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Use of Olefin Metathesis to Link Phosphinimide–Cyclopentadienyl Ligand Complexes: Synthesis, Structure, and Ethylene Polymerization Activity

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Efforts to link phosphinimide and cyclopentadienyl ligands via metathesis were undertaken. To this end, the allylic phosphinimine *t*-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNSiMe$_3$ (**1**) and the Ti complexes *t*-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNTi(Cp)Cl$_2$ (**2**), *t*-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNTi(C$_5$Me$_5$)Cl$_2$ (**3**), and *t*-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNTi(C$_5$H$_4$CH$_2$CH=CH$_2$)Cl$_2$ (**4**) were prepared. Attempts to effect olefin metathesis on **4** using either [Cl$_2$(PCy$_3$)$_2$Ru=CHPh] or [Cl$_2$(PCy$_3$)(H$_2$IMes)Ru=CHPh] as the catalyst were unsuccessful. Alternatively, the phosphinimine *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNSiMe$_3$ (**5**) was found to undergo olefin isomerization upon conversion to the phosphinimines *t*-Bu$_2$(MeCH=CH)PNH (**6**) and *t*-Bu$_2$(MeCH=CH)PNTi(NMe$_2$)$_3$ (**7**), *t*-Bu$_2$(MeCH=CH)PNTiCl$_3$ (**8**), and *t*-Bu$_2$(MeCH=CH)PNTiCl$_3$(THF) (**8**·THF). Direct reaction of **5** with TiCl$_4$ gave *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTiCl$_3$ (**9**), which was readily converted to *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(C$_5$H$_4$C(Me)=CH$_2$)Cl$_2$ (**10**). Repeated attempts to effect a ring closure by olefin metathesis resulted in no reaction. However, the species *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(CpCH$_2$CH=CH$_2$)Cl$_2$ (**11**) was readily methylated to give *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(CpCH$_2$CH=CH$_2$)Me$_2$ (**12**), and **11** in the presence of [Cl$_2$(PCy$_3$)$_2$Ru=CHPh] underwent olefin metathesis to give *t*-Bu$_2$(CpCH$_2$CH=CHCH$_2$)PNTiCl$_2$ (**13**). Subsequent reaction with 9-BBN gave *t*-Bu$_2$(CpCH$_2$CH$_2$CH(B(C$_8$H$_{14}$)CH$_2$)PNTiCl$_2$ (**14**), while alkylation gave *t*-Bu$_2$(CpCH$_2$CH=CHCH$_2$)PNTiMe$_2$ (**15**). In a similar fashion, the species *t*-Bu$_2$(C$_5$Me$_4$CH$_2$CH=CHCH$_2$)PNTiCl$_2$ (**20**), *t*-Bu$_2$(C$_5$Me$_4$CH$_2$CH=CHCH$_2$)PNTiMe$_2$ (**21**), *t*-Bu$_2$(C$_9$H$_6$CH$_2$CH=CHCH$_2$)PNTiCl$_2$ (**24**), and *t*-Bu$_2$(C$_9$H$_6$CH$_2$CH=CHCH$_2$)PNTiMe$_2$ (**25**) were prepared. A number of these compounds were screened for their ability to effect olefin polymerization using MAO, B(C$_6$F$_5$)$_3$, or [Ph$_3$C][B(C$_6$F$_5$)$_4$] as the activator. In general, active single-site catalysts were obtained, yielding high molecular weight polyethylene, although the activities were lower with MAO than with boron-based activators. Crystal structures of **3**, **8**·THF, **13**, **15**, and **20** are reported.

Introduction

For more than 25 years, researchers around the globe have been engaged in the development of homogeneous catalysts for olefin polymerization. Several reviews have described a variety of strategies employed toward this goal.[1−7] While it is fair to say that metallocenes garnered the lion's share of attention during the 1980s, subsequently non-cyclopentadienyl ligand systems came under intense scrutiny following the commercialization of the "constrained geometry catalysts"[8−11] derived from linked amide–cyclopentadienyl ligands introduced by Bercaw and co-workers.[12] Later in the 1990s the work of McConville and co-workers[13−16] revealed that titanium complexes containing bulky bis-amido-chelate ligands were effective living "non-metallocene" catalysts. More recently, the "FI" catalysts developed by researchers at Mitsui have drawn considerable attention.[7,17−21] Parallel to these efforts targeting

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high-activity catalysts for ethylene polymerizations, some very clever ligand design strategies were developed to provide stereoregularity control over the polymers derived from α-olefin polymerization.[22–25]

Almost 10 years ago, we first reported the utility of phosphinimide ligands in the development of highly active olefin polymerization catalysts.[26–28] Since the early reports we have explored a number of avenues in attempts to understand the structure−activity relationship, mechanisms of deactivations, and the impact of variations of the metal itself. Much of this work has been recently reviewed.[29] While the extension of these systems to give related catalysts designed for stereoselective polymerization of α-olefins seemed like a reasonable goal, this proved very challenging. In early trials[30] to prepare such catalysts, cyclopentadienyl ligands with pendant phosphines were oxidized in an effort to form a Ti−phosphinimide complex in which the phosphinimide and Cp were linked. Despite numerous perturbations, these efforts were not successful. Seeking an alternative strategy we noted the creative use of olefin metathesis by the groups of Hayashi[31] and Erker[23,32–37] to make metallocenes in which longer alkyl chains link the cyclopentadienyl ligands. This work inspired us to utilize a similar strategy toward Cp−phosphinimide linked ligand complexes. In this article we report synthetic efforts targeting new Ti complexes featuring a phosphinimide tethered to a cyclopentadienyl ligand. A synthetic strategy based on olefin metathesis makes such species accessible. The impact of such links between ligands on the olefin polymerization activity of the resulting catalysts is evaluated.

Experimental Section

General Considerations. All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers. Deuterated benzene, toluene, and methylene chloride were purchased from Cambridge Isotopes Laboratories, freeze−pump−thaw degassed (3 times), and vacuum distilled from the appropriate drying agents. Trace amounts of protonated solvents were used as references, and ^{1}H and ^{13}C NMR chemical shifts are reported relative to SiMe$_4$. ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{19}F NMR spectra were referenced to external 85% H$_3$PO$_4$, BF$_3\cdot$Et$_2$O, and CFCl$_3$, respectively. Combustion analyses were performed at the University of Windsor Chemical Laboratories employing a Perkin-Elmer CHN analyzer. High-temperature GPC data were provided by the technical staff at NOVA Chemicals Corporation. t-Bu$_2$PCH$_2$CH=CH$_2$,[38] [C$_5$H$_4$C(Me)=CH$_2$]Li,[39] t-Bu$_2$(Me$_2$CLi)PNSiMe$_3$,[40] (C$_5$H$_4$CH$_2$CH=CH$_2$)TiCl$_3$,[37] and (CH$_2$=CHCH$_2$)C$_5$Me$_4$H[41] were prepared via literature methods. 9-Borabicyclo[3.3.1]nonane (9-BBN), [Cl$_2$(PCy$_3$)$_2$Ru=CHPh], and [Cl$_2$(PCy$_3$)(H$_2$IMes)Ru=CHPh] were purchased from Aldrich Chemical Co.

Synthesis of t-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNSiMe$_3$ (1). t-Bu$_2$(Me$_2$CLi)PNSiMe$_3$ (0.80 g; 2.85 mmol) was dissolved in 10 mL of hexanes. CH$_2$=CHCH$_2$Br (0.30 mL; 3.55 mmol) was added dropwise at 25 °C. The cloudy solution was stirred for 3 h and then filtered through Celite. The hexanes were removed under vacuum to give a colorless oil (0.82 g; 2.60 mmol; 91%). ^{1}H NMR (C$_6$D$_6$): 5.73 (m, 1H, CH$_2$=C*H*CH$_2$CMe$_2$), 5.06 (dm, ^3J = 10 Hz, 1H, C*H$_2$*=CHCH$_2$CMe$_2$), 5.02 (dm, ^3J = 20 Hz, 1H, C*H$_2$*=CHCH$_2$CMe$_2$), 2.54 (t, J = 7 Hz, 2H, CH$_2$=CHC*H$_2$*CMe$_2$), 1.18 (d, ^{3}J$_{PH}$ = 14 Hz, 6H, CH$_2$=CHCH$_2$ C*Me$_2$*), 1.17 (d, $^3J_{PH}$ = 13 Hz, 18H, t-Bu), 0.41 (s, 9H, Si*Me$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 134.7 (d, $^3J_{PC}$ = 11 Hz, CH$_2$=*C*HCH$_2$CMe$_2$), 118.6 (*C*H$_2$=CHCH$_2$CMe$_2$), 43.5 (d, $^1J_{PC}$ = 55 Hz, CH$_2$=CHCH$_2$*C*Me$_2$), 43.1 (CH$_2$=CH*C*H$_2$CMe$_2$), 40.7 (d, $^1J_{PC}$ = 53 Hz, t-Bu), 30.2 (t-Bu), 25.4 (CH$_2$=CHCH$_2$C*Me$_2$*), 5.2 (Si*Me$_3$*). ^{31}P NMR (C$_6$D$_6$): 33.4. Anal. Calcd for C$_{17}$H$_{38}$NPSi: C, 64.71; H, 12.14; N, 4.44. Found: C, 64.24; H, 12.34; N, 4.23.

Synthesis of t-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNTi(Cp)Cl$_2$ (2). Compound **1** (0.79 g; 2.51 mmol) was added to a toluene solution (30 mL) containing CpTiCl$_3$ (0.55 g; 2.507 mmol) at 25 °C. The orange solution was heated at 90 °C for 8 h. Toluene was removed under vacuum to give a yellow precipitate. Pentane (20 mL) was added, and the mixture was stirred for 10 min and then filtered. The yellow solid was dried under vacuum (0.77 g; 1.81 mmol; 73%). ^{1}H NMR (C$_6$D$_6$): 6.45 (s, 5H, Cp), 5.51 (m, 1H, CH$_2$=C*H*CH$_2$CMe$_2$), 5.04 (m, 2H, C*H$_2$*=CHCH$_2$CMe$_2$), 2.53 (pseudo t, J = 6 Hz, 2H, CH$_2$=CHC*H$_2$*CMe$_2$), 1.21 (d, $^3J_{PH}$ = 15 Hz, 6H, CH$_2$=CHCH$_2$-C*Me$_2$*), 1.15 (d, $^3J_{PH}$ = 14 Hz, 18H, t-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 132.5 (d, $^3J_{PC}$ = 11 Hz, CH$_2$=*C*HCH$_2$CMe$_2$), 120.3 (*C*H$_2$=CHCH$_2$CMe$_2$), 115.5 (*C*p), 45.9 (d, $^1J_{PC}$ = 43 Hz, CH$_2$=CHCH$_2$ *C*Me$_2$), 42.7 (d, $^1J_{PC}$ = 38 Hz, t-Bu), 42.6 (CH$_2$=CH*C*H$_2$CMe$_2$), 30.0 (t-Bu), 25.4 (CH$_2$=CHCH$_2$C*Me$_2$*). ^{31}P NMR (C$_6$D$_6$): 45.9. Anal. Calcd for C$_{19}$H$_{34}$NPTiCl$_2$: C, 53.54; H, 8.04; N, 3.29. Found: C, 53.24; H, 7.93; N, 3.43.

