Cationic Methyl- and Chlorotitanium Phosphinimide Complexes

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A variety of donor-stabilized cationic complexes of the form $[Cp(NPt\text{-}Bu_3)TiMe(L)][MeB(C_6F_5)_3]$ and $[Cp(NPt\text{-}Bu_3)TiMe(L)][B(C_6F_5)_4]$ (L = Py, 4-EtPy, 4-*t*-BuPy, $NC_5H_4NMe_2$, PMe_3, P*n*-Bu_3, PPh_3, $P(p\text{-}MeC_6H_4)_3$) have been prepared and characterized. Prolonged storage in CH_2Cl_2 solution resulted in chloride for methyl exchange to afford species of the form $[CpTi(NPt\text{-}Bu_3)Cl(L)][B(C_6F_5)_4]$, $[\{CpTi(NPt\text{-}Bu_3)Me\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$, and $[CpTi(NPt\text{-}Bu_3)(\mu\text{-}Cl)]_2[MeB(C_6F_5)_3]_2$. The byproduct salt $[(o\text{-}MeC_6H_4)_3PCH_2Cl][B(C_6F_5)_4]$ was obtained from reactions employing the sterically demanding donor phosphine $P(o\text{-}MeC_6H_4)_3$, suggesting transient generation of the cation $[CpTi(NPt\text{-}Bu_3)Cl(CH_2Cl_2)]^+$. Analogous reactivity was not seen in C_6H_5Cl, although the species $[\{CpTi(NPt\text{-}Bu_3)Me\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$ could be formed in this solvent. The isolated zwitterionic complex $TiCp(NPt\text{-}Bu_3)Me(\mu\text{-}MeB(C_6F_5)_3)$ readily performs insertion chemistry into the Ti−methyl bonds with diisopropylcarbodiimide and diphenylacetylene substrates to afford the cationic species $[CpTi(NPt\text{-}Bu_3)((Ni\text{-}Pr)_2CMe)][MeB(C_6F_5)_3]$, $[TiCp(NPt\text{-}Bu_3)(PhCCPh(Me))][MeB(C_6F_5)_3]$, and $[TiCp(NPt\text{-}Bu_3)(PhCCPh(Me))(PMe_3)][MeB(C_6F_5)_3]$. The implications of this chemistry are considered.

Introduction

Post-metallocene, homogeneous, single-site olefin polymerization catalysts have been the focus of intense development and study over the last two decades.[1−3] Of the systems that have been commercialized, the best known non-metallocene catalyst is the titanium-based "constrained geometry" catalyst.[4] Other early metal non-metallocene systems provide living polymerization catalysts. These include chelating diamide complexes of the form $Ti(CH_2(CH_2NAr)_2)X_2$ (Ar = $(2,6\text{-}i\text{-}Pr_2)C_6H_3$, $(2,6\text{-}Me_2)C_6H_3$; X = Cl, Me), developed by McConville et al.[5−7] and the related Zr system, $Zr((t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O)Me_2$, described by Schrock et al.[8] More recently, Mitsui researchers have reported a series of highly active ethylene polymerization catalysts derived from precursors of the general formula ML_2Cl_2 (M = Ti, Zr; L = salicylaldehyde derivative).[9−12] In our own work, we have furthered the development of non-metallocene ethylene polymerization catalysts using Ti-phosphinimide complexes.[13−15] In particular, the zwitterionic species $CpTi(NPt\text{-}Bu_3)Me(\mu\text{-}MeB(C_6F_5)_3)$ acts as a single-component ethylene polymerization catalyst.[14] Cationic Zr analogues derived from $Cp'Zr(NPR_3)X_2$ also provide active ethylene polymerization catalysts, although these systems proved to be more sensitive to the activation strategy.[16] While numerous ethylene polymerization catalysts have been studied, phosphinimide-based systems are among the few to exhibit high activity under industrially relevant conditions.[15] More recently we showed that complexes of the form $Cp'Ti(NP(NR_2)_3)X_2$[17] also provide a family of highly active catalysts. In general, for Ti or Zr metallocene or non-metallocene polymerization catalyst systems,[1−3,18−27] it is accepted that the active species is the metal-based cation. Met-

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allocene cations have been stabilized by phosphines,[28−31] tethered donors,[32−34] and more recently Arduengo carbenes.[35] Similarly, stabilized constrained geometry cations have been studied.[26,27,36] While we have previously described the Ti-zwitterionic species $CpTi(NPBu_3)Me(MeBC_6F_5)_3$, it has only been in a very recent communication that Piers and co-workers[37] have described the chemistry of Ti-phosphinimide cationic species. In this article, we report the preparation and characterization of a series of base-stablized Ti-phosphinimide cationic complexes. In addition, some reactivity of these species is described.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an MBraun or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs type solvent purification system manufactured by Innovative Technologies. All organic reagents were purified by conventional methods. ^1H, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and 500 spectrometers. All spectra were recorded in CD_2Cl_2 at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as reference, and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and ^{19}F NMR spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively. Combustion analyses were performed in-house employing a Perkin-Elmer CHN analyzer. $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ were generously donated by NOVA Chemicals Corporation. $CpTi(NPt\text{-}Bu_3)X_2$ (X = Cl **1**, Me **2**) were prepared according to published procedures.[14] The reagents pyridine, 4-EtPy, 4-*t*-BuPy, 4-(NMe_2)Py, PMe_3 (1.0 M in toluene), PCy_3, and P*t*-Bu_3 were purchased from Aldrich Chemical Co. P*i*-Pr_3, P*n*-Bu_3, P(*p*-$C_6H_4Me)_3$, and P(*o*-$C_6H_4Me)_3$ were obtained from Strem Chemicals and were used as received.

Synthesis of $CpTi(NPt\text{-}Bu_3)Me(\mu\text{-}MeB(C_6F_5)_3)$, 3. A hexane solution (10 mL) of complex **2** (63 mg, 0.23 mmol) in 2 mL of hexane was added dropwise at 25 °C to a solution of $B(C_6F_5)_3$ (119 mg 0.23 mmol) in 3 mL of hexane. An orange solid precipitated out of solution immediately. The mixture was stirred for 30 min, the mother liquor was decanted, and the residue was washed with hexane (3 × 10 mL) and dried under vacuum to yield complex **3** as an orange solid (84% yield by NMR spectroscopy). ^1H NMR: 6.35 (s, 5H, Cp), 1.43 (d, J^3_{PH} = 14 Hz, 27H, *t*-Bu), 0.54 (br s, 6H, TiMe, MeB). $^{31}P\{^1H\}$ NMR: 52.2. ^{19}F NMR: −55.9 (s), −84.8 (br), −88.8 (br s). $^{11}B\{^1H\}$ NMR: −14.8. Anal. Calcd for $C_{37}H_{38}BF_{15}NPTi$: C, 51.00, H, 4.40, N, 1.61. Found: C, 50.82, H, 4.32, N, 1.42.

Synthesis of $[CpTi(NPt\text{-}Bu_3)Me(THF)][MeB(C_6F_5)_3]$, 4 Compound **2** (213 mg, 0.59 mmol) and $B(C_6F_5)_3$ (303 mg, 0.59 mmol) were dissolved separately in THF (5 mL each) before combining at −35 °C. The bright yellow solution was stirred at 25 °C for 1 h, after which time the solvent was removed in vacuo. The oily residue was washed with benzene (3 × 5 mL) before drying to afford **4** as a bright yellow solid (177 mg, 32%). ^1H NMR: 6.42 (s, 5H, Cp), 3.95 (br, 4H, OCH_2), 1.95 (br, 4H, CH_2CH_2), 1.49 (d, 27H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 1.10 (s, 3H, TiMe), 0.51 (br s, 3H, MeB). $^{13}C\{^1H\}$ NMR: 148.8 (dd, $^1J_{CF}$ = 230 Hz, $^2J_{CF}$ = 14 Hz, C_6F_5 (*o*-C)), 138.1 (d(m), $^1J_{CF}$ = 240 Hz, C_6F_5 (p−C)), 137.0 (ddd, $^1J_{CF}$ = 240 Hz, $^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 12 Hz, C_6F_5 (*m*-C)), 129.5 (br, C_6F_5 (*ipso*)), 114.8 (s, Cp), 77.0 (br, OCH_2), 69.1 (br, CH_2CH_2), 52.1 (s, TiMe), 42.0 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 29.8 (s, *t*-Bu), 10.6 (br q, J_{BC} = 54 Hz, MeB). $^{11}B\{^1H\}$ NMR: −19.1. ^{19}F NMR: −133.3 (d, 6F, $^3J_{FF}$ = 22 Hz, C_6F_5 (*o*-F)), −165.5 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (p−F)), −168.3 (m, 6F, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 52.4. Anal. Calcd for $C_{41}H_{46}BF_{15}NOPTi$: C, 52.20, H, 4.91, N, 1.48. Found: C, 51.79, H, 4.99, N, 1.39.

