), and

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Me_3SiN_3 were purchased from Strem Chemical Co. and Sigma-Aldrich Chemical Co., respectively, and employed without further purification. MAO and Al(*i*-Bu)$_3$, as well as GPC analysis service, were generously provided by NOVA Chemicals Corp.

Synthesis of Me_3SiNP-*t*-Bu_2(2-CH_2Py) (4)

To a solution of **2** (1.99 g, 8.38 mmol) in toluene (30 mL) was added Me_3SiN_3 (2.24 mL, 16.9 mmol). The resulting solution was heated at refluxing temperature for 48 h. The volume of the solution was reduced to ca. 5 mL, and the solution was filtered through Celite. The remaining solvent and excess Me_3SiN_3 were removed under vacuum, resulting in a pale yellow oil. Yield: 2.06 g, 6.36 mmol, 76%. ^{1}H NMR δ: 8.41 (d, 1H, $^3J_{H-H}$ = 4 Hz, Py), 7.44 (m, 1H, Py), 7.17 (m, 1H, Py), 6.65 (m, 1H, Py), 3.14 (d, 2H, $^2J_{P-H}$ = 11 Hz, CH_2), 1.04 (d, 18H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 0.30 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR δ: 157.0 (d, $^2J_{P-C}$ = 7 Hz, Py, (ipso-C)), 149.4 (s, Py), 135.3 (s, Py), 126.1 (s, Py), 121.6 (s, Py), 37.5 (d, $^1J_{P-C}$ = 61 Hz, *t*-Bu), 34.8 (d, $^1J_{P-C}$ = 53 Hz, CH_2), 27.8 (s, *t*-Bu), 5.3 (s, $SiMe_3$). ^{31}P{^{1}H} NMR δ: 25.9 (s).

Syntheses of Cp′$TiCl_2$[NPR_2(2-CH_2Py)] (Cp′ = Cp, *i*-Pr (5), *t*-Bu (6), Cp′ = Cp*, R = *i*-Pr (7), *t*-Bu (8))