Synthesis of t-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNTi(C$_5$Me$_5$)Cl$_2$ (3). Compound **1** (0.40 g; 1.27 mmol) was added to a toluene solution (25 mL) containing Cp*TiCl$_3$ (0.36 g; 1.24 mmol) at 25 °C. The orange solution was heated at 100 °C for 12 h. Toluene was removed under vacuum to give an orange precipitate. Pentane (20 mL) was added, and the mixture was stirred for 10 min and then filtered. The orange solid was dried under vacuum (0.53 g; 1.07 mmol; 77%). ^{1}H NMR (C$_6$D$_6$): 5.59 (m, 1H, CH$_2$=C*H*CH$_2$-CMe$_2$), 5.09 (m, 2H, C*H$_2$*=CHCH$_2$CMe$_2$), 2.67 (br, 2H, CH$_2$=CHC*H$_2$*CMe$_2$), 2.19 (s, 15H, C$_5$*Me$_5$*), 1.28 (d, $^3J_{PH}$ = 14.5 Hz, 6H, CH$_2$=CHCH$_2$C*Me$_2$*), 1.27 (d, $^3J_{PH}$ = 14 Hz, 18H, t-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 133.1 (d, $^3J_{PC}$ = 11 Hz,

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CH$_2$=*C*HCH$_2$CMe$_2$), 125.7 (*C*$_5$Me$_5$), 119.9 (*C*H$_2$=CHCH$_2$CMe$_2$), 45.7 (d, $^1J_{PC}$ = 44 Hz, CH$_2$=CHCH$_2$*C*Me$_2$), 42.9 (d, $^1J_{PC}$ = 40 Hz, *t*-Bu), 42.6 (CH$_2$=CH*C*H$_2$CMe$_2$), 30.4 (*t*-Bu), 25.4 (CH$_2$=CHCH$_2$C*Me*$_2$), 13.5 (C$_5$*Me*$_5$). ^{31}P NMR (C$_6$D$_6$): 45.7. Anal. Calcd for C$_{24}$H$_{44}$NPTiCl$_2$: C, 58.07; H, 8.93; N, 2.82. Found: C, 58.14; H, 8.91; N, 2.98.

Synthesis of *t*-Bu$_2$(CH$_2$=CHCH$_2$C(Me$_2$)PNTi(C$_5$H$_4$CH$_2$CH=CH$_2$)Cl$_2$ (4). Compound **1** (0.73 g; 2.32 mmol) was added to a toluene solution (30 mL) containing (C$_5$H$_4$CH$_2$CH=CH$_2$)TiCl$_3$ (0.60 g; 2.32 mmol) at 25 °C. The red solution was heated at 90 °C for 8 h. The toluene was removed under vacuum to give an orange oil (1.00 g; 2.14 mmol; 92%). ^{1}H NMR (C$_6$D$_6$): 6.43 (m, 2H, 3,4-H), 6.27 (m, 2H, 2,5-H), 6.11 (m, 1H, CH$_2$C*H*=CH$_2$), 5.55 (m, 1H, CH$_2$=C*H*CH$_2$CMe$_2$), 5.13–5.01 (m, 4H, CH$_2$CH=C*H*$_2$ and C*H*$_2$=CHCH$_2$CMe$_2$), 3.63 (d, ^2J = 7 Hz, C*H*$_2$CH=CH$_2$), 2.56 (t, *J* = 6.5 Hz, 2H, CH$_2$=CHC*H*$_2$CMe$_2$), 1.23 (d, $^3J_{PH}$ = 15 Hz, 6H, CH$_2$=CHCH$_2$C*Me*$_2$), 1.19 (d, $^3J_{PH}$ = 14 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 137.8 (CH$_2$*C*H=CH$_2$), 132.8 (*ipso*-C$_5$H$_4$), 132.5 (d, ^{3}J$_{PC}$ = 11 Hz, CH$_2$=*C*HCH$_2$CMe$_2$), 120.3 (*C*H$_2$=CHCH$_2$CMe$_2$), 116.4 (CH$_2$CH=*C*H$_2$), 115.9 (C2, C5), 113.7 (C3, C4), 45.8 (d, $^1J_{PC}$ = 43 Hz, CH$_2$=CHCH$_2$*C*Me$_2$), 42.8 (d, $^1J_{PC}$ = 38 Hz, *t*-Bu), 42.7 (CH$_2$=CH*C*H$_2$CMe$_2$), 35.7 (*C*H$_2$CH=CH$_2$), 30.1 (*t*-Bu), 25.4 (CH$_2$=CHCH$_2$C*Me*$_2$). ^{31}P NMR (C$_6$D$_6$): 45.7. Anal. Calcd for C$_{22}$H$_{38}$NPTiCl$_2$: C, 56.67; H, 8.21; N, 3.00. Found: C, 56.99; H, 8.19; N, 3.05.

Synthesis of *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNSiMe$_3$ (5). N$_3$SiMe$_3$ (6.10 g; 53.0 mmol) was added to a 35 mL toluene solution of *t*-Bu$_2$PCH$_2$CH=CH$_2$ (2.50 g; 13.4 mmol) at 25 °C. The cloudy solution was heated at 70 °C for 48 h. The toluene was removed under vacuum, and the product was extracted with pentane and then filtered through Celite. Removing pentane under vacuum gave a colorless oil (3.25 g; 11.89 mmol; 89%). ^{1}H NMR (C$_6$D$_6$): 6.02 (m, 1H, CH$_2$C*H*=CH$_2$), 5.04 (dm, ^{3}J = 10 Hz, 1H, =C*H*$_2$), 4.95 (dm, ^3J = 17 Hz, 1H, =C*H*$_2$), 2.26 (m, 2H, PC*H*$_2$), 1.02 (d, $^3J_{PH}$ = 14 Hz, 18H, *t*-Bu), 0.28 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 133.5 (d, $^2J_{PC}$ = 8 Hz, PCH$_2$*C*H=CH$_2$), 117.5 (d, $^3J_{PC}$ = 10 Hz, CH$_2$CH=*C*H$_2$), 37.1 (d, $^1J_{PC}$ = 62 Hz, *t*-Bu), 30.6 (d, $^1J_{PC}$ = 52 Hz, P*C*H$_2$), 27.6 (*t*-Bu), 5.3 (Si*Me*$_3$). ^{31}P NMR (C$_6$D$_6$): 24.3. Anal. Calcd for C$_{14}$H$_{32}$NPSi: C, 61.49; H, 11.79; N, 5.12. Found: C, 61.22; H, 11.73; N, 4.94.

Synthesis of *t*-Bu$_2$(MeCH=CH)PNH (6). Dry MeOH (30 mL) was added to compound **5** (1.60 g; 5.86 mmol) at 25 °C. The solution was stirred for 24 h. Excess MeOH was removed under vacuum to give a waxy material. Storage of the product under vacuum for 24 h afforded a colorless crystalline solid (1.00 g; 4.97 mmol; 85%). ^{1}H NMR (C$_6$D$_6$): 6.71 (m, 1H, MeC*H*=CHP), 5.81 (m, 1H, MeCH=C*H*P), 1.59 (dm, ^3J = 7.0 Hz, 3H, *Me*CH=CHP), 1.12 (d, $^3J_{PH}$ = 13.0 Hz, 18H, *t*-Bu), −0.31 (br, 1H, N*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 146.1 (Me*C*H=CHP), 123.1 (d, $^1J_{PC}$ = 68 Hz, MeCH=*C*HP), 34.8 (d, $^1J_{PC}$ = 61 Hz, *t*-Bu), 27.6 (*t*-Bu), 20.1 (d, $^3J_{PC}$ = 15 Hz, *Me*CH=CHP). ^{31}P NMR (C$_6$D$_6$): 43.4. Anal. Calcd for C$_{11}$H$_{24}$NP: C, 65.64; H, 12.02; N, 6.96. Found: C, 65.81; H, 12.33; N, 6.66.

Synthesis of *t*-Bu$_2$(MeCH=CH)PNTi(NMe$_2$)$_3$ (7). Compound **6** (0.45 g; 2.24 mmol) in 5 mL of toluene was added dropwise over a 15 min period to a toluene solution (10 mL) of Ti(NMe$_2$)$_4$ (0.50 g; 2.24 mmol). The solution was heated at 80 °C for 8 h. The toluene was removed under vacuum to give an orange oil (0.79 g; 2.08 mmol; 93%). ^{1}H NMR (C$_6$D$_6$): 7.03 (m, 1H, MeC*H*=CHP), 5.68 (dd, $^2J_{PH}$ = 30.0 Hz, ^3J = 16.5 Hz, 1H, MeCH=C*H*P), 3.39 (s, 18H, N*Me*$_2$), 1.67 (dm, ^3J = 6.5 Hz, 3H, *Me*CH=CHP), 1.15 (d, $^3J_{PH}$ = 13.5 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 147.4 (Me*C*H=CHP), 120.8 (d, $^1J_{PC}$ = 75 Hz, MeCH=*C*HP), 46.6 (N*Me*$_2$), 35.7 (d, $^1J_{PC}$ = 53 Hz, *t*-Bu), 27.5 (*t*-Bu), 20.4 (d, $^3J_{PC}$ = 15 Hz, *Me*CH=CHP). ^{31}P NMR (C$_6$D$_6$): 16.1. Anal. Calcd for C$_{17}$H$_{41}$N$_4$PTi: C, 53.68; H, 10.86; N, 14.73. Found: C, 53.47; H, 11.11; N, 14.51.

Synthesis of *t*-Bu$_2$(MeCH=CH)PNTiCl$_3$ (8). Me$_3$SiCl (0.25 mL; 1.97 mmol) was added to a toluene solution (5 mL) of compound **7** (0.15 g; 0.39 mmol) at 25 °C. The cloudy solution was stirred overnight, then pumped to dryness. The product was washed with pentane (5 mL) and then dried under vacuum (0.12 g; 0.34 mmol; 88%). ^{1}H NMR (C$_6$D$_6$): 7.41 (m, 1H, MeC*H*=CHP), 5.05 (dd, $^2J_{PH}$ = 30 Hz, ^3J = 17 Hz, 1H, MeCH=C*H*P), 1.44 (d, ^3J = 7 Hz, 3H, *Me*CH=CHP), 0.99 (d, $^3J_{PH}$ = 16 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 154.3 (Me*C*H=CHP), 112.2 (d, $^1J_{PC}$ = 75 Hz, MeCH=*C*HP), 37.9 (d, $^1J_{PC}$ = 53 Hz, *t*-Bu), 26.7 (*t*-Bu), 20.8 (d, $^3J_{PC}$ = 15 Hz, *Me*CH=CHP). ^{31}P NMR (C$_6$D$_6$, 121 MHz): δ 40.1. Anal. Calcd for C$_{11}$H$_{23}$NPTiCl$_3$: C, 37.27; H, 6.54; N, 3.95. Found: C, 37.37; H, 6.68; N, 3.95. Crystals of *t*-Bu$_2$(MeCH=CH)PNTiCl$_3$(THF) (**8**·THF) were grown from THF/hexane.

Synthesis of *t*-Bu$_2$(H$_2$C=CHCH$_2$)PNTiCl$_3$ (9). Compound **5** (1.0 g; 3.66 mmol) was dissolved in 8 mL of toluene and then added dropwise to a toluene (50 mL) solution of TiCl$_4$ (3.9 mL, 3.90 mmol, 1 M) at −78 °C. The dark red solution was stirred at −78 °C for 30 min, warmed slowly to 25 °C, refluxed for 12 h, and then filtered hot. The solvent was removed under vacuum to give a solid, which was washed with pentane (2 × 5 mL) and dried under vacuum (1.00 g; 2.82 mmol; 78%). ^{1}H NMR (C$_6$D$_6$): 5.95 (m, 1H, CH$_2$C*H*=CH$_2$), 5.04 (dm, ^3J = 10 Hz, 1H, =C*H*$_2$), 4.90 (dm, ^3J = 17 Hz, 1H, =C*H*$_2$), 2.09 (ddm, $^2J_{PH}$ = 11 Hz, ^3J = 10.4 Hz, 2H, PC*H*$_2$), 0.89 (d, $^3J_{PH}$ = 15 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 128.7 (CH$_2$*C*H=CH$_2$), 122.0 (d, $^3J_{PC}$ = 11 Hz, CH$_2$CH=*C*H$_2$), 38.9 (d, $^1J_{PC}$ = 48 Hz, *t*-Bu), 28.4 (d, $^1J_{PC}$ = 48 Hz, P*C*H$_2$), 26.9 (*t*-Bu). ^{31}P NMR (C$_6$D$_6$): 46.5. Anal. Calcd for C$_{11}$H$_{23}$NPTiCl$_3$: C, 37.27; H, 6.54; N, 3.95. Found: C, 36.99; H, 6.48; N, 3.65.