Synthesis of $[CpTi(NPt\text{-}Bu_3)Me(L)][MeB(C_6F_5)_3]$ (L = Py 5, 4-EtPy 6, 4-*t*-BuPy 7, 4-NMe_2Py 8, PMe_3 9, P*n*-Bu_3 10, PPh_3 11, P(*p*-$MeC_6H_4)_3$ 12), and $[CpTi(NPt\text{-}Bu_3)Me(L)][B(C_6F_5)_4]$ (L = Py 13, 4-EtPy 14, 4-*t*-BuPy 15, $NC_5H_4NMe_2$ 16, PMe_3 17, P*n*-Bu_3 18, PPh_3 19, P(*p*-$MeC_6H_4)_3$ 20). These compounds were prepared in a similar fashion, and thus one preparation is detailed. Pyridine (12 μL, 0.14 mmol) was added at 25 °C to a solution of **2** (50 mg, 0.14 mmol) in CH_2Cl_2 (3 mL), followed by the addition of a solution of $B(C_6F_5)_3$ (72 mg, 0.14 mmol) in CH_2Cl_2 (3 mL). The resulting solution was left to stir for 30 min. The solvent was removed in vacuo, and the oily residue was washed with pentane (3 × 5 mL) before drying to afford a bright yellow solid (yield 110 mg, 83%). **5**, ^1H NMR: 8.20 (br s, 2H, Py (α-H)), 8.02 (t, 1H, $^3J_{HH}$ = 8 Hz, Py (γ-H)), 7.56 (t, 2H, $^3J_{HH}$ = 7 Hz, Py (β-H)), 6.46 (s, 5H, Cp), 1.45 (d, 27H, $^3J_{P-H}$ = 14 Hz, t-Bu), 1.28 (s, 3H, TiMe), 0.50 (br s, 3H, MeB). $^{13}C\{^1H\}$ NMR: 148.8 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 148.3 (s, Py (α-C)), 143.5 (s, Py (γ-C)), 138.0 (d m, $^1J_{CF}$ = 237 Hz, C_6F_5 (*p*-C)), 137.0 (ddd, $^1J_{CF}$ = 247 Hz, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 129.3 (br s, C_6F_5 (*ipso*-C)), 126.7 (s, Py (β-C)), 115.6 (s, Cp), 54.9 (s, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, t-Bu), 29.8 (s, t-Bu), 10.6 (br q, $^1J_{BC}$ = 54 Hz, MeB). $^{11}B\{^1H\}$ NMR: −15.2. ^{19}F NMR: −133.4 (d, 6F, $^3J_{FF}$ = 23 Hz, C_6F_5 (*o*-F)), −165.5 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.1 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 51.7. Anal. Calcd for $C_{42}H_{43}BF_{15}N_2PTi$: C, 53.08, H, 4.56, N, 2.95. Found: C, 52.79, H, 4.29, N, 2.59. **6**: light yellow solid (60 mg, 88%). ^1H NMR: 8.00 (d, 2H, $^3J_{HH}$ = 6 Hz, C_5H_4N (β-H)), 7.42 (d, 2H, $^3J_{HH}$ = 6 Hz, C_5H_4N (α-H)), 6.43 (s, 5H, Cp), 1.76 (q, 2H, $^3J_{HH}$ = 8 Hz, Et), 1.45 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.27 (t, 3H, $^3J_{HH}$ = 8 Hz, Et), 1.24 (s, 3H, TiMe), 0.48 (br s, 3H, MeB). $^{13}C\{^1H\}$ NMR: 161.3 (s, C_5H_4N (γ-C)), 148.9 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 147.4 (s, C_5H_4N (α-C)), 138.0 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*p*-C)), 137.0 (ddd, $^1J_{CF}$ = 244 Hz, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 129.0 (br s, C_6F_5 (*ipso*-C)), 126.4 (s, C_5H_4N (α-C)), 115.4 (s, Cp), 54.5 (s, TiMe), 42.1 (d, $^1J_{PC}$ = 43 Hz, t-Bu), 29.8 (s, *t*-Bu), 29.1 (s, Et), 13.8 (s, Et), 10.6 (br q, $^1J_{B-C}$ = 54 Hz, MeB). $^{11}B\{^1H\}$ NMR: −15.1. ^{19}F NMR: −133.4 (d, 6F, $^3J_{FF}$ = 22 Hz, C_6F_5 (*o*-F)), −165.5 (t, 3F, $^3J_{FF}$ = 21 Hz, C_6F_5 (*p*-F)), −168.1 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 51.1. Anal. Calcd for $C_{44}H_{47}BF_{15}N_2PTi$: C, 53.85, H, 4.96, N, 2.93. Found: C, 53.75, H, 4.92, N, 2.83. **7**: yellow powder (62 mg, 88%). ^1H NMR: 8.17 (d, 2H, $^3J_{HH}$ = 6 Hz, C_5H_4N, (α-H)), 7.49 (d, 2H, $^3J_{HH}$ = 6 Hz, C_5H_4N, (β-H)), 6.44 (s, 5H, Cp), 1.45 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.31