These complexes were prepared in similar fashions and thus only one preparation is detailed. To a yellow slurry of $CpTiCl_3$ (0.370 g, 1.69 mmol) in toluene (40 mL) was added a solution of **3** (0.501 g, 1.69 mmol) in toluene (10 mL). The resulting solution was stirred for 12 h at room temperature. The solvent and volatile products were removed under vacuum to cause the formation of a yellow crystalline solid, which was washed with hexanes and dried under vacuum. Yield: 0.641 g, 1.57 mmol, 93%. **5**: ^{1}H NMR δ: 8.25 (br, 1H, Py), 7.40 (m, 1H, Py), 7.15 (m, 1H, Py), 6.58 (m, 1H, Py), 6.34 (s, 5H, Cp), 2.97 (d, 2H, $^2J_{P-H}$ = 13 Hz, CH_2), 1.68 (d(sept), 2H, $^3J_{P-H}$ = 10 Hz, $^3J_{H-H}$ = 7 Hz, CH), 0.94 (dd, 6H, $^3J_{P-H}$ = 16 Hz, $^3J_{H-H}$ = 7 Hz, Me) 0.86 (dd, 6H, $^3J_{P-H}$ = 17 Hz, $^3J_{H-H}$ = 7 Hz, Me). ^{13}C{^{1}H} NMR δ: 153.1 (d, $^2J_{P-C}$ = 7 Hz, Py (ipso-C)), 149.7 (s, Py), 135.6 (s, Py), 126.6 (s, Py), 122.6 (s, Py), 115.5 (s, Cp), 33.8 (d, $^1J_{P-C}$ = 51 Hz, CH_2), 27.3 (d, $^1J_{P-C}$ = 59 Hz, CH), 16.1 (d, $^2J_{P-C}$ = 6 Hz, Me). ^{31}P{^{1}H} NMR δ: 31.7 (s). Elemental anal. calcd.: C 50.15, H 6.19, N 6.88; found: C 49.95, H 6.41, N 6.76. X-ray quality crystals were obtained via slow evaporation of a toluene solution. **6**: Yield: 0.320 g, 0.735 mmol, 75%. ^{1}H NMR δ: 8.32 (d, 1H, $^3J_{H-H}$ = 5 Hz, Py), 7.65 (d, 1H, $^3J_{H-H}$ = 8 Hz, Py), 7.26 (m, 1H, Py), 6.63 (dd, 1H, $^3J_{H-H}$ = 6 Hz, $^3J_{H-H}$ = 6 Hz, Py), 6.26 (s, 5H, Cp), 3.06 (d, 2H, $^2J_{P-H}$ = 11 Hz, CH_2), 1.07 (d, 18H, $^3J_{P-H}$ = 15 Hz, *t*-Bu). ^{13}C{^{1}H} NMR δ: 153.7 (d, $^2J_{P-C}$ = 8 Hz, Py, (ipso-C)), 149.6 (s, Py), 136.7 (s, Py), 127.7 (d, $^3J_{P-C}$ = 3 Hz, Py), 122.6 (s, Py), 115.7 (s, Cp), 39.5 (d, $^1J_{P-C}$ = 51 Hz, *t*-Bu), 33.0 (d, $^1J_{P-C}$ = 46 Hz, CH_2), 27.4 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 36.6 (s). Elemental anal. calcd.: C 52.44, H 6.72, N 6.44; found: C 52.34, H 6.69, N 6.33. X-ray quality crystals were obtained via slow evaporation of a toluene solution. **7**: Yield: 0.748 g, 1.57 mmol, 92%. ^{1}H NMR δ: 8.24 (d, 1H, $^3J_{H-H}$ = 4 Hz, Py), 7.18 (d, 1H, $^3J_{H-H}$ = 6 Hz, Py), 7.06 (m, 1H, Py), 6.55 (dd, 1H, $^3J_{H-H}$ = 6 Hz, $^3J_{H-H}$ = 6 Hz, Py), 3.39 (d, 2H, $^2J_{P-H}$ = 15 Hz, CH_2), 2.18 (s, 15H, Cp*), 1.93 (d(sept), 2H, $^3J_{P-H}$ = 10 Hz, $^3J_{H-H}$ = 7 Hz, CH), 1.07 (dd, 6H, $^3J_{P-H}$ = 16 Hz, $^3J_{H-H}$ = 7 Hz, Me), 0.94 (dd, 6H, $^3J_{P-H}$ = 16 Hz, $^3J_{H-H}$ = 7 Hz, Me). ^{13}C{^{1}H} NMR δ: 154.2 (d, $^2J_{P-C}$ = 7 Hz, Py, (ipso-C)), 149.7 (s, Py), 135.8 (s, Py), 126.3 (s, Cp*), 126.2 (s, Py), 122.1 (s, Py), 35.1 (d, $^1J_{P-C}$ = 51 Hz, CH_2), 27.6 (d, $^1J_{P-C}$ = 59 Hz, CH), 16.6 (d, $^2J_{P-C}$ = 2 Hz, Me), 16.3 (d, δ: $^2J_{P-C}$ = 2 Hz, Me), 13.5 (s, Cp*). Elemental anal. calcd.: C 55.36, H 7.39, N 5.87; found: C 55.13, H 7.49, N 5.58. ^{31}P{^{1}H} NMR δ: 30.6 (s). X-ray quality crystals were obtained via slow evaporation of a toluene solution. **8**: Yield: 0.561 g, 1.11 mmol, 72%. ^{1}H NMR δ: 8.28 (d, 1H, $^3J_{H-H}$ = 4 Hz, Py), 7.61 (d, 1H, $^3J_{H-H}$ = 6 Hz, Py), 7.16 (m, 1H, Py), 6.59 (dd, 1H, $^3J_{H-H}$ = 6 Hz, $^3J_{H-H}$ = 6 Hz, Py), 3.59 (d, 2H, $^2J_{P-H}$ = 14 Hz, CH_2), 2.19 (s, 15H, Cp*), 1.17 (d, 18H, $^3J_{P-H}$ = 15 Hz, *t*-Bu). ^{13}C{^{1}H} NMR δ: 154.9 (d, $^2J_{P-C}$ = 7 Hz, Py, (ipso-C)), 149.4 (s, Py), 136.7 (s, Py), 127.1 (d, $^3J_{P-C}$ = 4 Hz, Py), 126.2 (s, Cp*), 122.3 (s, Py), 39.5 (d, $^1J_{P-C}$ = 52 Hz, *t*-Bu), 35.7 (d, $^1J_{P-C}$ = 45 Hz, CH_2), 28.1 (s, *t*-Bu), 13.5 (s, Cp*). ^{31}P{^{1}H} NMR δ: 38.0 (s). Elemental anal. calcd.: C 56.23, H 7.59, N 5.70; found: C 56.52, H 7.75, N 5.65. X-ray quality crystals were obtained via slow evaporation of a toluene solution.