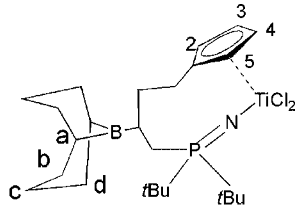
Synthesis of *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(C$_5$H$_4$C(Me)=CH$_2$)Cl$_2$ (10). [C$_5$H$_4$C(Me)=CH$_2$]Li (0.08 g; 0.71 mmol) was dissolved in 3 mL of THF and then added dropwise to a THF solution of compound **9** (0.25 g; 0.714 mmol) at 25 °C. The solution was stirred for 6 h and then pumped to dryness. Toluene was added (10 mL), and the mixture was heated at 100 °C for 5 min. After filtration, the toluene was removed under vacuum to give a dark orange powder (0.21 g; 0.50 mmol; 70%). ^{1}H NMR (C$_6$D$_6$): 6.60 (m, 2H, 3,4-H), 6.37 (m, 2H, 2,5-H), 6.09 (m, 1H, CH$_2$C*H*=CH$_2$), 5.50 and 5.07 (s each, 1H, (Me)C=C*H*$_2$), 5.02 (dm, ^3J = 10 Hz, 1H, CH$_2$CH=C*H*$_2$), 4.90 (dm, ^3J = 17 Hz, 1H, CH$_2$CH=C*H*$_2$), 2.27 (dd, $^2J_{PH}$ = 10 Hz, ^3J = 7 Hz, 2H, PC*H*$_2$), 2.18 (s, 3H, (*Me*)C=CH$_2$), 1.01 (d, $^3J_{PH}$ = 15 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): 119.9 (CH$_2$CH=*C*H$_2$), 114.1 (C2, C5), 113.7 (C3, C4), 112.7 ((Me)C=*C*H$_2$), 39.1 (d, $^1J_{PC}$ = 53 Hz, *t*-Bu), 28.4 (d, $^1J_{PC}$ = 53 Hz, P*C*H$_2$), 27.1 (*t*-Bu), 22.1 ((*Me*)C=CH$_2$). ^{31}P NMR (C$_6$D$_6$): 37.1. Anal. Calcd for C$_{19}$H$_{32}$NPTiCl$_2$: C, 53.79; H, 7.60; N, 3.30. Found: C, 53.52; H, 7.49; N, 2.99.

Synthesis of *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(CpCH$_2$CH=CH$_2$)Cl$_2$ (11). (CpCH$_2$CH=CH$_2$)TiCl$_3$ (2.81 g; 10.84 mmol) was dissolved in 50 mL of toluene. Compound **5** (2.96 g; 10.84 mmol) was added dropwise with stirring at 25 °C. The orange solution was heated at 80 °C for 12 h. Toluene was removed under vacuum to give a yellow solid, which was washed with pentane (2 × 5 mL) and dried under vacuum (4.43 g; 10.5 mmol; 96%). ^{1}H NMR (C$_6$D$_6$): 6.40 (m, 2H, 3,4-H), 6.27 (m, 2H, 2,5-H), 6.07 (m, 2H, CH$_2$C*H*=CH$_2$), 5.03 (m, 4H, CH$_2$CH=C*H*$_2$), 3.61 (d, ^2J = 6 Hz, CpC*H*$_2$CH=CH$_2$), 2.25 (ddm, $^2J_{PH}$ = 11 Hz, ^3J = 7 Hz, 2H, PC*H*$_2$CH=CH$_2$), 1.02 (d, $^3J_{PH}$ = 15 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 137.7 (CpCH$_2$*C*H=CH$_2$), 132.6 (*ipso*-C$_5$H$_4$), 130.6 (d, $^2J_{PC}$ = 8 Hz, PCH$_2$*C*H=CH$_2$), 120.1 (d, $^3J_{PC}$ = 10 Hz, PCH$_2$CH=*C*H$_2$), 116.4 (CpCH$_2$CH=*C*H$_2$), 115.9 (C2, C5), 113.9 (C3, C4), 39.0 (d, $^1J_{PC}$ = 52 Hz, *t*-Bu), 35.6 (Cp*C*H$_2$CH=CH$_2$), 29.1 (d, $^1J_{PC}$ = 50 Hz, P*C*H$_2$CH=CH$_2$), 27.3 (P*t*-Bu). ^{31}P NMR (C$_6$D$_6$): 36.9. Anal. Calcd for C$_{19}$H$_{32}$NPTiCl$_2$: C, 53.79; H, 7.60; N, 3.30. Found: C, 53.99; H, 7.56; N, 3.30.

Synthesis of *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(CpCH$_2$CH=CH$_2$)Me$_2$ (12). MeMgBr (0.98 mL; 3 M, 2.95 mmol) was added dropwise to a diethyl ether (10 mL) solution of compound **11** (0.25 g; 0.59 mmol) at −35 °C. The cloudy solution was stirred for 8 h at 25 °C. The solvent was removed under vacuum, and the product was extracted with 5 mL of hexanes and then filtered through Celite. Removing hexanes under vacuum gave a red oil (0.20 g; 0.52 mmol; 89%). ^{1}H NMR (C$_6$D$_6$): 6.15 (m, 2H, CH$_2$C*H*=CH$_2$), 6.12 (m, 2H, 3,4-H), 5.91 (m, 2H, 2,5-H), 5.19 (d, ^{3}J = 17 Hz, 1H, CpCH$_2$C*H*=CH$_2$), 5.06 (d, ^3J = 10 Hz, 1H, CpCH$_2$C*H*=CH$_2$), 5.03 (d, ^{3}J = 10 Hz, 1H, PCH$_2$C*H*=CH$_2$), 4.93 (d, ^3J = 17 Hz, 1H, PCH$_2$C*H*=CH$_2$), 3.47 (d, ^3J = 7 Hz, 2H, CpC*H*$_2$CH=CH$_2$), 2.33 (m, 2H, PC*H*$_2$CH=CH$_2$), 1.09 (d, $^3J_{PH}$ = 14 Hz, 18H, *t*-Bu), 0.64 (s, Ti*Me*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 138.9 (CpCH$_2$*C*H=CH$_2$), 132.3 (d, $^2J_{PC}$ = 7 Hz, PCH$_2$CH=CH$_2$), 126.3 (*ipso*-C$_5$H$_4$), 118.4 (d, $^3J_{PC}$ = 11 Hz, PCH$_2$CH=*C*H$_2$), 115.5 (CpCH$_2$CH=*C*H$_2$), 111.7 (C2, C5), 109.4 (C3, C4), 41.1 (Ti*Me*$_2$), 38.4 (d, $^1J_{PC}$ = 54 Hz, *t*-Bu), 35.5 (Cp*C*H$_2$CH=CH$_2$), 30.1 (d, $^1J_{PC}$ = 52 Hz, P*C*H$_2$CH=CH$_2$), 27.6 (*t*-Bu). ^{31}P NMR (C$_6$D$_6$): 22.4. Anal. Calcd for C$_{21}$H$_{38}$NPTi: C, 65.79; H, 9.99; N, 3.65. Found: C, 65.97; H, 9.63; N, 3.39.

Synthesis of *t*-Bu$_2$(CpCH$_2$CH=CHCH$_2$)PNTiCl$_2$ (13). [Cl$_2$(PCy$_3$)$_2$Ru=CHPh] (0.08 g; 0.097 mmol, 8 mol%) was dissolved in 350 mL of toluene in a round-bottom flask and heated at 50 °C. Compound **9** (0.5 g; 1.18 mmol) was dissolved in 15 mL of toluene and slowly added over a 6 h period using a syringe pump. The resulting red solution was stirred for 10 h. The solution was concentrated to ca. 30 mL and filtered through Celite. Cooling the red solution at −35 °C for 3 days gave a yellow precipitate, which was collected and washed with pentane (2 × 3 mL) and dried under vacuum (0.22 g; 0.56 mmol; 49%). ^{1}H NMR (C$_6$D$_6$): 6.51 (m, 2H, 3,4-H), 5.97 (m, 2H, 2,5-H), 5.83 (m, 1H, C*H*), 5.09 (m, 1H, C*H*), 3.13 (m, CpC*H*$_2$), 1.90 (m, PC*H*$_2$), 0.97 (d, $^3J_{PH}$ =14 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 132.6 (d, J_{PC} = 7 Hz, *C*H), 131.1 (*ipso*-C$_5$H$_4$), 120.8 (d, J_{PC} = 10 Hz, *C*H), 118.2 (C-3,4), 112.2 (C-2,5), 39.1 (d, $^1J_{PC}$ = 52 Hz, *t*-Bu), 29.3 (Cp*C*H$_2$), 27.4 (*t*-Bu), 20.1 (d, $^1J_{PC}$ = 50 Hz, P*C*H$_2$). ^{31}P NMR (C$_6$D$_6$): 42.0. Anal. Calcd for C$_{17}$H$_{28}$NPTiCl$_2$: C, 51.54; H, 7.12; N, 3.54. Found: C, 52.09; H, 6.90; N, 3.56.

Synthesis of *t*-Bu$_2$(CpCH$_2$CH$_2$CH(B(C$_8$H$_{14}$)CH$_2$)PNTiCl$_2$ (14). Compound **13** (0.30 g; 0.76 mmol) and 9-BBN (0.90 g; 7.38 mmol; 10 equiv) were dissolved in 10 mL of CH$_2$Cl$_2$ and refluxed for 48 h. The solvent was removed under vacuum, and the solid was washed with hexanes (3 × 10 mL) to remove unreacted 9-BBN. The remaining solid was redissolved in 3 mL of CH$_2$Cl$_2$ and cooled at −35 °C for 3 days to give a yellow precipitate. The solid was filtered cold, washed with 3 mL of pentane, and dried under vacuum (0.11 g; 0.21 mmol; 28%). ^{1}H NMR (CD$_2$Cl$_2$): 6.39, 6.33, 6.24 6.08 (each m, Cp-*H*), 3.26 (ddd, ^2J = 16 Hz, ^3J = 6 Hz, ^3J = 2.5 Hz, 1H, CpC*H*), 2.87 (ddd, ^2J = 17 Hz, ^3J = 7 Hz, ^3J = 3 Hz, 1H, CpC*H′*), 2.53 (m, 1H, BC*H*), 2.32 (m, 1H, CpCH2C*H*), 2.14 (m, 1H, PC*H*), 1.97, 1.86, 1.82 (each brm, b, a and d-H), 1.73 (m, 1H, PC*H′*), 1.65 (m, 1H, CpCH$_2$C*H′*), 1.38 (d, $^2J_{PC}$ =15 Hz, *t*-Bu), 1.33 (d, $^2J_{PC}$ =15 Hz, *t*-Bu). 1.32 (m, c-H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 131.1 (*ipso*-C$_5$H$_4$), 118.5, 117.8 (each CH, C-2,5), 113.8, 112.5 (each CH, C-3,4), 40.5 (d, $^1J_{PC}$ = 53 Hz, *t*-Bu), 38.6 (d, $^1J_{PC}$ = 51 Hz, *t*-Bu), 34.6, 34.1 (each CH$_2$, C- b, d), 31.6 (br, C- a), 29.2 (PCH$_2$*C*HB), 27.8 (CpCH$_2$*C*H$_2$), 27.7 (*t*-Bu), 27.5 (*t*-Bu), 26.7 (Cp*C*H$_2$), 23.7 (CH$_2$, C- c), 20.9 (d, $^1J_{PC}$ = 45 Hz, P*C*H$_2$). ^{31}P NMR (CD$_2$Cl$_2$): 44.1. ^{11}B NMR (CD$_2$Cl$_2$): 86.8 (br). Anal. Calcd for C$_{25}$H$_{43}$NPTiBCl$_2$: C, 57.95; H, 8.36; N, 2.70. Found: C, 57.66; H, 8.22; N, 2.51.