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(s, 9H, 4-t-Bu), 1.27 (s, 3H, TiMe), 0.48 (br s, 3H, MeB).^{13}C-{^{1}H} NMR: 148.8 (d m, $^1J_{CF}$ = 230 Hz, C_6F_5 (*o*-C)), 147.2 (s, C_5H_4N (α-C)), 137.9 (d m), $^1J_{CF}$ = 250 Hz, C_6F_5 (*p*-C)), 137.0 (d m, $^1J_{CF}$ = 253 Hz, C_6F_5 (*m*-C)), 128.6 (br s, C_6F_5 (*ipso*-C)), 123.4 (s, C_5H_4N), 115.4 (s, Cp), 54.4 (s, TiMe), 42.1 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 35.4 (s, *t*-Bu), 30.3 (s, *t*-Bu), 29.8 (s, *t*-Bu), 10.7 (br q, $^1J_{BC}$ = 54 Hz, MeB). ^{11}B{^{1}H} NMR: −15.1. ^{19}F NMR: −133.4 (d, 6F, $^3J_{FF}$ = 22 Hz, C_6F_5 (*o*-F)), −165.6 (t, 3F, $^3J_{FF}$ = 21 Hz, C_6F_5 (*p*-F)), −168.1 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 51.1. Anal. Calcd for $C_{46}H_{51}BF_{15}N_2PTi$: C, 54.89, H, 5.11, N, 2.78. Found: C, 54.79, H, 4.99, N, 2.43. **8**: yellow solid (65 mg, 93%). ^{1}H NMR: 7.62 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4N, (α-H)), 6.52 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4N, (*β*-H)), 6.37 (s, 5H, Cp), 3.07 (s, 6H, 4-Me_2N), 1.46 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.10 (s, 3H, TiMe), 0.48 (br s, 3H, MeB). ^{13}C{^{1}H} NMR: 155.9 (s, C_5H_4N, (*γ*-C)), 148.7 (d m, $^1J_{CF}$ = 255 Hz, C_6F_5 (*o*-C)), 146.9 (s, C_5H_4N, (α-C)), 138.0 (d m, $^1J_{CF}$ = 233 Hz, C_6F_5 (*p*-C)), 136.9 (d m, $^1J_{CF}$ = 234 Hz, C_6F_5 (*m*-C)), 128.6 (br s, C_6F_5 (*ipso*-C)), 114.7 (s, Cp), 107.3 (s, C_5H_4N, (*β*-C)), 52.1 (s, TiMe), 42.1 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 39.8 (s, Me_2N), 29.8 (s, *t*-Bu), 10.7 (br q, $^1J_{BC}$ = 54 Hz, MeB). ^{11}B{^{1}H} NMR: −15.2. ^{19}F NMR: −133.4 (d, 6F, $^3J_{FF}$ = 22 Hz, C_6F_5 (*o*-F)), −165.5 (t, 3F, $^3J_{FF}$ = 21 Hz, C_6F_5 (*p*-F)), −168.2 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 49.1. Anal. Calcd for $C_{46}H_{48}BF_{15}N_3$-PTi: C, 54.30, H, 4.75, N, 4.13. Found: C, 54.09, H, 4.25, N, 4.01. **9**: yellow solid (50 mg, 75%). ^{1}H NMR: 6.45 (s, 5H, Cp), 1.54 (d, 27H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 1.37 (d, 9H, $^2J_{PH}$ = 8 Hz, PMe), 0.80 (s, 3H, TiMe), 0.48 (br s, 3H, MeB). ^{13}C{^{1}H} NMR: 148.7 (d m, $^1J_{CF}$ = 238, C_6F_5 (*o*-C)), 138.1 (d m, $^1J_{CF}$ = 243 Hz, C_6F_5 (*p*-C)), 136.9 (ddd, $^1J_{CF}$ = 245 Hz, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 12 Hz, C_6F_5 (*m*-C)), 129.2 (br s, C_6F_5 (*ipso*-C)), 114.9 (s, Cp), 63.9 (d, $^2J_{PC}$ = 5 Hz, TiMe), 42.0 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 30.0 (s, *t*-Bu), 26.4 (d, $^1J_{PC}$ = 23 Hz, PMe), 10.6 (br q, $^1J_{BC}$ = 54 Hz, MeB). ^{11}B{^{1}H} NMR: −15.2. ^{19}F NMR: −133.7 (d, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*o*-F)), −165.6 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.1 (m, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 52.1 (s, NP), −18.6 (s, PMe_3). Anal. Calcd for $C_{40}H_{47}BF_{15}NP_2Ti$: C, 50.71, H, 5.00, N, 1.48. Found: C, 50.35, H, 4.69, N, 1.39. **10**: bright yellow solid (112 mg, 61%). ^{1}H NMR: 6.44 (d, 5H,$^3J_{PH}$ = 1 Hz, Cp), 1.76 (m, 6H, PCH_2), 1.56 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.38 (m, 6H, PCH_2CH_2), 1.29 (m, 6H, CH_2Me), 0.94 (t, 9H, $^3J_{HH}$ = 7 Hz, CH_2Me), 0.83 (s, 3H, TiMe), 0.50 (br s, 3H, MeB). ^{13}C{^{1}H} NMR: 148.9 (d m, $^1J_{CF}$ = 120 Hz, $^2J_{CF}$ = 14 Hz, C_6F_5 (*o*-C)), 138.1 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (p−C)), 137.0 (ddd, $^1J_{CF}$ = 250 Hz,$^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 129.2 (br, C_6F_5 (*ipso*)), 114.6 (s, Cp), 64.1 (d,$^2J_{PC}$ = 5 Hz, TiMe), 42.1 (d, $^1J_{PC}$ = 43 Hz, t-Bu), 30.1 (s, *t*-Bu), 26.4 (s, CH_2CH_2), 25.0 (d, $^2J_{PC}$ = 13 Hz, PCH_2), 24.3 (d, $^3J_{PC}$ = 18 Hz, PCH_2-CH_2), 13.7 (s, CH_2Me), 10.6 (br q, J_{B-C} = 54 Hz, MeB). ^{11}B-{^{1}H} NMR: −15.2. ^{19}F NMR: −133.34 (d, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*o*-F)), −165.64 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.15 (m, 6F, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 52.1 (s, NP), 3.0 (s, P*n*-Bu_3). Anal. Calcd for $C_{49}H_{65}BF_{15}NP_2Ti$: C, 54.82, H, 6.10, N, 1.30. Found: C, 54.54, H, 5.88, N, 1.08. **11**: bright yellow solid (69 mg, 87%). ^{1}H NMR: 7.54 (m, 9H, PPh (*o*,*p*-H)), 7.39 (t m, 6H, $^3J_{P-H}$ = 2 Hz, PPh (*m*-H)), 6.31 (d, 5H, $^3J_{PH}$ = 1 Hz, Cp), 1.41 (d, 27 H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.20 (s, 3H, TiMe), 0.50 (br s, 3H, MeB). ^{13}C{^{1}H} NMR: 148.8 (d m, $^1J_{CF}$ = 232 Hz, C_6F_5 (*o*-C)), 138.0 (d m, $^1J_{CF}$ = 245 Hz, C_6F_5 (*p*-C)), 136.9 (ddd, $^1J_{CF}$ = 246 Hz, $^2J_{CF}$ = 23 Hz, $^3J_{CF}$ = 12 Hz, C_6F_5 (*m*-C)), 134.2 (d, $^2J_{PC}$ = 12 Hz, PPh, (*o*-C)), 132.5 (d, $^4J_{PC}$ = 2 Hz, PPh, (*p*-C)), 130.2 (d, $^3J_{PC}$ = 10 Hz, PPh, (*m*-C)), 128.0 (d, $^1J_{PC}$ = 36 Hz, PPh (*ipso*-C)), 129.2 (br s, C_6F_5 (*ipso*-C)), 115.9 (s, Cp), 65.7 (d, $^2J_{PC}$ = 5 Hz, TiMe), 42.2 (d, $^1J_{PC}$ = 42 Hz, *t*-Bu), 30.0 (s, *t*-Bu), 10.4 (br q, $^1J_{BC}$ = 54 Hz, MeB). ^{11}B{^{1}H} NMR: −15.2. ^{19}F NMR: −133.4 (d, 6F, $^3J_{FF}$ = 22 Hz, C_6F_5 (*o*-F)), −165.6 (t, 3F, $^3J_{FF}$ = 21 Hz, C_6F_5 (*p*-F)), −168.1 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 54.3 (s, NP), 15.1 (s, PPh_3). Anal. Calcd for $C_{55}H_{53}BF_{15}NP_2Ti$: C, 58.27, H, 4.71, N, 1.24. Found: C, 58.01, H, 4.58, N, 1.11. **12**: yellow solid (72 mg, 87%). ^{1}H NMR: 7.30 (m, 12H, C_6H_4), 6.29 (s, 5H, Cp), 2.41 (s, 9H, Me), 1.40 (d, 27 H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 1.17 (s, 3H, TiMe), 0.50 (br s, 3H, MeB). ^{13}C{^{1}H} NMR: 148.9 (d m, $^1J_{CF}$ = 235 Hz, C_6F_5 (*o*-C)), 143.2 (d, $^4J_{PC}$ = 2 Hz, P(*p*-$CH_3C_6H_4$) (*p*-C)), 138.1 (d m), $^1J_{CF}$ = 243 Hz, C_6F_5 (*p*-C)), 137.0 (ddd, $^1J_{CF}$ = 247 Hz, $^2J_{CF}$ = 23 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 134.1 (d, $^2J_{PC}$ = 13 Hz, C_6H_4 (*o*-C)), 130.8 (d, $^3J_{PC}$ = 10 Hz, C_6H_4 (*m*-C)), 129.2 (br s, C_6F_5 (*ipso*-C)), 125.8 (d, $^1J_{PC}$ = 38 Hz, C_6H_4 (*ipso*-C)), 115.8 (s, Cp), 65.1 (d, $^2J_{PC}$ = 5 Hz, TiMe), 42.2 (d, $^1J_{PC}$ = 42 Hz, *t*-Bu), 30.0 (s, *t*-Bu), 21.7 (s, Me), 10.6 (br q, $^1J_{BC}$ = 54 Hz, MeB). ^{11}B{^{1}H} NMR: −15.2. ^{19}F NMR: −133.7 (d, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*o*-F)), −165.6 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.1 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 53.6 (s, NP), 13.6 (s, TiP). Anal. Calcd for $C_{58}H_{59}BF_{15}NP_2Ti$: C, 59.25, H, 5.06, N, 1.19. Found: C, 59.02, H, 4.93, N, 1.01. **13**: yellow solid (147 mg, 93%). ^{1}H NMR: 8.20 (s, br, 2H, Py (α-H)), 8.05 (t, 1H, $^3J_{HH}$ = 8 Hz, Py (*γ*-H)), 7.61 (t, 2H, $^3J_{HH}$ = 7 Hz, Py (*β*-H)), 6.46 (s, 5H, Cp), 1.46 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.29 (s, 3H, TiMe). ^{13}C{^{1}H} NMR: 148.8 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 148.0 (s, Py (α-C)), 142.4 (s, Py (*γ*-C)), 138.9 (d m, $^1J_{CF}$ = 243 Hz, C_6F_5 (*p*-C)), 136.9 (d m, $^1J_{CF}$ = 247 Hz, C_6F_5 (*m*-C)), 127.0 (s, Py (*β*-C)), 124.8 (br s, C_6F_5 (*ipso*-C)), 115.5 (s, Cp), 54.9 (s, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, t-Bu), 29.7 (s, *t*-Bu). ^{11}B{^{1}H} NMR: −16.8. ^{19}F NMR: −133.2 (s, 8F, C_6F_5 (*o*-F)), −163.9 (t, 4F, $^3J_{FF}$ = 21 Hz, C_6F_5 (*p*-F)), −167.7 (t, 8F, $^3J_{FF}$ = 17 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 51.7. Anal. Calcd for $C_{47}H_{40}BF_{20}N_2PTi$: C, 51.20, H, 3.66, N, 2.54. Found: C, 51.07, H, 3.32, N, 2.27. **14**: yellow solid (72 mg, 91%). ^{1}H NMR: 8.16 (d, 2H, $^3J_{HH}$ = 6 Hz, C_5H_4N (*β*-H)), 7.23 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4N (α-H)), 6.44 (d, 5H, Cp), 2.78 (q, 2H, $^3J_{HH}$ = 8 Hz, Et), 1.45 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.27 (t, 3H, $^3J_{HH}$ = 8 Hz, Et), 1.24 (s, 3H, TiMe). ^{13}C{^{1}H} NMR: 160.0 (s, C_5H_4N (*γ*-C)), 148.8 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 148.0 (s, C_5H_4N (α-C)), 138.9 (d m), $^1J_{CF}$ = 240 Hz, C_6F_5 (*p*-C)), 137.0 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*m*-C)), 126.2 (s, C_5H_4N (*β*-C), 124.6 (br s, C_6F_5 (*ipso*-C)), 115.5 (s, Cp), 54.6 (s, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 29.9 (s, *t*-Bu), 29.1 (s, Et), 13.9 (s, Et). ^{11}B{^{1}H} NMR: −16.8. ^{19}F NMR: −133.3 (s, 6F, C_6F_5 (*o*-F)), −163.9 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (m, 6F, C_6F_5 (*m*-F)). ^{31}P-{^{1}H} NMR: 51.2. Anal. Calcd $C_{49}H_{44}BF_{20}N_2PTi$: C, 52.06, H, 3.92, N, 2.48. Found: C, 51.88, H, 3.64, N, 2.12. **15**: yellow solid (70 mg, 86%). ^{1}H NMR: 8.06 (br s, 2H, C_5H_4N, (α-H)), 7.56 (br s, 2H, C_5H_4N, (*β*-H)), 6.44 (s, 5H, Cp), 1.44 (d, 27 H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 1.32 (s, 9H, *t*-Bu), 1.27 (s, 3H, TiMe). ^{13}C{^{1}H} NMR: 160.0 (s, C_5H_4N (*γ*-C)), 148.8 (d m, $^1J_{CF}$ = 235 Hz, C_6F_5 (*o*-C)), 147.7 (s, C_5H_4N (α-C)), 138.8 (d m, $^1J_{CF}$ = 246 Hz, C_6F_5 (*p*-C)), 136.9 (d m), $^1J_{CF}$ = 250 Hz, C_6F_5 (*m*-C)), 125.2 (br s, C_6F_5 (*ipso*-C)), 123.8 (s, C_5H_4N (*β*-C)), 115.4 (s, Cp), 54.5 (s, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 34.7 (s, *t*-Bu), 30.2 (s, *t*-Bu), 29.8 (s, *t*-Bu). ^{11}B{^{1}H} NMR: −16.8. ^{19}F NMR: −133.2 (s, 8F, C_6F_5 (*o*-F)), −163.9 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (br s, 8F, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 51.1. Anal. Calcd for $C_{51}H_{48}BF_{20}N_2PTi$: C, 52.87, H, 4.18, N, 2.41. Found: C, 52.66, H, 3.87, N, 2.23. **16**: yellow solid (66 mg, 82%). ^{1}H NMR: 7.65 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4N, (α-H)), 6.53 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4N), (*β*-H)), 6.38 (s, 5H, Cp), 3.08 (s, 6H, 4-Me_2N), 1.48 (d, 27 H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.12 (s, 3H, TiMe). ^{13}C{^{1}H} NMR: 155.9 (s, C_5H_4N, (*γ*-C)), 148.8 (d m, $^1J_{CF}$ = 253 C_6F_5 (*o*-C)), 147.0 (s, C_5H_4N, (α-C)), 138.9 (d m), $^1J_{CF}$ = 245 Hz, C_6F_5 (*p*-C)), 137.0 (d m, $^1J_{CF}$ = 238 Hz, C_6F_5 (*m*-C)), 125.1 (br s, C_6F_5 (*ipso*-C)), 114.6 (s, Cp), 107.4 (s, C_5H_4N, (*β*-C)), 52.3 (s, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 39.7 (s, Me_2N), 29.9 (s, *t*-Bu). ^{11}B{^{1}H} NMR: −16.8. ^{19}F NMR: −133.3 (s, 8F, C_6F_5 (*o*-F)), −163.9 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (br s, 8F, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 48.9. Anal. Calcd for $C_{49}H_{45}BF_{20}N_3$-PTi: C, 51.38, H, 3.96, N, 3.67. Found: C, 51.23, H, 3.59, N, 3.39. **17**: bright yellow solid (58 mg, 75 %). ^{1}H NMR: 6.45 (s, 5H, Cp), 1.55 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.37 (d, 9H, $^2J_{PH}$ = 8 Hz, PCH_3), 0.80 (s, 3H, TiMe). ^{13}C{^{1}H} NMR: 148.3 (d m, $^1J_{CF}$ = 244 Hz, C_6F_5 (*o*-C)), 138.5 (d m, $^1J_{CF}$ = 234 Hz, C_6F_5 (*p*-C)), 136.5 (ddd, $^1J_{CF}$ = 240 Hz, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 124.0 (br s, C_6F_5 (*ipso*-C)), 114.8 (s, Cp), 63.9 (s,