Syntheses of $CpTiCl_2$[NPR_2(2-CH_2Py)]·$B(C_6F_5)_3$ (R = *i*-Pr (9), *t*-Bu (10))

These complexes were prepared in similar fashions and thus only one preparation is detailed. To a yellow solution of $CpTiCl_2$[NP(*i*-Pr)$_2$(2-CH_2Py)] (**5**) (0.020 g, 0.49 mmol) in benzene (2 mL) was added a solution of $B(C_6F_5)_3$ (0.025 g, 0.049 mmol) in benzene (2 mL). The resulting clear yellow solution was stirred for 5 min. The solvent was removed under vacuum to produce a yellow solid. Yield: 0.044 g, 0.48 mmol, 98%. **9**: ^{1}H NMR δ: 9.46 (d, 1H, $^3J_{H-H}$ = 8 Hz, Py), 8.35 (m, 1H, Py), 7.53 (m, 1H, Py), 6.35 (m, 1H, Py), 6.24 (s, 5H, Cp), 3.43 (dd, 1H, $^2J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 16 Hz, CH_2), 3.13 (dd, 1H, $^2J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 16 Hz, CH_2), 1.69 (d(sept), 1H, $^2J_{P-H}$ = 9 Hz, $^3J_{H-H}$ = 7 Hz, CH), 0.94 (m, 1H, CH), 0.76 (dd, 3H, $^3J_{P-H}$ = 17 Hz, $^3J_{H-H}$ = 7 Hz, Me), 0.74 (dd, 3H, $^3J_{P-H}$ = 17 Hz, $^3J_{H-H}$ = 7 Hz, Me), 0.69 (dd, 3H, $^3J_{P-H}$ = 17 Hz, $^3J_{H-H}$ = 7 Hz, Me), 0.29 (dd, 3H, $^3J_{P-H}$ = 17 Hz, $^3J_{H-H}$ = 7 Hz, Me). ^{13}C{^{1}H} NMR (partial, some resonances in the C_6F_5 rings could not be observed) δ: 153.4 (s, Py (ipso-C)), 148.9 (s, Py), 148.2 (br d, $^1J_{C-F}$ ~ 240 Hz, C_6F_5), 143.8 (s, Py), 138.1 (br d, $^1J_{C-F}$ ~ 230 Hz, C_6F_5), 131.6 (s, Py), 124.2 (s, Py), 116.3 (s, Cp), 28.3 (d, $^1J_{P-C}$ = 51 Hz, CH_2), 28.2 (d, $^1J_{P-C}$ = 60 Hz, CH), 28.1 (d, $^1J_{P-C}$ = 59 Hz, CH), 16.2 (s, Me), 15.8 (d, $^2J_{P-C}$ = 3 Hz, Me), 15.3 (s, Me), 15.2 (d, $^2J_{P-C}$ = 3 Hz, Me). ^{11}B{^{1}H} NMR δ: –3.4 (s). ^{19}F NMR δ: –126.4 (dd, 1F, $^3J_{F-F}$ = 25 Hz, $^3J_{F-F}$ = 25 Hz), –127.0 (br, 1F), –130.4 (d, 1F, $^3J_{F-F}$ = 23 Hz), –132.6 (br, 2F), –135.2 (dd, 1F, $^3J_{F-F}$ = 25 Hz, $^3J_{F-F}$ = 25 Hz), –153.7 (dd, 1F, $^3J_{F-F}$ = 21 Hz, $^3J_{F-F}$ = 21 Hz), –154.1 (dd, 1F, $^3J_{F-F}$ = 21 Hz, $^3J_{F-F}$ = 21 Hz), –155.8 (dd, 1F, $^3J_{F-F}$ = 21 Hz, $^3J_{F-F}$ = 21 Hz), –160.8 (m, 1F), –162.0 (m, 1F), –162.1 (m, 1F), –162.6 (m, 1F), –163.3 (m, 1F), –164.0 (m, 1F). ^{31}P{^{1}H} NMR δ: 30.2 (s). Elemental anal. calcd.: C 45.74, H 2.74, N 3.05; found: C 45.33, H 3.04, N 2.93. **10**: Yield: 0.037 g, 0.39 mmol, 85%. ^{1}H NMR δ: 9.63 (d, 1H, $^3J_{H-H}$ = 8 Hz, Py), 8.42 (m, 1H, Py), 7.52 (m, 1H, Py), 6.37 (m, 1H, Py), 6.30 (s, 5H, Cp), 3.59 (dd, 1H, $^2J_{P-H}$ = 13 Hz, $^3J_{H-H}$ = 18 Hz, CH_2), 2.88 (dd, 1H, $^2J_{P-H}$ = 9 Hz, $^3J_{H-H}$ = 18 Hz, CH_2), 0.85 (d, 9H, $^3J_{P-H}$ = 15 Hz, *t*-Bu), 0.68