Synthesis of *t*-Bu$_2$(CpCH$_2$CH=CHCH$_2$)PNTiMe$_2$ (15). MeMgBr (0.55 mL; 3 M, 1.64 mmol) was added dropwise to a diethyl ether (10 mL) solution of compound **13** (0.13 g; 0.33 mmol) at −35 °C. The cloudy solution was stirred for 12 h at 25 °C. The solvent was removed under vacuum, and the residue was extracted with hot hexanes (2 × 5 mL) and filtered through Celite. After removing the hexanes, the solid was dried under vacuum (0.10 g; 0.28 mmol; 86%). ^{1}H NMR (C$_6$D$_6$): 6.66 (m, 2H, 3,4-H), 5.79 (m, 1H, C*H*), 5.69 (m, 2H, 2,5-H), 5.13 (m, 1H, C*H*), 2.97 (d, ^3J = 8 Hz, 2H, CpC*H*$_2$), 2.08 (m, 2H, PC*H*$_2$), 1.08 (d, $^3J_{PH}$ = 14 Hz, 18H, *t*-Bu), 0.67 (s, Ti*Me*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 132.5 (*C*H), 123.5 (*ipso*-C$_5$H$_4$), 120.9 (*C*H), 112.9 (C-3,4), 109.4 (C-2,5), 40.1 (Ti*Me*$_2$), 38.2 (d, $^1J_{PC}$ = 55 Hz, *t*-Bu), 28.7 (Cp*C*H$_2$), 27.7 (*t*-Bu), 22.3 (d, $^1J_{PC}$ = 43 Hz, P*C*H$_2$). ^{31}P NMR (C$_6$D$_6$): 27.4. Anal. Calcd for C$_{19}$H$_{34}$NPTi: C, 64.22; H, 9.64; N, 3.94. Found: C, 64.15; H, 9.54; N, 3.85.

Synthesis of (CH$_2$=CHCH$_2$)C$_5$Me$_4$SiMe$_3$ (16). (CH$_2$=CHCH$_2$)C$_5$Me$_4$H (7.90 g; 48.68 mmol; mixture of isomers) was dissolved in 200 mL of THF. *n*-BuLi (19.5 mL; 48.7 mmol; 2 M) was added dropwise at 25 °C. The resulting dark orange solution was refluxed for 2 h. The THF was removed under vacuum to give a red residue, which was suspended in pentane (50 mL) and stirred overnight. A white solid precipitated out, which was filtered, washed with pentane (4 × 20 mL), and dried under vacuum (3.70 g of (CH$_2$=CHCH$_2$)C$_5$Me$_4$Li. The solid was redissolved in 100 mL of THF and cooled to 0 °C. Me$_3$SiCl (2.50 mL) was added slowly, and the solution was stirred for 6 h. The THF was removed under vacuum, extracted with pentane (15 mL), and filtered through Celite. Removal of the pentane under vacuum gave a yellow oil (4.00 g; 17.06 mmol; 35%). ^{1}H NMR of predominant isomer (C$_6$D$_6$, 70 °C): 5.87 (m, 1H, C$_5$Me$_4$CH$_2$C*H*=CH$_2$), 5.03−4.88 (m, 2H, C$_5$Me$_4$CH$_2$CH=C*H*$_2$), 2.96−2.89 (m, 2H, C$_5$Me$_4$C*H*$_2$CH=CH$_2$), 1.85−1.56 (m, 12H, Me), −0.9 (s, 9H, Si*Me*$_3$). Anal. Calcd for C$_{15}$H$_{26}$Si: C, 76.84; H, 11.18. Found: C, 76.29; H, 11.07.

Synthesis of (CH$_2$=CHCH$_2$C$_5$Me$_4$)TiCl$_3$ (17). Compound **16** (2.00 g; 8.53 mmol) was dissolved in 5 mL of hexanes, then added dropwise to a hexanes (100 mL) solution of TiCl$_4$ (8.6 mL, 8.60 mmol, 1 M) at −78 °C. The orange solution turned dark red with some black precipitate. The solution was warmed slowly to 25 °C and refluxed for 30 min. It was filtered through Celite and cooled to −35 °C overnight. The product precipitated as a red solid, which was collected and dried under vacuum (1.60 g; 5.07 mmol; 60%). ^{1}H NMR (C$_6$D$_6$): 5.93 (m, 1H, C$_5$Me$_4$CH$_2$C*H*=CH$_2$), 4.79 (dd, ^3J = 10 Hz, ^2J = 1.6 Hz, 1H, C$_5$Me$_4$CH$_2$CH=C*H*$_2$), 4.61 (dd, ^3J = 17 Hz, ^2J = 1.6 Hz, 1H, C$_5$Me$_4$CH$_2$CH=C*H*$_2$), 3.34 (d, ^3J = 6 Hz, 2H, C$_5$Me$_4$C*H*$_2$CH=CH$_2$), 1.99 (s, 6H, *Me*), 1.91 (s, 6H, *Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 137.9 (C$_5$), 137.7 (C$_5$), 134.8 (C$_5$Me$_4$CH$_2$*C*H=CH$_2$), 116.5 (C$_5$Me$_4$CH$_2$CH=*C*H$_2$), 33.6 (C$_5$Me$_4$*C*H$_2$CH=CH$_2$), 14.3 (*Me*). Anal. Calcd for C$_{12}$H$_{17}$Cl$_3$Ti: C, 45.68; H, 5.43. Found: C, 45.75; H, 5.80.

Synthesis of *t*-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(C$_5$Me$_4$CH$_2$CH=CH$_2$)Cl$_2$ (18). Compound **5** (0.81 g; 2.57 mmol) was dissolved in 50 mL of toluene. Compound **17** (0.70 g; 2.57 mmol) was added dropwise with stirring at 25 °C. The red solution was heated at 80 °C for 12 h. Toluene was removed under vacuum to give a red solid, which was suspended in 10 mL of pentane, then stirred for 2 h to form an orange solid. The solid was filtered off and dried under vacuum (0.95 g; 1.98 mmol; 77%). ^{1}H NMR (C$_6$D$_6$): 6.31 (m, 1H, C$_5$Me$_4$CH$_2$C*H*=CH$_2$), 5.83 (m, 1H, PCH$_2$C*H*=CH$_2$), 4.95 (m, 4H, =C*H*$_2$), 3.57 (dm, ^3J = 6 Hz, 2H, C$_5$Me$_4$C*H*$_2$CH=CH$_2$), 2.62 (ddm, $^2J_{PH}$ = 10 Hz, ^3J = 7 Hz, 2H, PC*H*$_2$CH=CH$_2$), 2.24 (s, 6H, *Me*), 2.18 (s, 6H, *Me*), 1.10 (d, $^3J_{PH}$ = 15 Hz, 18H, P*t*-Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 137.3 (C$_5$Me$_4$CH$_2$*C*H=CH$_2$), 131.7 (d, $^2J_{PC}$ = 7 Hz, PCH$_2$*C*H=CH$_2$), 127.0 (C$_5$), 126.5 (C$_5$), 126.1 (C$_5$), 119.4 (d, $^3J_{PC}$

= 12 Hz, $\mathrm{PCH_2}\mathit{CH}\mathrm{{=}CH_2}$), 115.1 ($\mathrm{C_5Me_4CH_2CH{=}}\mathit{CH_2}$), 39.1 (d, $^1J_{\mathrm{PC}}$ = 52 Hz, *t*-Bu), 33.1 ($\mathrm{C_5Me_4}\mathit{CH_2}$), 31.4 (d, $^1J_{\mathrm{PC}}$ = 50 Hz, $\mathrm{P}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 27.8 (*t*-Bu), 13.5 (*Me*). ^{31}P NMR ($\mathrm{C_6D_6}$): 35.9. Anal. Calcd for $\mathrm{C_{23}H_{40}NPTiCl_2}$: C, 57.51; H, 8.39; N, 2.92. Found: C, 57.16; H, 8.63; N, 2.84.

Synthesis of *t*-$\mathrm{Bu_2(CH_2{=}CHCH_2)PNTi(C_5Me_4CH_2CH{=}CH_2)Me_2}$ (19). MeMgBr (0.62 mL; 3 M, 1.88 mmol) was added dropwise to a diethyl ether (7 mL) solution of compound **18** (0.18 g; 0.38 mmol) at −35 °C. The cloudy solution was stirred for 5 h at 25 °C. The solvent was removed under vacuum, and the product was extracted with 5 mL of hexanes and filtered through Celite. Removing the hexanes under vacuum gave a dark red oil (0.16 g; 0.36 mmol; 96%). ^{1}H NMR ($\mathrm{C_6D_6}$): 6.29 (m, 1H, $\mathrm{C_5Me_4CH_2}\mathit{CH}\mathrm{{=}CH_2}$), 5.97 (m, 1H, $\mathrm{PCH_2}\mathit{CH}\mathrm{{=}CH_2}$), 5.02 (m, 4H, $=\mathit{CH_2}$), 3.27 (dm, ^3J = 6 Hz, 2H, $\mathrm{C_5Me_4}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 2.54 (dd, $^2J_{\mathrm{PH}}$ = 10 Hz, ^3J = 7 Hz, 2H, $\mathrm{P}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 2.08 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.04 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.17 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 18H, *t*-Bu), 0.4 (s, $\mathrm{Ti}\mathit{Me_2}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 138.39 ($\mathrm{C_5Me_4CH_2}\mathit{CH}\mathrm{{=}CH_2}$), 133.0 (d, $^2J_{\mathrm{PC}}$ = 7 Hz, $\mathrm{PCH_2}\mathit{CH}\mathrm{{=}CH_2}$), 120.1 ($\mathrm{C_5}$), 119.2 ($\mathrm{C_5}$), 118.9 ($\mathrm{C_5}$), 118.2 (d, $^3J_{\mathrm{PC}}$ = 11 Hz, $\mathrm{PCH_2CH{=}}\mathit{CH_2}$), 114.5 ($\mathrm{C_5Me_4CH_2CH{=}}\mathit{CH_2}$), 43.7 ($\mathrm{Ti}\mathit{Me_2}$), 38.9 (d, $^1J_{\mathrm{PC}}$ = 52 Hz, *t*-Bu), 32.4 ($\mathrm{C_5Me_4}\mathit{CH_2}$), 32.0 (d, $^1J_{\mathrm{PC}}$ = 51 Hz, $\mathrm{P}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 28.1 (*t*-Bu), 12.5 ($\mathrm{C_5}\mathit{Me_4}$), 12.4 ($\mathrm{C_5}\mathit{Me_4}$). ^{31}P NMR ($\mathrm{C_6D_6}$): 21.7 Anal. Calcd for $\mathrm{C_{25}H_{46}NPTi}$: C, 68.32; H, 10.55; N, 3.19. Found: C, 67.95; H, 10.56; N, 2.81.