TiMe), 41.9 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 30.0 (s, *t*-Bu), 14.8 (d, $^1J_{PC}$ = 23 Hz, PMe). $^{11}B\{^1H\}$ NMR: −16.9. ^{19}F NMR: −133.3 (s, 8F, C_6F_5 (*o*-F)), −163.9 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (t, 8F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 52.2 (s, NP), −18.9 (s, PMe_3). Anal. Calcd for $C_{45}H_{44}BF_{20}NP_2Ti$: C, 49.16; H, 4.03, N, 1.27. Found: C, 49.00, H, 3.93, N, 1.01. **18**: yellow solid (68 mg, 80%). ^1H NMR: 6.45 (d, 5H, $^3J_{PH}$ = 1 Hz, Cp), 1.76 (m, 6H, PCH_2CH_2), 1.56 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.36 (m, 6H, PCH_2CH_2), 1.30 (m, 6H, CH_2CH_2), 0.95 (t, 9H, $^3J_{HH}$ = 7 Hz, Me), 0.83 (s, 3H, TiMe). $^{13}C\{^1H\}$ NMR: 148.9 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 138.9 (d m, $^1J_{CF}$ = 236 Hz, C_6F_5 (*p*-C)), 137.0 (d m, $^1J_{CF}$ = 250 Hz, C_6F_5 (*m*-C)), 124.8 (br s, C_6F_5 (*ipso*-C)), 114.7 (s, Cp), 64.5 (d, $^2J_{PC}$ = 5 Hz, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 30.2 (s, *t*-Bu), 26.3 (s, CH_2CH_2), 25.1 (d, $^2J_{PC}$ = 13 Hz, PCH_2CH_2), 24.4 (d, $^3J_{PC}$ = 18 Hz, PCH_2CH_2), 13.8 (s, Me). $^{11}B\{^1H\}$ NMR: −16.9. ^{19}F NMR: −133.3 (s, 8F, C_6F_5 (*o*-F)), −163.9 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (t, 8F, $^3J_{FF}$ = 18 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 52.2 (s, NP), 3.0 (s, P*n*-Bu_3). Anal. Calcd for $C_{54}H_{62}BF_{20}NP_2Ti$: C, 52.92, H, 5.10, N, 1.14. Found: C, 52.86, H, 5.09, N, 1.02. **19**: amber-yellow solid (70 mg, 78%). ^1H NMR: 7.65 (t m, 3H, $^3J_{PH}$ = 2 Hz, PPh (*p*-H)), 7.51 (t m, 6H, $^3J_{PH}$ = 2 Hz, PPh (*o*-H)), 7.39 (t m, 6H, $^3J_{PH}$ = 2 Hz, PPh (*m*-H)), 6.31 (d, 5H, $^3J_{PH}$ = 1 Hz, Cp), 1.40 (d, 27 H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.21 (s, 3H, TiMe). $^{13}C\{^1H\}$ NMR: 148.7 (d m, $^1J_{CF}$ = 242 Hz, C_6F_5 (*o*-C)), 138.8 (d m, $^1J_{CF}$ = 234 Hz, C_6F_5 (*p*-C)), 135.4 (d m, $^1J_{CF}$ = 251 Hz, C_6F_5 (*m*-C)), 134.1 (d, $^2J_{PC}$ = 12 Hz, PPh_3, (*o*-C)), 132.5 (d, $^4J_{PC}$ = 2 Hz, PC_6H_5, (*p*-C)), 130.1 (d, $^3J_{PC}$ = 10 Hz, PPh_3, (*m*-C)), 128.0 (d, $^1J_{PC}$ = 36 Hz, PPh, (*ipso*-C)), 124.2 (br s, C_6F_5 (*ipso*-C)), 115.9 (s, Cp), 65.7 (s, TiMe), 42.2 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 30.0 (s, *t*-Bu). $^{11}B\{^1H\}$ NMR: −16.9. ^{19}F NMR: −133.3 (s, 8F, C_6F_5 (*o*-F)), −164.0 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.8 (t, 8F, $^3J_{FF}$ = 18 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 54.3 (s, NP), 15.1 (s, PPh_3). Anal. Calcd for $C_{60}H_{50}BF_{20}NP_2Ti$: C, 56.05, H, 3.92, N, 1.09. Found: C, 55.91, H, 3.76, N, 0.99. **20**: orange solid (71 mg, 76%). ^1H NMR: 7.32 (m, 12H, C_6H_4), 6.30 (s, 5H, Cp), 2.41 (s, 9H, Me), 1.40 (d, 27 H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.19 (s, 3H, TiMe). $^{13}C\{^1H\}$ NMR: 148.8 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 143.1 (d, $^4J_{PC}$ = 2 Hz, C_6H_4) (*p*-C)), 138.7 (d m, $^1J_{CF}$ = 236 Hz, C_6F_5 (*p*-C)), 136.1 (d m, $^1J_{CF}$ = 250 Hz, C_6F_5 (*m*-C)), 134.0 (d, $^2J_{PC}$ = 13 Hz, C_6H_4 (*o*-C)), 130.8 (d, $^3J_{PC}$ = 10 Hz, C_6H_4 (*m*-C)), 124.7 (br s, C_6F_5 (*ipso*-C)), 125.9 (d, $^1J_{PC}$ = 38 Hz, C_6H_4) (*ipso*-C)), 115.9 (s, Cp), 65.2 (d, $^2J_{PC}$ = 5 Hz, TiMe), 42.2 (d, $^1J_{PC}$ = 42 Hz, *t*-Bu), 29.9 (s, *t*-Bu), 21.8 (s, Me). $^{11}B\{^1H\}$ NMR: −16.9. ^{19}F NMR: −133.4 (s, 8F, C_6F_5 (*o*-F)), −164.0 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.8 (t, 8F, $^3J_{FF}$ = 18 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 53.6 (s, NP), 13.6 (s, P(*p*-Me-C_6H_4)$_3$). Anal. Calcd for $C_{63}H_{56}BF_{20}NP_2Ti$: C, 56.99, H, 4.25, N, 1.05. Found: C, 56.69, H, 4.04, N, 1.00.

Isolation of [CpTi(NP*t*-Bu_3)Cl($NC_5H_4NMe_2$)][$B(C_6F_5)_4$], 21. A solution of **16** in CH_2Cl_2 was allowed to stand at 25 °C for several weeks. Concentration of the solution afforded the isolation of crystals of **21** (20 mg, 25% yield). ^1H NMR: 7.64 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4), 6.51 (d, 2H, $^3J_{HH}$ = 7 Hz, C_5H_4), 6.35 (s, 5H, Cp), 3.06 (s, 6H, Me_2N), 1.46 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu). $^{13}C\{^1H\}$ NMR: 155.6 (s, C_5H_4), 148.8 (d m), $^1J_{CF}$ = 252 C_6F_5 (*o*-C)), 146.7 (s, C_5H_4,), 138.9 (d m, $^1J_{CF}$ = 245 Hz, C_6F_5 (*p*-C)), 136.9 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*m*-C)), 125.0 (br s, C_6F_5 (*ipso*-C)), 115.0 (s, Cp), 107.0 (s, C_5H_4), 42.1 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 39.7 (s, Me), 29.9 (s, *t*-Bu). $^{11}B\{^1H\}$ NMR: −16.8 (s). ^{19}F NMR: −133.3 (s, 8F, C_6F_5 (*o*-F)), −163.9 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (br s, 8F, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 49.0. Anal. Calcd for $C_{48}H_{42}BClF_{20}N_3PTi$: C, 49.44, H, 3.63, N, 3.60. Found: C, 49.19, H, 3.29, N,3.47.