(d, 9H, $^3J_{P-H}$ = 16 Hz, *t*-Bu). $^{13}C\{^1H\}$ NMR (partial): 153.8 (s, Py, (ipso-C)), 149.4 (s, Py), 143.6 (s, Py), 137.8 (br d, $^1J_{C-F}$ ~ 260 Hz, C_6F_5), 131.8 (s, Py), 124.1 (s, Py), 116.5 (s, Cp), 40.3 (d, $^1J_{P-C}$ = 53 Hz, $C(CH_3)_3$), 39.6 (d, $^1J_{P-C}$ = 53 Hz, *t*-Bu), 26.9 (s, *t*-Bu), 26.6 (s, *t*-Bu), 26.1 (d, $^1J_{P-C}$ = 41 Hz, CH_2). $^{11}B\{^1H\}$ NMR δ: –3.4 (s). ^{19}F NMR δ: –125.8 (dd, 1F, $^3J_{F-F}$ = 25 Hz, $^3J_{F-F}$ = 25 Hz), –126.6 (br, 1F), –130.9 (d, 1F, $^3J_{F-F}$ = 25 Hz), –131.7 (br, 1F), –132.8 (m, 1F), –135.5 (m, 1F), –153.6 (dd, 1F, $^3J_{F-F}$ = 20 Hz, $^3J_{F-F}$ = 20 Hz), –154.6 (dd, 1F, $^3J_{F-F}$ = 20 Hz, $^3J_{F-F}$ = 20 Hz), –155.8 (dd, 1F, $^3J_{F-F}$ = 20 Hz, $^3J_{F-F}$ = 20 Hz), –160.8 (m, 1F), –160.8 (m, 1F), –161.7 (m, 1F), –162.4 (m, 2F), –162.8 (m, 1F), –163.6 (m, 1F). $^{31}P\{^1H\}$ NMR δ: 36.3 (s). Elemental anal. calcd.: C 46.92, H 3.09, N 2.96; found: C 47.33, H 2.94, N 2.70.

Synthesis of $Cp^*TiMe_2[NP\text{-}t\text{-}Bu_2(2\text{-}CH_2Py)]$ (11)

To a yellow suspension of **8** (0.306 g, 0.605 mmol) in a mixture of diethyl ether (30 mL) and toluene (50 mL) cooled to –78 °C was added 3.0 mol/L MeMgCl in THF (0.38 mL, 1.14 mmol). The resulting yellow suspension was stirred at –78 °C for ~20 min and then was slowly warmed to room temperature over a period of 1.5 h. The solvent was removed under vacuum, and the crude residue was extracted with hexanes. The suspension was filtered through Celite and the solvent was removed under vacuum to yield a crude brown solid. Subsequent recrystallization attempts from hexanes produced a yellow solid that was 95% pure by NMR analysis. Yield: 0.155 g, 0.336 mmol, 59%. ^1H NMR δ: 8.39 (d, 1H, $^3J_{H-H}$ = 4 Hz, Py), 7.61 (d, 1H, $^3J_{H-H}$ = 6 Hz, Py), 7.16 (m, 1H, Py), 6.63 (m, 1H, Py), 3.35 (d, 2H, $^2J_{P-H}$ = 12 Hz, CH_2), 2.04 (s, 15H, Cp*), 1.21 (d, 18H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 0.41 (s, 6H, $TiMe_2$). $^{13}C\{^1H\}$ NMR δ: 156.2 (d, $^2J_{P-C}$ = 6 Hz, Py, (ipso-C)), 149.6 (s, Py), 135.9 (s, Py), 127.1 (s, Py), 122.0 (s, Py), 118.8 (s, Cp*), 44.5 (s, $TiMe_2$, 39.4 (d, $^1J_{P-C}$ = 54 Hz, *t*-Bu), 36.1 (d, $^1J_{P-C}$ = 45 Hz, CH_2), 28.2 (s, *t*-Bu), 12.6 (s, Cp*). $^{31}P\{^1H\}$ NMR δ: 22.9 (s). Elemental anal. calcd.: C 67.23, H 9.76, N 6.03; found: C 66.16, H 9.97, N 6.25.

Polymerization protocol

Polymerization experiments were performed using a glass Büchi polymerization reactor. Toluene (600 mL) was transferred into the reactor, heated to 30 °C ± 2 °C, and presaturated with ethylene prior to injection of catalyst and cocatalyst. The solution was stirred at 1000 rpm for the duration of the polymerization experiment. At the end of the experiments, the polymer was collected and treated as previously described (9). For the catalyst precursors (**5**–**10**), polymerization experiments were conducted for 30 min employing MAO as the cocatalyst. In these polymerizations, 500 equiv. of MAO was injected into the reactor and the solution was stirred for 5 min prior to injecting a toluene solution of the precatalyst. Catalyst concentrations of 100 μmol/L were employed, thus 0.060 mmol of catalyst in 8 mL of toluene was injected. In the case of **11**, 1, 2, and 10 equiv. of $B(C_6F_5)_3$ were used as the cocatalyst, while 20 equiv. of $Al(i\text{-}Bu)_3$ was used as a scavenger. Catalyst concentrations of 20 μmol/L were employed, thus 0.012 mmol of catalyst in 4 mL of toluene was injected. These polymerization experiments were conducted for 10 min.

X-ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glovebox, 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 ($4.5° < 2\theta < 45–50.0°$). A measure of decay was obtained by recollecting 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. 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 operating on a Pentium computer.