Synthesis of *t*-$\mathrm{Bu_2(C_5Me_4CH_2CH{=}CHCH_2)PNTiCl_2}$ (20). $[\mathrm{Cl_2(PCy_3)_2Ru{=}CHPh}]$ (0.068 g; 0.083 mmol, 8 mol%) was dissolved in 350 mL of toluene in a round-bottom flask and heated to 50 °C. Compound **18** (0.50 g; 1.04 mmol) was dissolved in 15 mL of toluene and slowly added over a 6 h period using a syringe pump. The resulting red solution was stirred for 12 h. The solution was concentrated to approximately 30 mL, then filtered through Celite. Cooling the red solution at −35 °C for 3 days gave a yellow precipitate, which was collected, washed with pentane (2 × 3 mL), and dried under vacuum (0.23 g; 0.51 mmol; 49%). ^{1}H NMR ($\mathrm{C_6D_6}$) partial: 6.15 (m, 1H, CH), 5.19 (m, 1H, CH), 2.23 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.06 (br s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.02 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 18H, *t*-Bu), ^{1}H NMR ($\mathrm{C_6D_6}$, 70 °C): 6.21 (m, 1H, CH), 5.29 (m, 1H, CH), 3.37 (m, $\mathrm{C_5Me_4}\mathit{CH_2}$), 2.23 (m, $\mathrm{P}\mathit{CH_2}$), 2.21 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.06 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.09 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 70 °C): 133.6 (d, J_{PC} = 7 Hz, CH), 126.9 ($\mathrm{C_5}$), 124.8($\mathrm{C_5}$), 123.6 ($\mathrm{C_5}$), 120.8 (d, J_{PC} = 10 Hz, CH), 39.8 (d, $^1J_{\mathrm{PC}}$ = 53 Hz, *t*-Bu), 30.4 ($\mathrm{C_5Me_4}\mathit{CH_2}$), 27.9 (*t*-Bu), 21.7 (d, $^1J_{\mathrm{PC}}$ = 43 Hz, $\mathrm{P}\mathit{CH_2}$), 14.3 ($\mathrm{C_5}\mathit{Me_4}$), 12.7 ($\mathrm{C_5}\mathit{Me_4}$). ^{31}P NMR ($\mathrm{C_6D_6}$): 41.3. Anal. Calcd for $\mathrm{C_{21}H_{36}NPTiCl_2}$: C, 55.77; H, 8.02; N, 3.10. Found: C, 55.81; H, 8.30; N, 3.07.

Synthesis of *t*-$\mathrm{Bu_2(C_5Me_4CH_2CH{=}CHCH_2)PNTiMe_2}$ (21). MeMgBr (0.27 mL; 3 M, 0.83 mmol) was added dropwise to a diethyl ether (4 mL) solution of compound **20** (0.075 g; 0.17 mmol) at −35 °C. The cloudy solution was stirred for 3 h at 25 °C. The solvent was removed under vacuum, and the product was extracted with hot hexanes (2 × 3 mL) and filtered through Celite. After removing the hexanes, the solid was dried under vacuum (0.066 g; 0.160 mmol; 97%). ^{1}H NMR ($\mathrm{C_6D_6}$): 6.10 (m, 1H, CH), 5.20 (m, 1H, CH), 3.08 (br, 2H, $\mathrm{C_5Me_4}\mathit{CH_2}$), 2.24 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.90 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.11 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 18H, *t*-Bu), 0.42 (s, 6H, $\mathrm{Ti}\mathit{Me_2}$), $\mathrm{P}\mathit{CH_2}$ not seen. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz, 70 °C): 6.17 (m, 1H, CH), 5.25 (m, 1H, CH), 3.10 (d, $^3J_{\mathrm{PH}}$ = 8 Hz, $\mathrm{C_5Me_4}\mathit{CH_2}$), 2.29 (m, 2H, $\mathrm{P}\mathit{CH_2}$), 2.29 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.89 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 1.16 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 18H, *t*-Bu), 0.33 (s, 6H, $\mathrm{Ti}\mathit{Me_2}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 133.3 (d, J_{PC} = 8 Hz, CH), 120.7 (d, J_{PC} = 9 Hz, CH), 119.2 ($\mathrm{C_5}$), 118.9 ($\mathrm{C_5}$), 116.4 ($\mathrm{C_5}$), 41.8 ($\mathrm{Ti}\mathit{Me_2}$), 38.6 (d, $^1J_{\mathrm{PC}}$ = 55 Hz, *t*-Bu), 29.2 ($\mathrm{C_5Me_4}\mathit{CH_2}$), 28.0 (*t*-Bu), 22.7 (d, $^1J_{\mathrm{PC}}$ = 44 Hz, $\mathrm{P}\mathit{CH_2}$), 13.4 ($\mathrm{C_5}\mathit{Me_4}$), 12.2 ($\mathrm{C_5}\mathit{Me_4}$). ^{31}P NMR ($\mathrm{C_6D_6}$): 27.2. Anal. Calcd for $\mathrm{C_{23}H_{42}NPTi}$: C, 67.14; H, 10.29; N, 3.40. Found: C, 66.97; H, 9.98; N, 3.11.

Synthesis of *t*-$\mathrm{Bu_2(CH_2{=}CHCH_2)PNTi(C_9H_6CH_2CH{=}CH_2)Cl_2}$ (22). $[\mathrm{C_9H_6CH_2CH{=}CH_2}]$Li (0.36 g; 2.22 mmol) was dissolved in 15 mL of a toluene/THF (1:1) mixture, then added dropwise to a toluene (30 mL) solution of compound **9** (0.79 g; 2.23 mmol) at 25 °C. The solution was stirred overnight and pumped down to dryness. The resulting solid was suspended in 50 mL of hexanes, heated to reflux, and filtered hot. The solvent was removed under vacuum to give an orange solid (0.73 g; 1.54 mmol; 69%). ^{1}H NMR ($\mathrm{C_6D_6}$): 7.74 (m, 2H, phenyl), 7.19 (m, 2H, phenyl), 6.69 (d, ^3J = 3 Hz, 1H, C3), 6.54 (d, ^3J = 3 Hz, 1H, C2), 6.11 (m, 2H, $\mathrm{CH_2{=}}\mathit{CH}\mathrm{CH_2}$), 5.15 (dm, J = 17 Hz, 1H, $\mathrm{CH_2CH{=}}\mathit{CH_2}$), 5.05 (dm, J = 10 Hz, 2H, $\mathrm{CH_2CH{=}}\mathit{CH_2}$), 4.92 (dm, J = 17 Hz, 1H, $\mathrm{CH_2CH{=}}\mathit{CH_2}$), 3.93 (m, 2H, $\mathrm{C_9H_6}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 2.29 (ddm, $^2J_{\mathrm{PH}}$ = 12 Hz, ^3J = 7 Hz, 2H, $\mathrm{P}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 1.06 (d, $^3J_{\mathrm{PH}}$ = 15 Hz, 18H, *t*-Bu). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 136.7 ($\mathrm{C_9H_6CH_2}\mathit{CH}\mathrm{{=}CH_2}$), 129.7 (d, $^2J_{\mathrm{PC}}$ = 8 Hz, $\mathrm{PCH_2}\mathit{CH}\mathrm{{=}CH_2}$), 125.4, 125.3, 124.5, and 122.5 phenyl CH), 119.1 (d, $^3J_{\mathrm{PC}}$ = 11 Hz, $\mathrm{PCH_2CH{=}}\mathit{CH_2}$), 115.3 ($\mathrm{C_9H_6CH_2CH{=}}\mathit{CH_2}$), 114.6 (Cp-*C*, C3), 102.0 (Cp-*C*, C2), 38.1 (d, $^1J_{\mathrm{PC}}$ = 49 Hz, *t*-Bu), 33.5 ($\mathrm{C_9H_6}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 28.6 (d, $^1J_{\mathrm{PC}}$ = 51 Hz, $\mathrm{P}\mathit{CH_2}$), 26.5 (*t*-Bu). ^{31}P NMR ($\mathrm{C_6D_6}$): 36.3. Anal. Calcd for $\mathrm{C_{23}H_{34}NPTiCl_2}$: C, 58.25; H, 7.23; N, 2.95. Found: C, 58.05; H, 6.97; N, 2.65.

Synthesis of *t*-$\mathrm{Bu_2(CH_2{=}CHCH_2)PNTi(C_9H_6CH_2CH{=}CH_2)Me_2}$ (23). MeMgBr (0.87 mL; 3 M, 2.64 mmol) was added dropwise to a diethyl ether (10 mL) solution of compound **21** (0.25 g; 0.53 mmol) at −35 °C. The cloudy solution was stirred overnight at 25 °C. The solvent was removed under vacuum, and the product was extracted with hexanes (2 × 10 mL) and filtered through Celite. The solvent was removed under vacuum to give a brown solid (0.18 g; 0.415 mmol; 79%). ^{1}H NMR ($\mathrm{C_6D_6}$): 7.74 (m, 1H, $\mathrm{C_6}$-ring), 7.57 (m, 1H, $\mathrm{C_6}$-ring), 7.17 (m, 2H, $\mathrm{C_6}$-ring), 6.13 (m, 2H, $\mathrm{CH_2{=}}\mathit{CH}\mathrm{CH_2}$), 6.10 (d, ^3J = 4 Hz, 1H, C3), 5.89 (d, ^3J = 4 Hz, 1H, C2), 5.17 (dm, J = 17 Hz, 1H, $\mathrm{CH_2CH{=}}\mathit{CH_2}$), 5.05 (dm, J = 10 Hz, 2H, $\mathrm{CH_2CH{=}}\mathit{CH_2}$), 4.94 (dm, J = 17 Hz, 1H, $\mathrm{CH_2CH{=}}\mathit{CH_2}$), 3.81 (dm, J = 7 Hz, 1H, $\mathrm{C_9H_6}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 3.57 (dm, J = 6 Hz, 1H, $\mathrm{C_9H_6}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 2.33 (m, 2H, $\mathrm{P}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 1.07 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 18H, *t*-Bu), 0.35 (s, 3H, $\mathrm{Ti}\mathit{Me}$), −0.04 (s, 3H, $\mathrm{Ti}\mathit{Me}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 138.5 ($\mathrm{C_9H_6CH_2}\mathit{CH}\mathrm{{=}CH_2}$), 132.2 (d, $^2J_{\mathrm{PC}}$ = 8 Hz, $\mathrm{PCH_2}\mathit{CH}\mathrm{{=}CH_2}$), 126.2, 123.7, 123.4, and 123.1 ($\mathrm{C_6}$-ring), 118.7 (d, $^3J_{\mathrm{PC}}$ = 11 Hz, $\mathrm{PCH_2CH{=}}\mathit{CH_2}$), 115.6 ($\mathrm{C_9H_6CH_2CH{=}}\mathit{CH_2}$), 113.0 (Cp-*C*, C3), 97.8 (Cp-*C*, C2), 46.0 ($\mathrm{Ti}\mathit{Me}$), 44.8 ($\mathrm{Ti}\mathit{Me}$), 38.5 (d, $^1J_{\mathrm{PC}}$ = 55 Hz, *t*-Bu), 33.6 ($\mathrm{C_9H_6}\mathit{CH_2}\mathrm{CH{=}CH_2}$), 30.1 (d, $^1J_{\mathrm{PC}}$ = 51 Hz, $\mathrm{P}\mathit{CH_2}$), 27.6 (*t*-Bu). ^{31}P NMR ($\mathrm{C_6D_6}$): 22.7. Anal. Calcd for $\mathrm{C_{25}H_{40}NPTi}$: C, 69.28; H, 9.30; N, 2.23. Found: C, 69.64; H, 8.99; N, 2.42.

Synthesis of *t*-$\mathrm{Bu_2(C_9H_6CH_2CH{=}CHCH_2)PNTiCl_2}$ (24). $[\mathrm{Cl_2(PCy_3)(H_2IMes)Ru{=}CHPh}]$ (0.070 g; 0.082 mmol, 8 mol%) was dissolved in 350 mL of toluene in a round-bottom flask and heated to 50 °C. Compound **22** (0.50 g; 1.05 mmol) was dissolved in 15 mL of $\mathrm{CH_2Cl_2}$ and slowly added over a 6 h period using a syringe pump. Another aliquot of $[\mathrm{Cl_2(PCy_3)(H_2IMes)Ru{=}CHPh}]$ (0.070 g) was added after 2 h. The resulting red solution was stirred for 12 h. The solution was concentrated to approximately 40 mL and filtered through Celite. Cooling the red solution to −35 °C for 3 days gave a red precipitate, which was collected, washed with pentane (2 × 3 mL), and dried under vacuum (0.23 g; 0.51 mmol; 49%). ^{1}H NMR ($\mathrm{C_6D_6}$): 7.57 (m, 1H, $\mathrm{C_6}$-ring), 7.41 (m, 1H, $\mathrm{C_6}$-ring), 7.14 (m, 2H, $\mathrm{C_6}$-ring), 6.85 (d, ^3J = 3 Hz, 1H, C3), 6.42 (d, ^3J = 3 Hz, 1H, C2), 6.03 (m, 1H, CH), 5.25 (m, 1H, CH), 3.85 (m, 1H, CH), 3.17 (m, 1H, CH), 2.53 (m, 1H, CH), 1.65 (m, 1H, CH), 0.97 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 9H, *t*-Bu), 0.94 (d, $^3J_{\mathrm{PH}}$ = 14 Hz, 9H, *t*-Bu). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 133.0 (d, J_{PC} = 8 Hz, CH), 126.7, 126.3, 126.1, and 123.0 (Phenyl CH), 121.5 (d, J_{PC} = 11 Hz, CH), 115.6 (Cp-*C*, C3), 109.2 ($\mathrm{C_9H_6}$, C2), 39.4 and 39.1 (each d, $^1J_{\mathrm{PC}}$ = 51 Hz, *t*-Bu), 28.0 ($\mathrm{C_9H_6}\mathit{CH_2}$), 27.8 and 27.2 (each s, *t*-Bu), 22.0 (d, $^1J_{\mathrm{PC}}$ = 44 Hz, $\mathrm{P}\mathit{CH_2}$). ^{31}P NMR ($\mathrm{C_6D_6}$): 43.6. Anal. Calcd for

$C_{21}H_{30}NPTiCl_2$: C, 56.53; H, 6.78; N, 3.14. Found: C, 56.48; H, 7.01; N, 3.08.