Synthesis of [(*o*-$MeC_6H_4)_3PCH_2Cl$][$B(C_6F_5)_4$], 22. A solution of **2** (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was combined at 25 °C with a solution of [Ph_3C][$B(C_6F_5)_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), followed by the addition of a solution of P(*o*-$MeC_6H_4)_3$ (21 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 30 min. The solvent was removed in vacuo, and the recovered orange oil was washed with pentanes (3 × 5 mL) and dried to provide an orange solid. NMR data revealed the presence of **22** and **23**. Recrystallization of this residue from CH_2Cl_2 (1 mL) layered with pentanes (3 mL) provided colorless crystals of **22** (49 mg, 68%). ^1H NMR: 7.81 (m, 3H, C_6H_4), 7.60−7.47 (m, 9H, C_6H_4), 4.93 (br s, 2H, PCH_2), 2.25 (s, 9H, Me). ^1H NMR (233 K): 7.81 (m, 3H, C_6H_4), 7.60−7.47 (m, 9H, C_6H_4), 5.17 (dd $^2J_{PH}$ = 5 Hz, $^2J_{HH}$ = 15 Hz), 4.71 (dd $^2J_{PH}$ = 3 Hz, $^2J_{HH}$ = 15 Hz), 2.25 (s, 9H, Me). $^{13}C\{^1H\}$ NMR: (partial) 148.7 (d m, $^1J_{CF}$ = 243 Hz, C_6F_5 (*o*-C)), 144.2 (d, $^2J_{PC}$ = 9 Hz, C_6H_4), 138.7 (d m), $^1J_{CF}$ = 250 Hz, C_6F_5 (*p*-C)), 137.0 (d, $^4J_{PC}$ = 3 Hz, C_6H_4), 136.8 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*m*-C)), 135.5 (d, $^2J_{PC}$ = 12 Hz, C_6H_4), 134.7 (d, $^3J_{PC}$ = 11 Hz, C_6H_4), 128.9 (d, $^3J_{PC}$ = 13 Hz, C_6H_4), 24.7 (br s, C_6F_5 (*ipso*-C)), 42.2 (d, $^1J_{PC}$ = 57 Hz, PCH_2), 23.0 (d, Me). $^{11}B\{^1H\}$ NMR: −16.9. ^{19}F NMR: −133.8 (s, 8F, C_6F_5 (*o*-F)), −163.8 (t, 4F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (br s, 8F, $^3J_{FF}$ = 18 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 29.1. Anal. Calcd for $C_{22}H_{23}PCl$: C, 74.68, H, 6.55. Found: C, 74.55, H, 6.43.

Synthesis of [{CpTi(NP*t*-Bu_3)Me}$_2$(*μ*-Cl)][$B(C_6F_5)_4$], 23. A solution of **2** (0.025 g, 0.07 mmol) in CH_2Cl_2 (2 mL) was combined with a solution of [CPh_3][$B(C_6F_4)_4$] (0.064 g, 0.07 mmol) in CH_2Cl_2 (2 mL) at 25 °C and left to stir for 30 min. A second equivalent of **2** (0.025 g, 0.07 mmol) in CH_2Cl_2 (2 mL) was then added, and the solution was stirred for an additional 30 min. The solvent was removed in vacuo and the recovered oil washed with pentanes (3 × 5 mL) and dried under vacuum to give a red solid (0.088 g, 89%). The *rac*/*meso* isomers of **23** were present in a 1:1 ratio and could not be specifically assigned. ^1H NMR: 6.40, 6.36 (s, 10H, Cp), 1.51, 1.49 (d, 54H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.11, 1.05 (s, 6H, TiMe). $^{13}C\{^1H\}$ NMR: 148.8 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*o*-C)), 138.8 (d m, $^1J_{CF}$ = 243 Hz, C_6F_5 (*p*-C)), 136.9 (d m, $^1J_{CF}$ = 246 Hz, C_6F_5 (*m*-C)), 124.2 (br s, C_6F_5 (*ipso*-C)), 114.8, 114.7 (s, Cp), 42.4 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 29.9 (s, *t*-Bu), 25.4 (s, TiMe). $^{11}B\{^1H\}$ NMR: −16.8. ^{19}F NMR: −133.2 (s, 8F, C_6F_5 (*o*-F)), −164.0 (t, 4F, $^3J_{FF}$ = 21 Hz, C_6F_5 (*p*-F)), −167.8 (s, 8F, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (233 K): 50.1, 49.9. Anal. Calcd for $C_{58}H_{70}BF_{20}N_2P_2Ti_2Cl$: C, 50.51, H, 5.11, N, 2.03. Found: C, 50.34, H, 5.03, N, 2.00.

Synthesis of [{CpTi(NP*t*-Bu_3)(*μ*-Cl)}$_2$][$MeB(C_6F_5)_3$]$_2$, 24. A solution of **2** (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at 25 °C to a solution of $B(C_6F_5)_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) and was left to stir for 30 min. The solvent was removed in vacuo and the recovered oil was washed with pentanes (3 × 5 mL) before drying to afford an amber solid (106 mg, 85 %). ^1H NMR: 6.76 (s, 10H, Cp), 1.47 (d, 54H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 0.54 (br s, 6H, MeB). $^{13}C\{^1H\}$ NMR: 148.9 (d m, $^1J_{CF}$ = 236 Hz, C_6F_5 (*o*-C)), 138.3 (d m, $^1J_{CF}$ = 242 Hz, C_6F_5 (*p*-C)), 137.0 (d m, $^1J_{CF}$ = 247 Hz, C_6F_5 (*m*-C)), 127.6 (br s, C_6F_5 (*ipso*-C)), 117.6 (s, Cp), 42.7 (d, $^1J_{PC}$ = 40 Hz, *t*-Bu), 29.9 (s, *t*-Bu), 10.5 (br s, MeB). $^{11}B\{^1H\}$ NMR: −15.2 (s). ^{19}F NMR: −133.4 (d, 12F, $^3J_{FF}$ = 23 Hz, C_6F_5 (*o*-F)), −165.6 (t, 6F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.1 (t, 12F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR: 60.7. Anal. Calcd for $C_{72}H_{70}B_2Cl_2F_{30}N_2P_2Ti_2$: C, 48.49, H, 3.96, N, 1.57. Found: C, 48.23, H, 3.67, N, 1.29.

Synthesis of [{CpTi(NP*t*-Bu_3)Me}$_2$(*μ*-Me)][$B(C_6F_5)_4$], 25. A solution of **2** (25 mg, 0.07 mmol) in C_6H_5Cl (2 mL) was combined at 25 °C with a solution of [CPh_3][$B(C_6F_5)_4$] (64 mg, 0.07 mmol) in C_6H_5Cl (2 mL) and left to stir for 30 min. A second equivalent of **2** (25 mg, 0.07 mmol) in C_6H_5Cl (2 mL) was added to the reaction mixture. The solution was stirred at 25 °C for another 30 min. The solvent was removed in vacuo, and the recovered purple oil was washed with pentanes (3 × 5 mL) before drying to afford a purple solid (77 mg, 79%). The *rac*/*meso* isomers were present in a 1:1 ratio and could not be specifically assigned. ^1H NMR: 6.29, 6.25 (s, 10H, Cp), 1.51, 1.50 (d, 54H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 0.69, 0.66 (s, 6H, TiMe), 0.14, 0.13 (s, 3H, *μ*-TiMe). $^{13}C\{^1H\}$ NMR: 148.9 (d m, $^1J_{CF}$ = 236 Hz, C_6F_5 (*o*-C)), 139.0 (d m, $^1J_{CF}$ = 244 Hz, C_6F_5 (*p*-C)), 137.0 (d m, $^1J_{CF}$ = 247 Hz, C_6F_5 (*m*-C)), 126.6 (s, br, C_6F_5 (*ipso*-C)), 113.6, 113.5 (s, Cp), 49.1, 49.0 (s, *μ*-TiMe) 42.2 (d, $^1J_{PC}$ = 44 Hz, *t*-Bu), 30.7, 30.6 (s, TiMe), 30.0 (s, *t*-Bu). $^{11}B\{^1H\}$ NMR:

−16.8. ^{19}F NMR: −133.3 (s, 6F, C_6F_5 (*o*-F)), −163.9 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −167.7 (s, 6F, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 47.0. Anal. Calcd for $C_{61}H_{73}BF_{20}N_2P_2Ti_2$: C, 52.99, H, 5.32, N, 2.03. Found: C, 52.69, H, 5.21, N, 1.93.