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations (33). 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*, 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, respectively. 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 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 they 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. Additional details are provided in the supplementary data.[2]

Results and discussion

The phosphinimine ligands, $Me_3SiNPR_2(2\text{-}CH_2Py)$ (R = *i*-Pr (**3**) (32), *t*-Bu (**4**)), were prepared in conventional fashion

[2] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5031. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 233404–233407 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Scheme 1.

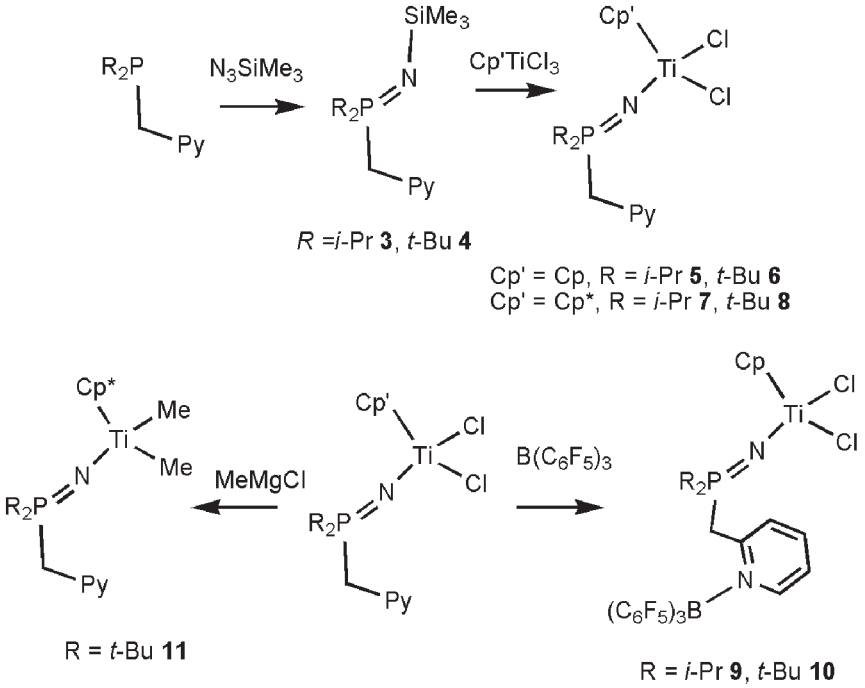


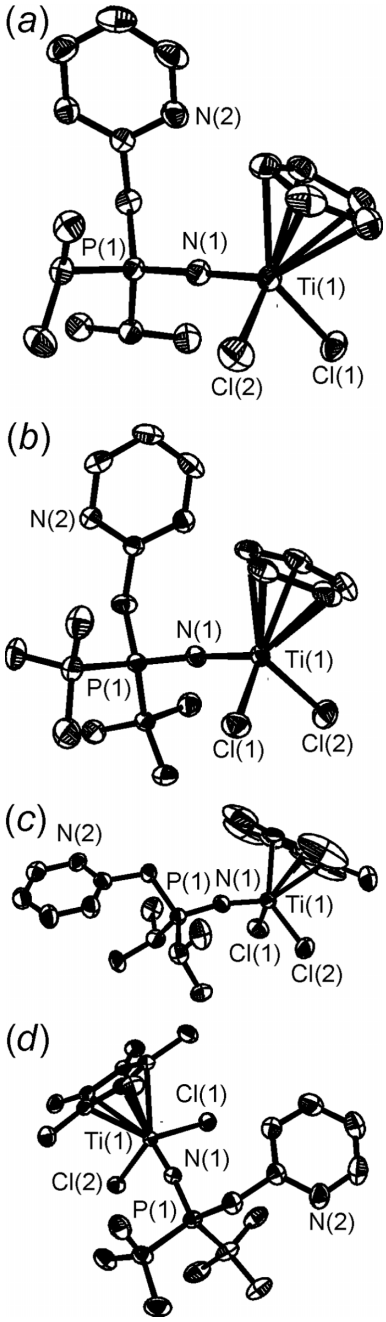
Table 1. Crystallographic data for **5**–**8**.

	5	**6**	**7**	**8**
Formula	$C_{17}H_{25}Cl_2N_2PTi$	$C_{19}H_{29}Cl_2N_2PTi$	$C_{22}H_{35}Cl_2N_2PTi$	$C_{24}H_{39}Cl_2N_2PTi$
Formula weight	407.16	435.21	477.29	505.34
a (Å)	26.51(1)	9.745(6)	20.41(1)	9.773(5)
b (Å)	8.170(4)	12.713(8)	7.769(4)	17.010(9)
c (Å)	18.58(1)	17.94(1)	16.455(9)	16.414(9)
β (°)	97.87(1)	98.34(1)	102.29(1)	99.04(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P2_1/c$	$P2_1/c$
Volume (Å^3)	3987(4)	2199(2)	2549(2)	2695(3)
D_{calcd} (g cm^{-3})	1.357	1.314	1.244	1.246
Z	8	4	4	4
Abs. coeff. (μ, mm^{-1})	0.778	0.710	0.618	0.589
θ Range (°)	2.21–23.29	1.97–23.24	2.04–23.38	1.74–23.23
Total reflections	8193	9012	10 674	11 234
Data $F_o^2 > 3\sigma(F_o^2)$	2839	3138	3676	3839
Parameters	208	226	253	271
R (%)	0.0312	0.0351	0.0554	0.0349
R_w (%)	0.0849	0.0909	0.1270	0.0895
Goodness-of-fit	1.010	1.026	0.859	1.031