Synthesis of *t*-$Bu_2(C_9H_6CH_2CH{=}CHCH_2)PNTiMe_2$ (25). MeMgBr (0.71 mL; 3 M, 2.13 mmol) was added dropwise to a diethyl ether (10 mL) suspension of compound **24** (0.19 g; 0.43 mmol) at −35 °C. The cloudy solution was stirred overnight at 25 °C. The solvent was removed under vacuum, and the product was extracted with hot hexanes (3 × 10 mL) and filtered through Celite. The solvent was removed under vacuum to give a yellow solid (0.14 g; 0.35 mmol; 82%). ^1H NMR (C_6D_6): 7.79 (m, 1H, C_6-ring), 7.34 (m, 1H, C_6-ring), 7.18 (m, 2H, C_6-ring), 6.77 (d, $^3J = 3$ Hz, 1H, C3), 5.99 (m, 1H, C*H*), 5.91 (d, $^3J = 3$ Hz, 1H, C2), 5.27 (m, 1H, C*H*), 3.48 (dd, $J = 13$ Hz, $J = 11.0$ Hz,1H, $C_9H_6CH_2$), 3.09 (m, 1H, $C_9H_6CH_2$), 2.50 (m, 1H, PCH_2), 1.90 (m, 1H, PCH_2), 1.07 (d, $^3J_{PH} = 13.5$ Hz, 9H, *t*-Bu), 1.03 (d, $^3J_{PH} = 14$ Hz, 9H, *t*-Bu), 0.68 and −0.33 (each s, Ti*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 132.6 (d, $J_{PC} = 8$ Hz, *C*H), 128.7, 126.6, 125.9, 123.8, 123.7, 123.6, and 111.7 (phenyl), 121.7 (d, $J_{PC} = 10$ Hz, *C*H), 114.2 (Cp-*C*, C3), 101.5 (Cp-*C*, C2), 45.3 and 40.4 (Ti*Me*), 38.4 (d, $^1J_{PC} = 55$ Hz, *t*-Bu), 37.9 (d, $^1J_{PC} = 55$ Hz, *t*-Bu), 28.0 (s, *t*-Bu), 27.5 (s, *t*-Bu), 27.4 ($C_9H_6CH_2$), 22.2 (d, $^1J_{PC} = 44$ Hz, PCH_2). ^{31}P NMR (C_6D_6): 28.5. Anal. Calcd for $C_{23}H_{36}NPTi$: C, 68.15; H, 8.95; N, 3.46. Found: C, 67.92; H, 8.66; N, 3.17.

Polymerization Protocol. The polymerizations were performed in a 1 L Buchi reactor system. Following assembly, the reactor vessel and solvent storage unit were refilled with nitrogen with four refill/evacuation cycles over at least 90 min. Approximately 600 mL of toluene was transferred to the solvent storage container from a Grubbs-type purification column. The solvent was purged with dry nitrogen for 20 min and then transferred to the reactor vessel by differential pressure. The solvent was stirred at 1500 ± 10 rpm, and the temperature was kept constant at 30 ± 2 °C. The system was then exposed to ethylene via five vent/refill cycles. The activator, precatalyst, and solvent scrubber stock solutions were prepared in an inert atmosphere glovebox. Stock solutions were loaded into syringes and transferred to the reactor. *i*-Bu_3Al was used as a solvent scrubber for polymerizations using either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4)]$ as the cocatalyst. When experiments employed MAO, it served as both the activator and solvent scrubber. CpTi(NP*t*-$Bu_3)Cl_2$ and CpTi(NP*t*-$Bu_3)Me_2$[27] were used as standards, and these standards were tested regularly to ensure consistent performance of the reactor system. All trials reported have been done in duplicate to ensure reproducibility. In a typical experiment, 3.00 mL of *i*-Bu_3Al solution (0.125 mmol, 20.8 equiv) was injected into the reactor via the catalyst injection inlet. The solvent scrubber was allowed to stir for 5 min. Then 1.50 mL of toluene solution of $B(C_6F_5)_3$ (0.006 mmol) was injected followed immediately by 1.0 mL of precatalyst solution of CpTi(NP*t*-$Bu_3)Me_2$ (0.006 mmol). The reactor was allowed to stir (1500 ± 10 rpm) for 5 min at 30 ± 2 °C under 2 atm of ethylene. The polymerization was halted by closing off the ethylene inlet and venting the reactor to air. Stirring was stopped, the reactor was disassembled, and the reactor contents were transferred to a 4 L beaker containing approximately 100 mL of 10% HCl in MeOH. The polymer was collected via filtration, washed with toluene, and dried overnight.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data ($4.5° < 2\theta < 45-50.0°$) 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. 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 SHELXTL processing packages. An empirical absorption correction 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.[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, 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, 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 Supporting Information.

Discussion

Our strategy to linking phosphinimide to cyclopentadienyl ligands requires the preparation of complexes containing olefin-functionalized phosphinimide and cyclopentadienyl ligands. Initially, we targeted a system that incorporated a phosphinimide fragment similar to that seen in the unlinked complexes CpTi(NP*t*-$Bu_3)X_2$. To that end, we noted that we had previously described the synthesis of *t*-$Bu_2(Me_2CLi)PNSiMe_3$ via metalation of *t*-Bu_2(*i*-Pr)$PNSiMe_3$.[40] This species reacts with $CH_2{=}CHCH_2Br$ to give the allylic phosphinimine *t*-$Bu_2(CH_2{=}CHCH_2C(Me_2)PNSiMe_3$ (**1**). ^1H, ^{13}C, and ^{31}P NMR spectra showed the expected resonances. Subsequent reaction of **1** with $CpTiCl_3$ or Cp^*TiCl_3 afforded the desired products as yellow and orange solids in 73% and 77% yields, respectively. These products (**2** and **3**) were formulated as *t*-$Bu_2(CH_2{=}CHCH_2C(Me_2)PNTi(Cp)Cl_2$ and *t*-$Bu_2(CH_2{=}CHCH_2C(Me_2)PNTi(C_5Me_5)Cl_2$ based on ^1H, ^{13}C, and ^{31}P NMR spectra. The nature of **3** was also confirmed by X-ray crystallography (Figure 1). The Ti−N distance was found to be 1.776(4) Å, while the Ti−Cl distances were 2.3095(16) and 2.3212(15) Å, typical of this class of compounds. Similarly, the P−N distance of 1.608(4) and P−N−Ti angles of 164.6(2)° also fall in the range typical of Ti−phosphinimide complexes. The C(23)−C(24) distance of 1.312(11) Å confirms the presence of the olefinic fragment.

The isolation of **2** and **3** confirms that the addition of the olefin-functionalized phosphinimide onto Ti proceeds smoothly without ligand isomerization. With that established, reaction of **1** with $(C_5H_4CH_2CH{=}CH_2)TiCl_3$ was performed. This reaction proceeded upon heating at 90 °C for 8 h in toluene to give the complex *t*-$Bu_2(CH_2{=}CHCH_2C(Me_2)PNTi(C_5H_4CH_2CH{=}CH_2)Cl_2$ (**4**). The resulting complex was isolated as an orange oil in excellent yield of 92%. The downfield shift of the ^{31}P NMR resonance to 45.7 ppm is consistent with formation of the Ti−phosphinimide complex. Ring-closing metathesis reactions using **4** as the substrate were explored using either $[Cl_2(PCy_3)_2Ru{=}CHPh]$ or $[Cl_2(PCy_3)(H_2IMes)Ru{=}CHPh]$ as the catalyst, and under a variety of reaction conditions no

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[42] Cromer, D. T.; Waber, J. T. *Int. Tables X-Ray Crystallogr.* **1974**, *4*, 71–147.

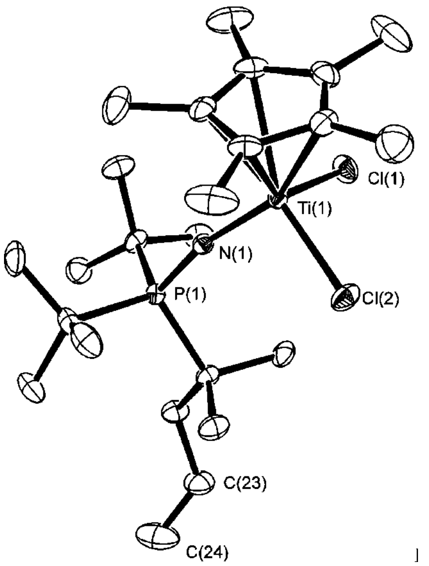
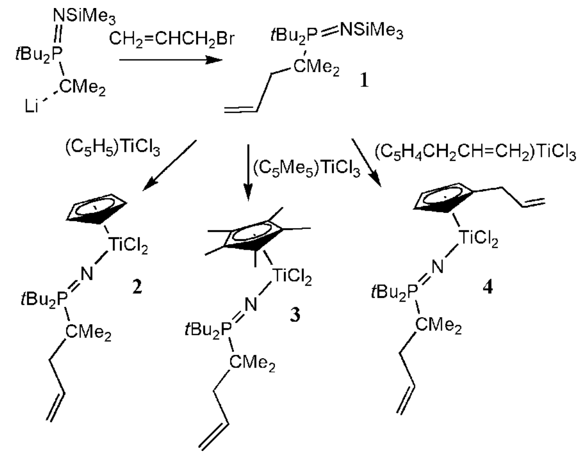
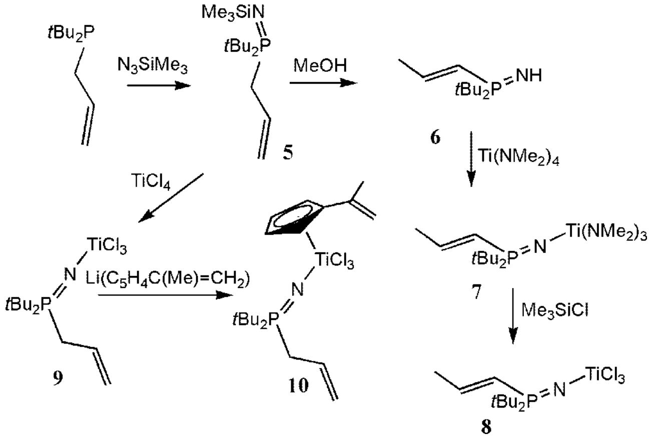


Figure 1. ORTEP drawing of one of the two molecules in the asymmetric unit of **3**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(1) 1.776(4), Ti(1)−Cl(1) 2.3095(16), Ti(1)−Cl(2) 2.3212(15), P(1)−N(1) 1.608(4), C(23)−C(24) 1.312(11), N(1)−Ti(1)−Cl(1) 101.99(12), N(1)−Ti(1)−Cl(2) 101.72(13), Cl(1)−Ti(1)−Cl(2) 102.96(7), P(1)−N(1)−Ti(1) 164.6(2).