Synthesis of [CpTi(NP*t*-Bu$_3$)((N*i*-Pr)$_2$CMe)][MeB(C$_6$F$_5$)$_3$], 26, and [TiCp(NP*t*-Bu$_3$)(PhCCPh(Me))][MeB(C$_6$F$_5$)$_3$], 27. These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of **2** (100 mg, 0.28 mmol) and $B(C_6F_5)_3$ (142 mg, 0.28 mmol) were prepared separately in CH_2Cl_2 (5 mL). (N*i*-Pr)$_2$C (0.044 mL, 0.28 mmol) was added to the solution containing the Ti-precursor, followed by addition of the borane reagent. The mixture became dark red immediately, and after stirring for an additional 5 min, the solvent was removed in vacuo. The residue was washed with benzene (5 × 3 mL) to afford a dark red solid, **26** (132 mg, 47%). ^{1}H NMR: 6.64 (s, 5H, Cp), 3.89 (sept, 2H, $^3J_{HH}$ = 6 Hz, N*i*-Pr), 2.17 (s, 3H, CMe), 1.47 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.20 (d, 6H, $^3J_{HH}$ = 6 Hz, N*i*-Pr), 1.12 (d, 6H, $^3J_{HH}$ = 6 Hz, N*i*-Pr), 0.50 (br, 3H, MeB). ^{13}C{^{1}H} NMR: 163.5 (s, CMe), 148.8 (dd, $^1J_{CF}$ = 240 Hz, $^2J_{CF}$ = 11 Hz, C_6F_5 (*o*-C)), 138.1 (d m, $^1J_{CF}$ = 240 Hz, C_6F_5 (*p*-C)), 136.9 (ddd, $^1J_{CF}$ = 240 Hz,$^2J_{CF}$ = 23 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 128.9 (br s, C_6F_5 (*ipso*)), 116.6 (s, Cp), 51.2 (s, N*i*-Pr), 42.3 (d, $^1J_{PC}$ = 43 Hz, *t*-Bu), 29.8 (s, *t*-Bu), 26.3 (s, N*i*-Pr), 25.2 (s, N*i*-Pr), 12.9 (s, CMe), 10.6 (br q, J_{BC} = 58 Hz, MeB). ^{11}B{^{1}H} NMR: −19.1. ^{19}F −133.4 (d, 6F, $^3J_{FF}$ = 23 Hz, C_6F_5 (*o*-F)), −163.6 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.2 (m, 6F, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 53.4. Anal. Calcd for $C_{44}H_{53}BF_{15}N_3PTi$: C, 52.92, H, 5.35, N, 4.21. Found: C, 52.60, H, 5.43, N, 4.09. **27**: deep red oil, despite exhaustive washing (54%). ^{1}H NMR: 7.59 (d, 2H, $^3J_{HH}$ = 10 Hz, Ph), 7.40 (m, 3H, Ph), 7.15 (m, 3H, Ph), 7.08 (d, 2H, $^3J_{HH}$ = 7 Hz, Ph), 6.32 (s, 5H, Cp), 1.65 (d, 27H, $^3J_{PH}$ = 14 Hz, *t*-Bu), 1.89 (s, 3H, CMe), 0.52 (br s, 3H, MeB). ^{13}C{^{1}H} NMR: 198.1 (s, Ti−CPh), 148.3 (d m, $^1J_{CF}$ = 226 Hz, C_6F_5 (*o*-C)), 137.5 (d m, $^1J_{CF}$ = 233 Hz, C_6F_5 (*p*-C)), 136.4 (ddd, $^1J_{CF}$ = 263 Hz,$^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 11 Hz, C_6F_5 (*m*-C)), 135.9 (s, Ph), 135.0 (s, Ph), 134.5 (s, Ph), 131.5 (s, Ph), 129.7 (br, C_6F_5 (*ipso*)), 128.8 (s, Ph), 128.0 (s, Ph), 127.0 (s, Ph), 125.8 (s, Ph), 116.6 (s, Cp), 42.1 (d, $^1J_{PC}$ = 41 Hz, *t*-Bu), 29.5 (s, *t*-Bu), 24.8 (s, CMe), 10.0 (br q, $^1J_{BC}$ = 43 Hz, MeB). ^{11}B{^{1}H} NMR: −19.1. ^{19}F NMR: −133.3 (d, 6F, $^3J_{FF}$ = 23 Hz, C_6F_5 (*o*-F)), −163.5 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.1 (m, 6F, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR: 56.7. Anal. Calcd for $C_{51}H_{63}BF_{15}NPTi$: C, 58.36, H, 4.61, N, 1.33. Found: C, 57.99, H, 4.16, N, 1.35.

Generation of [TiCp(NP*t*-Bu$_3$)(PhCCPh(Me))(PMe$_3$)][MeB(C$_6$F$_5$)$_3$], 28. To a solution of **3** (0.065 g, 0.075 mmol) in CD_2Cl_2 (2 mL) was added excess neat PMe_3 (0.020 mL, 0.192 mmol). The mixture became dark red immediately, and after stirring for an additional 5 min, NMR spectroscopy revealed that the conversion to **39** was 90%. ^{1}H NMR: 7.16 (t, 2H, Ph, J_{HH} = 7 Hz), 6.97 (t, 4H, Ph, J_{HH} = 7 Hz), 6.74 (dd, 2H, Ph, J_{HH} = 8 Hz, 1 Hz), 6.48 (d, 2H, Ph, J_{HH} = 8 Hz), 6.43 (s, 5H, Cp), 2.18 (s, 3H, Me), 1.57 (d, 27H, *t*-Bu, J_{PH} = 13 Hz), 0.95 (d, 9H, PMe, J_{PH} = 8 Hz), 0.48 (br s, 3H, MeB). ^{19}F NMR: −133.3 (d, 6F, $^3J_{FF}$ = 23 Hz, C_6F_5 (*o*-F)), −163.5 (t, 3F, $^3J_{FF}$ = 20 Hz, C_6F_5 (*p*-F)), −168.1 (m, 6F, C_6F_5 (*m*-F)). ^{11}B NMR: −19.3. ^{31}P{^{1}H} NMR: 52.5, −18.2.

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° < 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. 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.

Structure Solution and Refinement, Non-hydrogen atomic scattering factors were taken from the literature tabulations.[38] 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 $w(|F_o| - |F_c|)^2$ where the weight w 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 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 Supporting Information.

Results and Discussion

Zwitterions. We have previously communicated that reaction of **2** with $B(C_6F_5)_3$ affords the zwitterionic species CpTi(NP*t*-Bu$_3$)Me(μ-MeB(C$_6$F$_5$)$_3$), **3** (Scheme 1).[14] The NMR data for **3** are consistent with molecular symmetry that infers a rapid exchange of the Ti-bound and B-bound methyl groups. This process was not slowed even upon cooling to −80 °C. Analogous exchange processes have been observed in metallocene systems,[39] although such exchange was not seen for the pentamethylcyclopentadienyl complex Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$.[40,41] Nonetheless, the previously reported solid state structure of **3** confirms the zwitterionic formulation, in which one methyl group is terminal on Ti while a second borate-bound methyl group interacts through the C−H bonds with the cationic Ti center (Scheme 1). The structural details of **3** are reminiscent of ($C_5H_3Me_2$)$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$[42] and ($C_5H_3(SiMe_3)_2$)$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$[43] and reinforce the analogy between phosphinimide ligands and Cp. It is also noteworthy that our previous report demonstrated that **3** was an effective single-component olefin polymerization catalyst.[14]

Donor-Stabilized Cations. Efforts were made to isolate donor-stabilized phosphinimide-based cations. Reaction of **2** with $B(C_6F_5)_3$ in the donor solvent THF afforded the species [TiCp(NP*t*-Bu$_3$)Me(THF)][MeB(C$_6$F$_5$)$_3$], **4**. Compound **4** polymerizes this solvent if left in solution for several hours, and for this reason, timely removal of the solvent was critical. In a similar reaction

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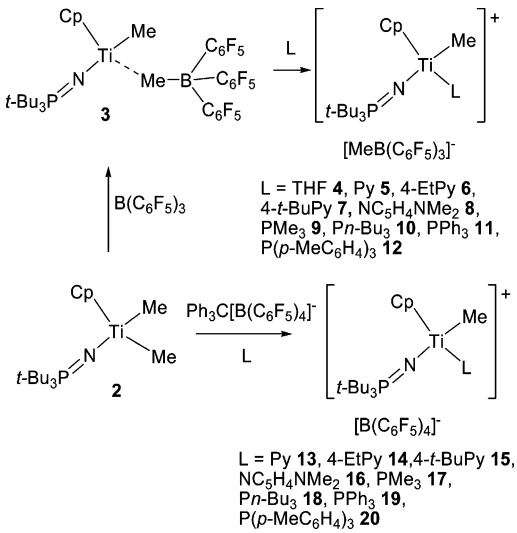
Table 1. Crystallographic Parameters[a]

	17	**21**·0.25CH_2Cl_2	**22**	**24**·CH_2Cl_2
formula	$C_{45}H_{44}BF_{20}NP_2Ti$	$C_{48.25}H_{39.5}BCl_{1.5}F_{20}N_3PTi$	$C_{46}H_{23}BClF_{20}P$	$C_{83}H_{68}B_2Cl_4F_{40}N_2P_2Ti_2$
fw	1099.46	1184.18	1032.87	2174.54
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2/c$	$P\bar{1}$
a (Å)	15.707(9)	10.899(5)	21.297(14)	12.489(6)
b (Å)	18.379(10)	27.244(13)	7.996(5)	13.693(7)
c (Å)	18.198(10)	18.146(9)	25.302(16)	14.974(7)
α (deg)				93.120(10)
β (deg)	108.838(10)	97.102(9)	91.693(12)	109.771(9)
γ (deg)				107.766(9)
V (Å^3)	4972(5)	5347(4)	4307(5)	2259.1(19)
Z	4	4	4	1
d(calc) (g cm^{-1})	1.469	1.474	1.593	1.597
abs coeff, μ (cm^{-1})	0.344	0.371	0.248	0.459
no. of data collected	20 949	22 741	17 533	9658
no. of data $F_o^2 > 3\sigma(F_o^2)$	7065	7609	6134	6399
no. of variables	631	684	623	613
R	0.0399	0.0573	0.0329	0.0328
R_w	0.0931	0.1567	0.0800	0.0845
GOF	0.820	0.947	0.851	0.924

[a] The data were collected at 20 °C with Mo Kα radiation (λ = 0.71073 Å).