Note: Data collected at 20 °C; Mo Kα radiation (λ = 0.710 69 Å); $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

from reaction of the precursor phosphines (30) with Me_3SiN_3 in toluene at refluxing temperatures. These products were characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and all data were consistent with the proposed formulation. The corresponding Ti complexes, $Cp'TiCl_2[NPR_2(2\text{-}CH_2Py)]$ (Cp′ = Cp, R = *i*-Pr (**5**), *t*-Bu (**6**); Cp′ = Cp*, R = *i*-Pr (**7**), *t*-Bu (**8**)), were prepared via reaction of the phosphinimine ligands, $Me_3SiNPR_2(2\text{-}CH_2Py)$ (R = *i*-Pr (**3**) (32), R = *t*-Bu (**4**)), with the precursors $CpTiCl_3$ and Cp^*TiCl_3, respectively (Scheme 1). Similar preparative methods for species of the form $Cp'Ti(NPR_3)Cl_2$ have been previously described (9). Spectroscopic data for **5**–**8** were as expected and elemental analyses were consistent with the formulations. Single crystal X-ray data were also obtained for these complexes (Table 1) (Fig. 1). All of these complexes are monomeric as expected, with pseudo-tetrahedral geometries at Ti with the coordination sphere comprised of a η^5-bound Cp or Cp* ligand, an N-bound phosphinimide, and

Fig. 1. ORTEP diagrams (30% probability ellipsoids) of (*a*) **5**, (*b*) **6**, (*c*) **7**, (*d*) **8**. Hydrogen atoms have been omitted for clarity.



two chloride ligands. Metric parameters (Table 2) are similar to those reported for related compounds (4, 9, 34–37). The P-N-Ti bond angles for complexes **5**–**8** are approximately linear at 173.8(1)°, 170.9(2)°, 165.0(3)°, and 166.5(2)°, respectively, and are within the range of 158.7(1)° to 178.38(11)° for related titanium phosphinimide compounds (34, 37). The smaller P-N-Ti angles for **7** and **8** are attributable to the greater electron donation and steric demand of the Cp* ligand. This view is also consistent with the longer Ti—N distances for complexes **7** and **8** (1.775(4) and 1.792(2) Å) compared with those in **5** and **6** (1.768(2) and 1.761(2) Å). Similarly, the P—N bond lengths for compounds **5** and **6** (1.607(2) and 1.609(2) Å) are longer than those for **7** and **8** (1.600(4) and 1.597(2) Å). The orientation of the pyridyl substituent of the phosphinimide ligands varies. In **5** and **6**, this substituent is oriented in the general direction of the Cp ligand, while in **7** and **8**, it projects away from the Cp* ligand. This is presumably a steric effect. No preferred orientation of the nitrogen atom of the pyridyl group is observed and there is no intra- or inter-molecular interactions of this donor atom with the Lewis acidic Ti center.

Table 2. Metric parameters (bond lengths and angles) for **5**–**8**.

	5	**6**	**7**	**8**
Bond lengths (Å)				
Ti1—N1	1.768(2)	1.761(2)	1.775(4)	1.792(2)
N1—P1	1.607(2)	1.609(2)	1.599(4)	1.597(2)
Ti1—Cl1	2.337(1)	2.315(1)	2.307(2)	2.330(1)
Ti1—Cl2	2.320(1)	2.331(1)	2.319(2)	2.323(1)
Bond angles (°)				
Ti1-N1-P1	173.8(1)	170.9(2)	165.2(3)	166.5(2)
N1-Ti1-Cl1	103.12(8)	103.24(8)	102.8(1)	104.18(9)
N1-Ti1-Cl2	102.70(7)	104.23(8)	103.0(2)	101.47(8)
Cl1-Ti1-Cl2	101.48(3)	99.54(6)	101.31(9)	100.70(4)

Table 3. Ethylene polymerization data and MAO activation.