Scheme 1. Synthesis of 1−4



Scheme 2. Synthesis of 5−10



evidence of the desired reaction was observed. This was attributed to the sterically demanding environment about P that presumably restricts rotation about the P−N bond, thus inhibiting approach of the phosphinimide-bound olefinic unit to that on the cyclopentadienyl ring.

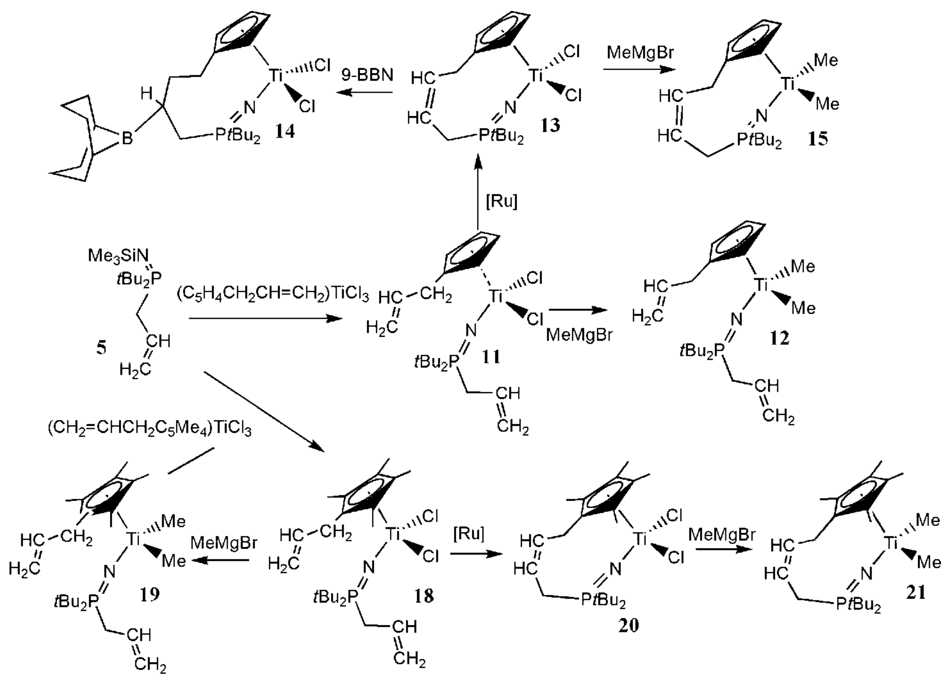
Adopting an alternative approach, the phosphinimine t-Bu$_2$(CH$_2$=CHCH$_2$)PNSiMe$_3$ (**5**) was prepared via a classical Staudinger oxidation of the phosphine t-Bu$_2$PCH$_2$CH=CH$_2$ with N$_3$SiMe$_3$ at 70 °C for 48 h, giving **5** in an overall 89% yield. The ^{1}H and ^{13}C{^{1}H} NMR data as well as the downfield shift of the ^{31}P NMR resonance to 24.3 ppm were consistent with the formulation. Treatment of **5** with methanol in an attempt to generate the corresponding parent phosphinimine via methanolysis of the SiMe$_3$ group gave rise to a new product (**6**). This species, isolated as a colorless crystalline solid in 85% yield, exhibited ^{1}H NMR multiplets at 6.71 and 5.81 ppm as well as a doublet at 1.59 ppm and a broad signal at −0.31 ppm. The corresponding ^{13}C{^{1}H} NMR resonances at 146.1, 123.1, and 20.1 ppm supported the formulation as the phosphinimine t-Bu$_2$(MeCH=CH)PNH (**6**), in which the allyl substituent had undergone isomerization. The mechanism of this isomerization is not fully understood, although the increased acidity of the CH$_2$ adjacent to P(V) must play a role in mediating proton transfer from N to the terminal C.

The phosphinimine **6** readily affects protonolysis of an amido group of Ti(NMe$_2$)$_4$ at 80 °C for 8 h to give an orange oil (**7**) in 93% isolated yield. On the basis of the NMR and analytical data, this product was formulated as t-Bu$_2$(MeCH=CH)PNTi(NMe$_2$)$_3$ (**7**). Subsequent treatment with Me$_3$SiCl gave the corresponding chloride derivative t-Bu$_2$(MeCH=CH)PNTiCl$_3$ (**8**) in 88% yield (Scheme 2). Crystals of t-Bu$_2$(MeCH=CH)PNTiCl$_3$(THF) (**8**·THF) were isolated by recrystallization of **8** from THF/hexane. A crystallographic study of **8**·THF (Figure 2) revealed the geometry about Ti is best described as a pseudotrigonal bipyramid, with the O atom of THF and Cl(1) atom adopting the pseudoaxial positions. The distortion from ideal *trans* geometry is evident in the O(1)−Ti(1)−Cl(1) angle of 164.00(5)°. The angles in the pseudoequatorial plane also deviate from ideal, as the N−Ti−Cl angles are 109.79(7)° and 114.37(7)°, while the Cl−Ti−Cl angle is 134.41(4)°. The Ti−Cl bond lengths range from 2.2996(9) to 2.3443(9) Å, while the Ti−N and Ti−O distances are 1.728(2) and 2.1494(17) Å, respectively. The geometry about the phosphinimide fragment is typical, with a P−N bond length of 1.612(2) Å and with an approximately linear P−N−Ti angle of 172.37(13)°. The location of the C=C double bond in the allylic fragment is evident with the observation of the C(8)−C(10) bond distance of 1.313(4) Å.

The isomerization of the allylic group can be avoided by direct reaction of **5** with suitable metal precursors. Thus, reaction of **5** with TiCl$_4$ with initial mixing at −78 °C proceeds smoothly to give the product t-Bu$_2$(CH$_2$=CHCH$_2$)PNTiCl$_3$ (**9**) in 78% yield. The NMR data are consistent with these formulations. Subsequent reaction of **9** with [C$_5$H$_4$C(Me)=CH$_2$]Li in THF afforded an orange powder (**10**) in 70% isolated yield. The NMR data for **10** were consistent with the formulation t-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(C$_5$H$_4$C(Me)=CH$_2$)Cl$_2$ (Scheme 2). Again repeated attempts to effect a ring closure by olefin metathesis employing either [Cl$_2$(PCy$_3$)$_2$Ru=CHPh] or [Cl$_2$(PCy$_3$)(H$_2$IMes)Ru=CHPh] as the catalyst resulted in no appreciable reaction.

The above results suggest that steric bulk proximal to the olefinic residues precludes metathesis, and thus an unsubstituted linkage was targeted. To that end (CpCH$_2$CH=CH$_2$)TiCl$_3$ was reacted with **5** to give the yellow solid t-Bu$_2$(CH$_2$=CHCH$_2$)PNTi(CpCH$_2$CH=CH$_2$)Cl$_2$ (**11**) in 96% isolated yield. This species can further be derivatized by methylation via

Scheme 3. Synthesis of 11−21



$[Ru] = [Cl_2(PCy_3)_2Ru=CHPh]$

treatment with MeMgBr. This affords the species t-$Bu_2(CH_2{=}CHCH_2)PNTi(CpCH_2CH{=}CH_2)Me_2$ (**12**) as a red oil in 89% yield. This species exhibits resonances in the ^1H NMR spectrum at 0.64 ppm attributable to the Ti-Me groups. Treatment of compound **11** with 8 mol % of the metathesis catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ with heating to 50 °C for 6 h afforded a yellow precipitate (**13**) in 49% isolated yield. Particularly diagnostic are the ^1H NMR resonances observed at 5.83, 5.09, 3.13, and 1.90 ppm, attributable to the CH and CH_2 groups in the linkage between the P atom and the cyclopentadienyl fragment. On the basis of the NMR data, **13** was formulated as t-$Bu_2(CpCH_2CH{=}CHCH_2)PNTiCl_2$, the product of ring-closing metathesis. This formulation was confirmed unequivocally by X-ray crystallography (Figure 3). Structural data for **13** revealed a geometry very similar to that described for **3** with Ti−N and Ti−Cl bond lengths of 1.748(3), 2.3020(13), and 2.3083(13) Å, respectively. The phosphinimide geometry is also similar, as the P−N bond distance was found to be 1.606(3) Å. It is notable however that the P−N−Ti is significantly closer to linearity at 178.1(2)°. The olefinic fragment in the linkage between the P atom and the cyclopentadienyl fragment is *cis*-substituted with a C(2)−C(3) distance of 1.382(6) Å.

Compound **13** reacts with 9-BBN to effect hydroboration of the olefinic residue in the linkage chain to give **14** in only 28% yield as a yellow solid. The product exhibits four distinct ^1H NMR signals at 6.39, 6.33, 6.24, and 6.08 ppm attributable to the cyclopentadienyl ring protons. In addition, the methylene

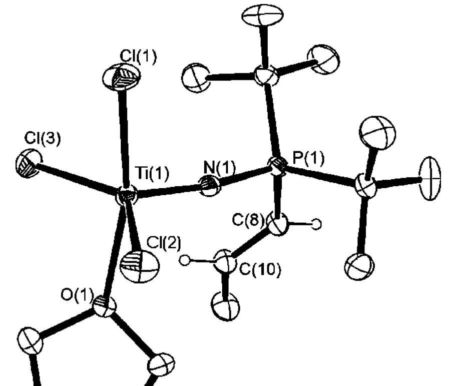


Figure 2. ORTEP drawing of **8**·THF. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(1) 1.728(2), Ti(1)−O(1) 2.1494(17), Ti(1)−Cl(3) 2.2996(9), Ti(1)−Cl(1) 2.3052(8), Ti(1)−Cl(2) 2.3443(9), P(1)−N(1) 1.612(2), C(8)−C(10) 1.313(4), N(1)−Ti(1)−O(1) 94.58(8), N(1)−Ti(1)−Cl(3) 109.79(7), O(1)−Ti(1)−Cl(3) 83.58(5), N(1)−Ti(1)−Cl(1) 101.36(7), O(1)−Ti(1)−Cl(1) 164.00(5), Cl(3)−Ti(1)−Cl(1) 92.27(4), N(1)−Ti(1)−Cl(2) 114.37(7), O(1)−Ti(1)−Cl(2) 82.23(5), Cl(3)−Ti(1)−Cl(2) 134.41(4), Cl(1)−Ti(1)−Cl(2) 89.83(4), P(1)−N(1)−Ti(1) 172.37(13).

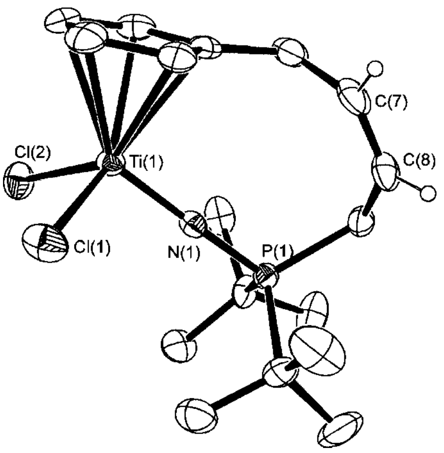


Figure 3. ORTEP drawing of one of the two molecules in the asymmetric unit of **13**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(1) 1.748(3), Ti(1)−Cl(2) 2.3020(13), Ti(1)−Cl(1) 2.3083(13), P(1)−N(1) 1.606(3), C(2)−C(3) 1.382(6), N(1)−Ti(1)−Cl(2) 103.43(10), N(1)−Ti(1)−Cl(1) 103.71(10), Cl(2)−Ti(1)−Cl(1) 100.23(5), P(1)−N(1)−Ti(1) 178.1(2).