Scheme 1. Synthesis of Complexes 3−20



sequence using the poorer donor solvent CH_2Cl_2, reaction of **2** with $B(C_6F_5)_3$ with subsequent addition of one of several substituted pyridines or tertiary phosphines afforded the donor-stabilized complexes [Cp(NP*t*-Bu_3)-TiMe(L)][$MeB(C_6F_5)_3$] (L = PyH **5**, 4-EtPy **6**, 4-*t*-BuPy **7**, $NC_5H_4NMe_2$ **8**, PMe_3 **9**, P*n*-Bu_3 **10**, PPh_3 **11**, P(*p*-$MeC_6H_4)_3$ **12**) (Scheme 1). The cations that were stabilized by the phosphine ligands were more robust than the corresponding pyridine-stabilized cations in solution. In a similar fashion, reaction of **2** with [CPh_3][$B(C_6F_5)_4$] in the presence of the appropriate donor ligand provided the analogous salts, [Cp(NP*t*-Bu_3)TiMe(L)][$B(C_6F_5)_4$] (L = PyH **13**, 4-EtPy **14**, 4-*t*-BuPy **15**, $NC_5H_4NMe_2$ **16**, PMe_3 **17**, P*n*-Bu_3 **18**, PPh_3 **19**, P(*p*-$MeC_6H_4)_3$ **20**). These products were completely characterized using ^{1}H, ^{13}C-{^{1}H}, ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{19}F NMR spectroscopy and elemental analysis. These salts exhibit ^{31}P{^{1}H} NMR signals corresponding to the phosphinimide ligand that are shifted about 20 ppm downfield relative to their precursor complexes, to ca. 50 ppm. Furthermore, a significant downfield shift is observed for the ^{31}P resonances upon coordination of the phosphine donor to the cationic titanium center. Similarly, the ^{1}H resonances attributed to the Cp ligand shift downfield from 6.07 to ca. 6.40 ppm, while the Ti-bound methyl group resonance shifts from 0.03 ppm to ca. 1.20 ppm. The ^{11}B{^{1}H} and ^{19}F NMR shifts are as expected for the free anions of both borate derivatives. In the case of **17**, this formulation was confirmed crystallographically (Figure 1). The Ti−N and Ti−methyl-C distances of 1.769(3) and 2.193(3) Å and a Ti−N−P angle of 172.20-(17)° are similar to those seen in **3** (Ti−N 1.765(3) Å, Ti−C 2.123(5) Å, P−N−Ti 176.0(2)°). The coordinated phosphine in **17** has a Ti−P distance of 2.6723(18) Å, while the Ti−N distance is similar to that seen in [Cp*Ti($NPBu_3$)H(THF)]$^+$ (1.781(2) Å). The Ti−P distance in **17** is considerably longer than the Ti−O bond length (2.075(2) Å) in the hydride cation, consistent with the oxophilicity of Ti and the greater steric demands of PMe_3 versus THF.[37]

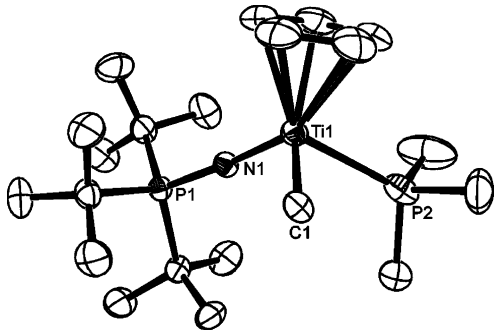


Figure 1. ORTEP drawing of the cation of **17**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Ti(1)−N(1) 1.769-(3), Ti(1)−C(1) 2.193(3), Ti(1)−P(2) 2.6723(18), P(1)−N(1) 1.618(3), N(1)−Ti(1)−C(1) 102.16(12), N(1)−Ti(1)−P(2) 105.08(9), C(1)−Ti(1)−P(2) 92.02(10), P(1)−N(1)−Ti(1) 172.2-(2).

Addition of donor to a solution of the neutral Ti precursor, followed by addition of a solution of $B(C_6F_5)_3$ or [CPh_3][$B(C_6F_5)_4$], led to the clean formation of **5**−**12** and **17**−**20**. Initial combination of the Lewis acid and donor resulted in the irreversible formation of borane-donor adducts or phosphonium borates, precluding methyl abstraction from Ti. In contrast, the pyridium borates [$PyCPh_3$][$B(C_6F_5)_4$] reversibly dissociate and thus react with **2**, to smoothly to give the salts **13**−**16**. In a recent paper Okuda et al. have also shown that silica-supported pyridium borate is an effective activator for constrained geometry catalysts.[36]

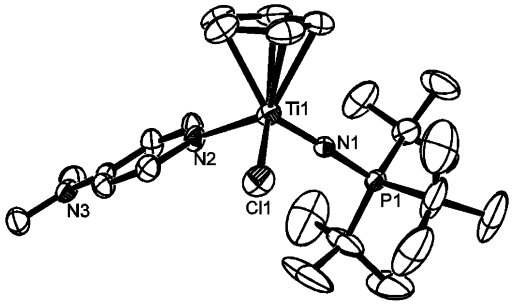


Figure 2. ORTEP drawings of the cation of **21**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Ti(1)−N(1) 1.764(3), Ti(1)−N(2) 2.112(4), Ti(1)−Cl(1) 2.3052(18), P(1)−N(1) 1.606(4), N(1)−Ti(1)−N(2) 100.79(16), N(1)−Ti(1)−Cl(1) 103.37(12), N(2)−Ti(1)−Cl(1) 99.84(12), P(1)−N(1)−Ti(1) 171.2(2).

Reactivity with CH_2Cl_2. Evidence of the reactivity of these salts with CH_2Cl_2 solvent was derived from attempts to isolate X-ray quality crystals of the cations and zwitterions. In the case of compound **16**, prolonged standing in CH_2Cl_2 at 25 °C for several weeks did indeed afford crystalline material in 25% yield. However, spectroscopic data revealed the formation of a new species, **21**, with a $^{31}P\{^1H\}$ NMR resonance at 49.0 ppm. The ^1H NMR spectrum revealed the absence of a methyl resonance, which would have been attributed to the Ti−Me fragment. These data, in addition to a crystallographic study, confirmed the formulation of **21** as $[CpTi(NPt\text{-}Bu_3)Cl(NC_5H_4NMe_2)][B(C_6F_5)_4]$ (Figure 2). The Ti−N distance for the phosphinimide N atom is 1.764(3) Å, while the P−N−Ti angle is 171.2(2)°, both similar to those determined for **17**. The Ti−N distance for the pyridine N atom is 2.112(4) Å, while the Ti−Cl distance is 2.305(2) Å. The formation of **21** clearly infers a reaction with CH_2Cl_2, although the mechanism in this case is unclear. Nonetheless, similar methyl for chloride exchange reactions in CH_2Cl_2 have been previously described in the formation of the dimers $[CpTi(\mu\text{-}Cl)(NPPh_2(NPt\text{-}Bu_3))]_2[B(C_6F_5)_4]_2$[44] and $[Cp^*Zr((Me_3SiNC)_2NPh)(\mu\text{-}Cl)]_2[B(C_6F_5)_4]_2$.[45,46]

Similarly, attempts to prepare the salt $[Cp(NPt\text{-}Bu_3)TiMe(P(o\text{-}MeC_6H_4)_3)][B(C_6F_5)_4]$ in CH_2Cl_2 revealed further evidence of reaction of the Ti cation with this solvent. In this case, two products, **22** and **23**, were observed spectroscopically in the reaction mixture. The former compound, **22**, gave rise to a $^{31}P\{^1H\}$ NMR resonance at 29.1 ppm. Crystals of **22** were obtained in 68% yield via layering reaction mixtures with pentanes, and a crystallographic study confirmed it to be the salt $[(o\text{-}MeC_6H_4)_3PCH_2Cl][B(C_6F_5)_4]$ (Figure 3). While the metric parameters were unexceptional, the X-ray data did affirm the helically chiral arrangement of the arene rings about P. This is consistent with the observation that the broad resonance at 4.94 ppm, assigned to the methylene protons in the ^1H NMR spectrum, is resolved to two doublets of doublets at −40 °C, as expected for diastereomeric methylene protons adjacent to P. The second product **23** gave rise to two sets of resonances

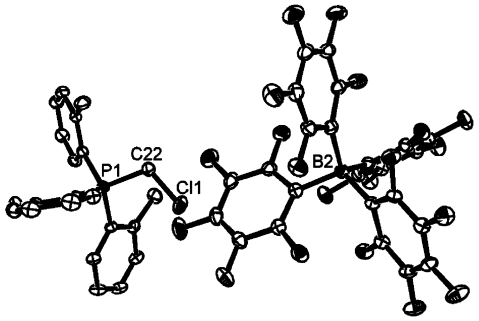


Figure 3. ORTEP drawings of the salt **22**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): P(1)−C(1) 1.804(3), P(1)−C(8) 1.809(2), P(1)−C(22) 1.837(2), Cl(1)−C(22) 1.775(3), Cl(1)−C(22)−P(1) 112.16(14).