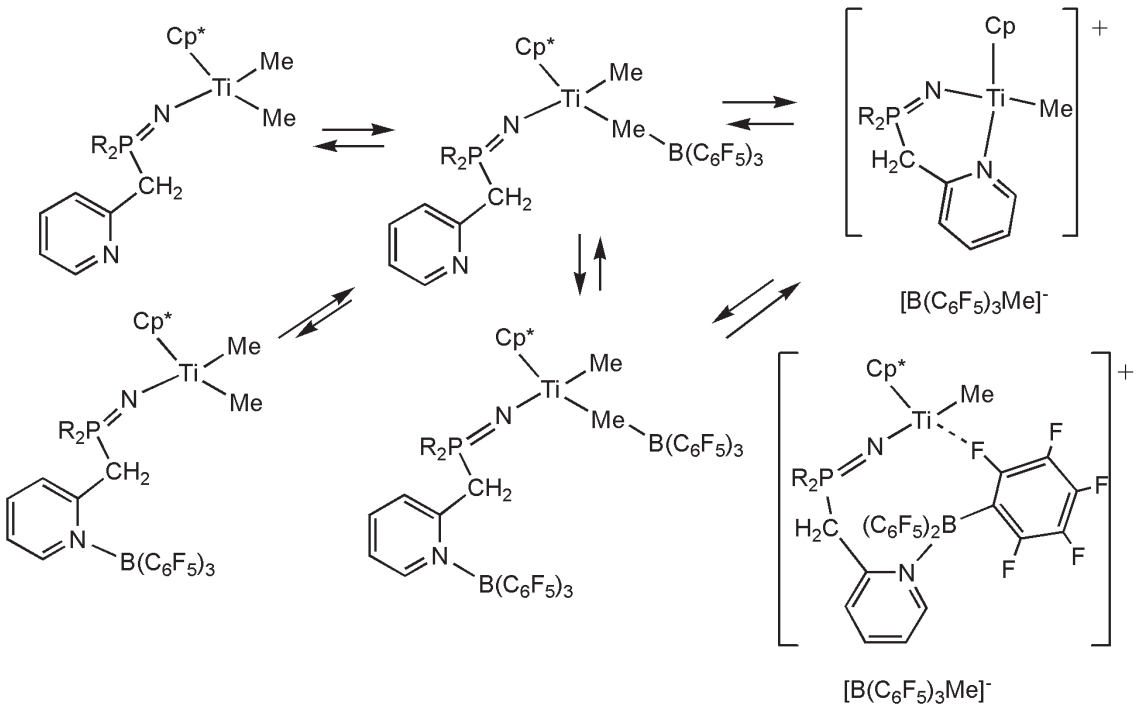
Precat.	M_n	M_w	PDI	Activity (g mmol^{-1} h^{-1} atm^{-1})
5	23 700	635 400	26.8	19
6	37 700	417 300	11.1	5.6
7	22 500	229 300	10.2	3
8	81 400	323 000	4	0.89
9	112 400	556 900	5	7.7
10	67 000	534 800	8	2

Note: Conditions for polymerization: ethylene pressure = 2 atm, T = 30 °C, toluene, [catalyst] = 100 µmol/L, 500 equiv. MAO.

Polymerization

The complexes **5**–**8** were tested as ethylene polymerization precatalysts using a Büchi polymerization reactor at 30 °C for 30 min in toluene, under an atmosphere of 2 atm of ethylene (1 atm = 101.325 kPa). A precatalyst concentration of 100 µmol/L was used and 500 equiv. of MAO was used as cocatalyst (Table 3). The resulting polymers have molecular weight (M_w) ranges from approximately 200 000 to 600 000 g/mol with polydispersity indices (PDI) varying from 4 to 26. These relatively high molecular weights together with high PDIs suggest that there may be several active catalyst species generated in solution. Certainly, these species do not behave as single site catalysts, nonetheless, such systems are of interest as they may provide polymers with desirable processability. In terms of activities, complex **5** displayed moderate activity (18 g mmol^{-1} h^{-1} atm^{-1}), while complexes **6**–**8** showed low activity. These results stand in contrast to previous results that demonstrated a high activity catalyst was derived from $CpTiCl_2(NP\text{-}t\text{-}Bu_3)$ under similar conditions (4, 9). These data also contrast the polymerization activity observed for $Cp^*TiCl_2[NP(t\text{-}Bu)_2(CH_2Ph)]$ under similar conditions (142 g mmol^{-1} h^{-1} atm^{-1}) (38). Clearly,

Scheme 2.



the only structural difference between **8** and $Cp^*TiCl_2[NP(t\text{-}Bu)_2(CH_2Ph)]$ is the N atom of the pyridine ring, and thus efforts to query the role of this atom were undertaken.

$B(C_6F_5)_3$ adducts

In an attempt to sequester any potential interference of the pyridyl group in the polymerization process, the complexes **5** and **6** were treated with $B(C_6F_5)_3$ producing donor–acceptor complexes of the general formula, $CpTiCl_2[NPR_2(2\text{-}CH_2Py)]\cdot B(C_6F_5)_3$ (R = *i*-Pr (**9**), *t*-Bu (**10**) (Scheme 1). $^{31}P\{^1H\}$, ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR data were consistent with the formulation. In particular, the $^{19}F\{^1H\}$ NMR spectra revealed 15 resonances for both **9** and **10**, indicating complexation and the inequivalence of all F atoms in the $B(C_6F_5)_3$ fragment. The downfield ^1H NMR shifts of the protons ortho to N in **5** and **6** upon reaction with the borane were greater than 1 ppm, consistent with B—N donor–acceptor bond formation. It is a noteworthy comparison that no reaction is observed between $CpTiCl_2(NP\text{-}t\text{-}Bu_3)$ and $B(C_6F_5)_3$ at 25 °C (39). The proposed structures of **9** and **10** were not confirmed crystallographically, despite numerous attempts to acquire suitable crystals.

The species **9** and **10** were evaluated as precatalysts for ethylene polymerization activity. Aliquots of the freshly prepared solutions were employed. The polymerization experiments were conducted in an identical fashion to those described previously (Table 3). The resulting activities of the catalysts derived from **9** and **10** were significantly lower than those derived from **5** and **6**, respectively. However, the causes of these observations remain unclear. It is likely that MAO competes with $B(C_6F_5)_3$ for coordination to the pyridyl N. Thus, the notion that one might use of coordination of borane to the pyridyl group to provide a sterically crowded phosphinimide ligand in situ is clearly simplistic.

Table 4. Ethylene polymerization data and $B(C_6F_5)_3$ activation.

Precat.	$B(C_6F_5)_3$ (equiv.)	Activity (g $mmol^{-1}$ h^{-1} atm^{-1})
11	1	47
11	2	120
11	10	75

Note: Conditions for polymerization: ethylene pressure = 2 atm, T = 30 °C, toluene, [catalyst] = 20 μmol/L, [TiBAl] = 400 μmol/L, 10 min.

Reaction of MeMgX with **5**–**7** resulted in mixtures of products that could not be separated despite exhaustive attempts to effect extraction, selective precipitation, or crystallization. These difficulties are thought to arise from the known acidity of the methylene protons of the pyridyl-phosphinimide ligand. For example, it is known that reaction of *n*-BuLi with **3** results in the formation of $Li(THF)_2[Me_3SiNP(i\text{-}Pr)_2(2\text{-}CHPy)]$ (32). Nonetheless, the species $Cp^*TiMe_2[NP(t\text{-}Bu)_2(2\text{-}CH_2Py)]$ (**11**) (Scheme 1) was successfully produced from reaction of MeMgCl with **8**, although multiple extractions with hexanes and subsequent reprecipitations were required to effect adequate purification.

Ethylene polymerization catalysis were examined using **11** and 1, 2, and 10 equiv. of $B(C_6F_5)_3$ as a cocatalyst (Table 4). These data reveal that **11**–$B(C_6F_5)_3$ is a much more active catalyst system than those derived from **8**–MAO. Interestingly, increasing the amount of borane from 1 to 2 equiv. prompted an increase in the polymerization activity from 47 to 120 g $mmol^{-1}$ h^{-1} atm^{-1}. In the presence of a larger excess of $B(C_6F_5)_3$, i.e., 10 equiv., a polymerization activity of 75 g $mmol^{-1}$ h^{-1} atm^{-1} was observed. Molecular weight distributions (GPC analysis) in these polymerizations were precluded by solubility problems, presumably a result of polymer molecular weights exceeding the limit of the instrumentation (i.e., >1 000 000 g mol^{-1}). It is noteworthy

that use of $B(C_6F_5)_3$ to activate Ti–phosphinimide catalysts has previously been shown to give rise to high molecular weight polymers in comparison to the similar systems in which MAO was employed as the activator (4–10).

The above polymerization data show that increasing from 1 to 2 equiv. of borane appears to increase the concentration of the active catalyst, while further increases in cocatalyst concentration reduce the observed activity. This suggests the involvement of several equilibria governing the concentration of the active catalyst(s). While the precise nature of these species involved remains unclear, it is tempting to speculate that such species could involve interaction of $B(C_6F_5)_3$ with the Ti-bound alkyl groups or the pyridyl group, chelation of the pyridyl fragment to Ti, or interaction of the Ti center with the pyridyl-bound $B(C_6F_5)_3$ (Scheme 2).

In conclusion, a series of Ti–pyridyl-phosphinimide complexes generate ethylene polymerization catalysts upon activation with MAO or $B(C_6F_5)_3$. While these catalysts do not exhibit the exceptional activity of previously reported Ti–phosphinimides, the presence of the pyridyl substituents appears to result in polymers with broadened molecular weight distributions. While the cause of this effect is the subject of speculation, the potential of a substituent modification approach to the alteration of the polydispersity remains a subject of on-going study.

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