in the proton NMR spectrum, attributable to Cp rings and methyl groups. Similarly, two resonances were observed at 50.1 and 49.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum at -40 °C. These data were consistent with the formulation of **23** as a 1:1 mixture of the *rac* and *meso* isomers of $[\{CpTi(NPt\text{-}Bu_3)Me\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$. While **23** was not isolated from the above reaction involving $P(o\text{-}MeC_6H_4)_3$, it was prepared and isolated independently in 89% yield via addition of 2 equiv of **2** with $[CPh_3][B(C_6F_4)_4]$. Analogous fluoride-bridged complexes $[\{(C_5H_3Me_2)_2ZrMe\}_2(\mu\text{-}F)][MeB(C_6F_5)_3]$ and $[\{Cp_2ZrMe\}_2(\mu\text{-}F)]$ [MePNB] (PNB = tris(β-perfluoronaphthyl)borane) have been previously described by Yang et al.[47]

The formation of **22** and **23** is consistent with the generation of the transient species $[Cp(NPt\text{-}Bu_3)TiMe(CH_2Cl_2)][B(C_6F_5)_4]$ with subsequent attack of the coordinated solvent by $P(o\text{-}MeC_6H_4)_3$. It is thought that the steric demands of $P(o\text{-}MeC_6H_4)_3$ preclude facile displacement of the coordinated CH_2Cl_2 and instead afford **22** and $Cp(NPt\text{-}Bu_3)TiMeCl$. The latter species displaces CH_2Cl_2 in $[Cp(NPt\text{-}Bu_3)TiMe(CH_2Cl_2)][B(C_6F_5)_4]$, ultimately affording the chloro-bridged species **23** (Scheme 2).

In a related reaction, treatment of **2** with $B(C_6F_5)_3$ in CH_2Cl_2 at 25 °C, without any added donor, afforded $[CpTi(NPt\text{-}Bu_3)(\mu\text{-}Cl)]_2[MeB(C_6F_5)_3]_2$ (**24**) in 85% yield. The ^1H NMR resonance for the cyclopentadienyl rings is a singlet seen at 6.76 ppm, while the $^{31}P\{^1H\}$ NMR resonance is seen at 60.7 ppm. These downfield signals are consistent with a symmetric dicationic formulation of **24**. Crystallographic data confirmed the nature of centrosymmetric dimeric **24** (Figure 4). The geometry about N, including the Ti−N distance of 1.751(2) Å, the P−N−Ti angle of 172.72(14)°, and the Ti−Cl distances of 2.455(1) and 2.461(1) Å, is similar to those found in the analogous dication of $[CpTi(\mu\text{-}Cl)(NPPh_2(NPt\text{-}Bu_3))]_2[B(C_6F_5)_4]_2$ (2.453(2) Å)[44] and the Ti(III)-chloro-bridged dimer $[CpTi(\mu\text{-}Cl)(NPt\text{-}Bu_3)]_2$ (2.484(1) Å).[48]

Chloride exchange is avoided when C_6H_5Cl is used as a solvent instead. Treatment of **2** with an equivalent of $[CPh_3][B(C_6F_5)_4]$ at 25 °C affords a transient species presumed to be $[CpTi(NPt\text{-}Bu_3)Me(C_6H_5Cl)][B(C_6F_5)_4]$. Subsequent treatment with a second equivalent of **2** afforded the isolation of the new species **25** in 79% yield.

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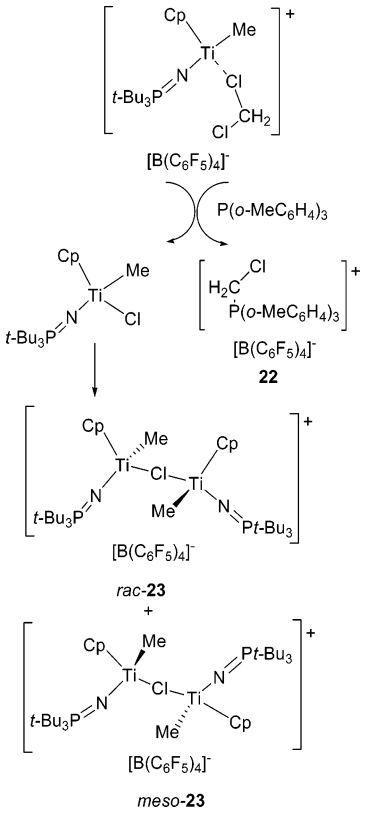
Scheme 2. Synthesis of 22 and 23



The observations of ^{1}H NMR signals at 6.29 and 6.25, 1.51 and 1.50, 0.69 and 0.66, and 0.14 and 0.13 ppm were attributed to Cp, *t*-Bu, TiMe, and μ-TiMeTi, groups, respectively. These data support the formulation of **25** as the methyl-bridged species [{CpTi(NP*t*-Bu$_3$)-Me}$_2$(μ-Me)][B(C$_6$F$_5$)$_4$]. Similar to **23**, the NMR data were consistent with a 1:1 mixture of the *rac* and *meso* isomers. Zhang and Piers[49] have previously reported a dimer analogous to **25**, in which ketimide ligands replace phosphinimides. In contrast to the ketimide species, **25** is stable at room temperature for days in a C$_6$H$_5$Cl solution.

Insertion Chemistry. Controlled stoichiometric insertion of the carbodiimide (N*i*-Pr)$_2$C into the Ti−Me bond of **3** results in the formation of **26** (Scheme 3). This species is isolated in 47% yield and exhibits ^{1}H NMR methyl resonances at 2.17 ppm, attributable to the central methyl group of an amidinate ligand. A broad resonance at 0.50 ppm is ascribed to the methyl group of the anion [MeB(C$_6$F$_5$)$_3$]$^-$. These and other NMR data are consistent with the formula of **26** as [CpTi(NP*t*-Bu$_3$)((N*i*-Pr)$_2$CMe)][MeB(C$_6$F$_5$)$_3$] (Scheme 3). The data are also consistent with a symmetric binding of the generated amidinate ligand and comparable to the recently reported Zr analogue [CpZr(NP*t*-Bu$_3$)((N*i*-Pr)$_2$-CMe)][MeB(C$_6$F$_5$)$_3$].[16] **26** is stable in solution for weeks at room temperature in CH$_2$Cl$_2$, in the absence of air and moisture.

In a similar fashion, the reaction of diphenylacetylene with **3** afforded [TiCp(NP*t*-Bu$_3$)(PhCCPh(Me))][MeB-(C$_6$F$_5$)$_3$] (**27**) in 54% yield. NMR data are consistent with the free anion. This suggests that steric crowding about

(49) Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088−2092.

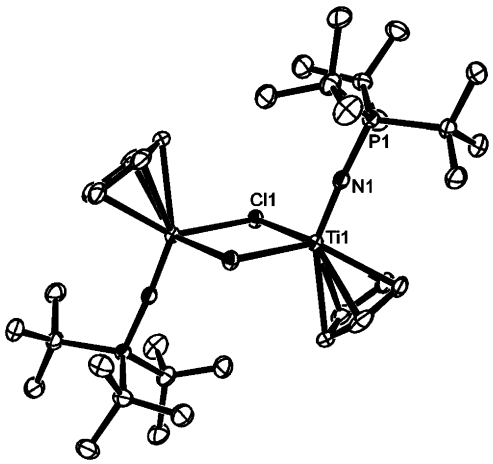
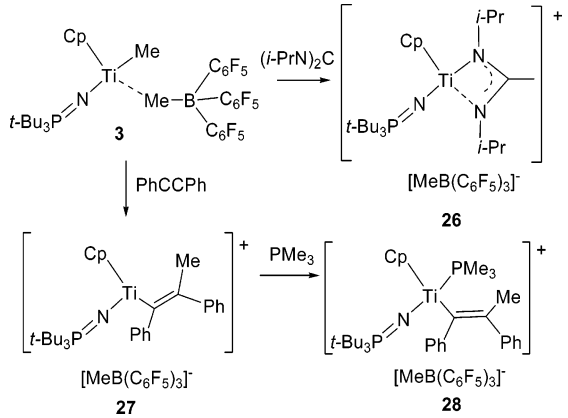


Figure 4. ORTEP drawing of the dication of **24**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Ti(1)−N(1) 1.751(2), Ti(1)−Cl(1) 2.4538(12), Ti(1)−Cl(1) 2.4608(13), P(1)−N(1) 1.651(2), N(1)−Ti(1)−Cl(1) 105.67(8), N(1)−Ti-(1)−Cl(1) 104.57(7), Cl(1)−Ti(1)−Cl(1) 85.82(4), Ti(1)−Cl-(1)−Ti(1) 94.18(4), P(1)−N(1)−Ti(1) 172.72(14).

Scheme 3. Synthesis of 26−28



Ti, combined with the Ti−sp^{2}C bond, imparts additional stability to the cation. Addition of PMe$_3$ results in coordination to Ti, generating the complex [TiCp(NP*t*-Bu$_3$)(PhCCPh(Me))(PMe$_3$)][MeB(C$_6$F$_5$)$_3$] (**28**) (Scheme 3).

Summary. A variety of cationic donor-stabilized Ti-phosphinimide complexes were prepared from the zwitterion **3** or by interception of the transient salt [CpTi-(NP*t*-Bu$_3$)Me][B(C$_6$F$_5$)$_4$]. The resulting species do not exhibit long-term stability in CH$_2$Cl$_2$, affording instead methyl for chloride exchange, as well as evidence of nucleophilic attack of CH$_2$Cl$_2$. The zwitterion **3** also undergoes stoichiometric insertions with unsaturated organic substrates. The reactive nature of the zwitterionic and cationic Ti-phosphinimide complexes are consistent with activity of ethylene polymerization catalysts derived from these systems.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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