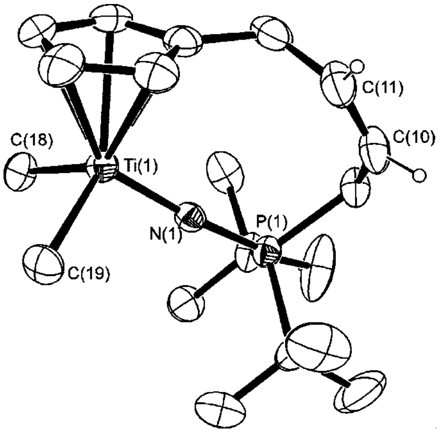


Figure 4. ORTEP drawing of one of the two molecules in the asymmetric unit of **15**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(1) 1.786(4), Ti(1)−C(18) 2.119(6), Ti(1)−C(19) 2.144(6), P(1)−N(1) 1.571(4), C(10)−C(11) 1.289(10), N(1)−Ti(1)−C(18) 102.5(2), N(1)−Ti(1)−C(19) 103.7(2), C(18)−Ti(1)−C(19) 98.5(3), P(1)−N(1)−Ti(1) 174.9(3).

protons of the chain between the P atom and cyclopentadienyl fragments are inequivalent (i.e., diastereotopic), consistent with the generation of a stereogenic center upon hydroboration. Similarly the *t*-Bu groups are inequivalent and give rise to distinct doublets at 1.38 and 1.33 ppm. These data, together with the other NMR data including the observation of a ^{11}B signal at 86.8 ppm, are consistent with the formulation of *t*-$Bu_2(CpCH_2CH_2CH(B(C_8H_{14})CH_2)PNTiCl_2$ (**14**).

Compound **13** was also derivatized by alkylation. Treatment with MeMgBr afforded the species *t*-$Bu_2(CpCH_2CH{=}CHCH_2)PNTiMe_2$ (**15**). Isolated in 86% yield, this species exhibits the expected NMR resonances, and the structure of **15** was also confirmed by X-ray crystallography (Figure 4). The structural data are similar to those reported above for **13**. The replacement of chlorides with methyl groups gives rise to Ti−C distances of 2.119(6) and 2.144(6) Å and, as a result, a longer Ti−N bond distance of 1.786(4) Å, consistent with a more electron-rich Ti center. Conversely, the P−N bond length of 1.571(4) Å in **15** is significantly shorter than that seen in **13**. On the other hand, the P−N−Ti angle varies only slightly, being 174.9(3)° in **15**.

Efforts to increase the steric demands about Ti involved use of tetramethylcyclopentadiene to give $(CH_2{=}CHCH_2)C_5Me_4SiMe_3$ (**16**) and subsequent addition of this to $TiCl_4$ to give $(CH_2{=}CHCH_2C_5Me_4)TiCl_3$ (**17**). Reaction of this precursor with compound **5** afforded an orange solid in 77% isolated yield. NMR data were consistent with the formulation *t*-$Bu_2(CH_2{=}CHCH_2)PNTi(C_5Me_4CH_2CH{=}CH_2)Cl_2$ (**18**). In a method similar to that used above methylation of **18** was achieved employing MeMgBr to give *t*-$Bu_2(CH_2{=}CHCH_2)PNTi(C_5Me_4CH_2CH{=}CH_2)Me_2$ (**19**) as a dark red oil in 96% yield. The methyl groups gave rise to ^{1}H NMR resonances at 0.40 ppm, while the ^{31}P NMR resonance was observed at 21.7 ppm. Compound **18** was also reacted with 8 mol % of $[Cl_2(PCy_3)_2Ru{=}CHPh]$ to effect ring-closing metathesis of the linkage between the phosphinimide and cyclopentadienyl ligand, affording *t*-$Bu_2(C_5Me_4CH_2CH{=}CHCH_2)PNTiCl_2$ (**20**). This species was isolated in 49% yield. The presence of the olefinic linkage was evidenced by the ^{1}H NMR signals at 6.15 and 5.19 ppm arising from the CH groups. The formulation of **20** was also confirmed via X-ray crystallography (Figure 5). The structure of **20** is analogous to that seen for **13** and **15**. The Ti−N distance in **20** is 1.767(3) Å, while the Ti−Cl distances are 2.3103(14) and 2.3185(14) Å. The P−N distance of 1.597(3) Å is slightly shorter than that seen in **13**, consistent with the stronger donor ability of the C_5Me_4 ring in **20**. The corresponding P−N−Ti angle is almost linear at 176.0(2)°. Again similar to **13** and **15**, the olefinic bond in the linker chain is *cis*-substituted with a C=C bond length of 1.316(6) Å. Compound **20** was further deriviatized by methylation to give *t*-$Bu_2(C_5Me_4CH_2CH{=}CHCH_2)PNTiMe_2$ (**21**) in 97% yield.

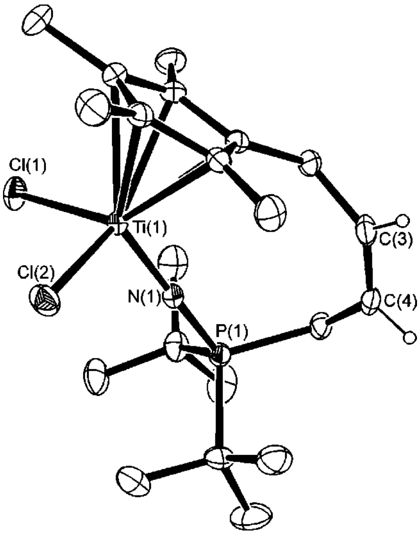


Figure 5. ORTEP drawing of one of the two molecules in the asymmetric unit of **20**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(1) 1.767(3), Ti(1)−Cl(2) 2.3103(14), Ti(1)−Cl(1) 2.3185(14), P(1)−N(1) 1.597(3), C(3)−C(4) 1.316(6), N(1)−Ti(1)−Cl(2) 104.90(12), N(1)−Ti(1)−Cl(1) 102.65(12), Cl(2)−Ti(1)−Cl(1) 101.21(5), P(1)−N(1)−Ti(1) 176.0(2).

Indenyl derivatives were also targeted and prepared. Treatment of **9** with $[C_9H_6CH_2CH{=}CH_2]Li$ afforded the species *t*-$Bu_2(CH_2{=}CHCH_2)PNTi(C_9H_6CH_2CH{=}CH_2)Cl_2$ (**22**) as an orange solid in 69% yield. This species was methylated to give the corresponding compound *t*-$Bu_2(CH_2{=}CHCH_2)PNTi(C_9H_6CH_2CH{=}CH_2)Me_2$ (**23**) in 79% yield, while treatment of **22** with 8 mol % $[Cl_2(PCy_3)(H_2IMes)Ru{=}CHPh]$ effected ring-closing metathesis to give the corresponding linked phosphinimide−indenyl species *t*-$Bu_2(C_9H_6CH_2CH{=}CHCH_2)PNTiCl_2$ (**24**). In this latter reaction, addition of a second aliquot of the Ru catalyst was necessary to give a total isolated yield of 49% after 8 h reaction time. The ^{1}H NMR spectrum of **24** revealed signals at 6.85, 6.42, 6.03, 5.25, 3.85, 3.17, 2.53, and 1.65 ppm attributable to the indenyl, methine, and methylene protons. The inherent dissymmetry of the molecule also gives rise to inequivalent resonances attributable to the *tert*-butyl groups at 0.94 and 0.97 ppm. An analogous situation is observed in the species *t*-$Bu_2(C_9H_6CH_2CH{=}CHCH_2)PNTiMe_2$ (**25**) derived from methylation of **24**.

Polymerization Catalysis. Screening of the ability of selected compounds to effect olefin polymerization was performed under a variety of conditions. Initially, using MAO as a solvent scrubber/activator resulted in a range of activities relative to $CpTi(NP\textit{t}\text{-}Bu_3)Cl_2$.[27] It is noteworthy that species **18** and **22**, in which pendant olefin groups are present on both the cyclopentadienyl and phosphinimide ligand, result in relatively high-activity catalysts (Table 2). In contrast, the corresponding species **20** and **24**, in which metathesis afforded a chain linking the ligands, gave much lower activity when it was observable

Table 1. Crystallographic Data

	3	**8**·THF	**13**	**15**	**20**
formula	$C_{24}H_{44}Cl_2NPTi$	$C_{15}H_{31}Cl_3NOPTi$	$C_{17}H_{28}Cl_2NPTi$	$C_{24}H_{36}Cl_2NPTi$	$C_{19}H_{34}NPTi$
fw	496.37	426.63	396.17	488.31	355.34
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	20.294(3)	8.0776(10)	9.6941(10)	16.188(4)	9.873(7)
b (Å)	13.630(2)	15.711(2)	12.5284(13)	9.838(2)	12.666(9)
c (Å)	20.3541(19)	17.107(2)	16.4667(16)	16.613(4)	16.654(12)
α (deg)			89.6710(10)		89.387(12)
β (deg)	105.854(10)	97.4340(10)	81.8720(10)	97.961(3)	82.408(12)
γ (deg)			88.5790(10)		88.980(12)
V (Å^3)	5415.7(13)	2152.7(5)	1979.2(3)	2620.3(11)	2064(3)
Z	8	4	4	4	4
d(calc) (g cm^{-1})	1.218	1.316	1.330	1.238	1.144
abs coeff, μ (cm^{-1})	0.583	0.845	0.780	0.602	0.490
data collected	50 520	20 283	13 276	24 383	13 159
data $F_o^2 > 3\sigma(F_o^2)$	11 607	3792	5226	4617	6248
variables	508	199	397	262	397
R	0.0652	0.0382	0.0451	0.0557	0.0624
R_w	0.1549	0.1080	0.0746	0.1402	0.1426
GOF	0.723	0.994	0.730	1.056	0.984

Table 2. Ethylene Polymerization Catalysis[a]

precat.	activator (equiv)	activity	M_n	M_w	PDI
$CpTiCl_2NPt\text{-}Bu_3$	MAO (500)	22250	588000	1193000	2.01
11	MAO (500)	870	96 115	235 056	2.45
13	MAO (500)	115			
18	MAO (500)	8208			
20	MAO (500)	260	185 878	554 210	2.98
22	MAO (500)	5652	327 620	642 112	1.97
24	MAO (500)	ns			
12	$B(C_6F_5)_3$ (2)	8058	357 931	847 100	2.37
15	$B(C_6F_5)_3$ (2)	6927	338 584	631 331	1.86
19	$B(C_6F_5)_3$ (2)	7528	577 457	1 138 761	1.97
21	$B(C_6F_5)_3$ (2)	12400	533 495	1 070 589	2.01
23	$B(C_6F_5)_3$ (2)	8769			
25)	$B(C_6F_5)_3$ (2)	5562			
$CpTiMe_2NPt\text{-}Bu_3$	$[Ph_3C][B(C_6F_5)_4]$ (2)	7958			
12	$[Ph_3C][B(C_6F_5)_4]$ (2)	9809	216 061	815 381	3.77
15	$[Ph_3C][B(C_6F_5)_4]$ (2)	5762	235 714	495 132	2.10
19	$[Ph_3C][B(C_6F_5)_4]$ (2)	7493	198 717	465 035	2.34
21	$[Ph_3C][B(C_6F_5)_4]$ (2)	6683	311 463	674 589	2.17
23	$[Ph_3C][B(C_6F_5)_4]$ (2)	9594	373 391	772 026	2.08
25	$[Ph_3C][B(C_6F_5)_4]$ (2)	6572	223 034	402 297	1.80

[a] MAO = methylalumoxane; activities are reported in g mmol^{-1} h^{-1} atm^{-1}. All reactions were performed at T = 30°C. ns = not soluble enough for determination.

at all. This in part can be attributable to significant reduction in solubility of the linked-ligand catalysts. The resulting polymers derived from these tests exhibited a polydispersity index (PDI) ranging from 1.97 to 2.98, consistent with single-site catalysis. In addition, the molecular weights were relatively high. Indeed, in several cases, the molecule weights of the polymers could not be determined due to extremely poor solubility (even at 160 °C in $C_6H_4Cl_2$), suggesting molecular weights well above 1×10^6.

Use of alternative activation strategies by treatment of $TiMe_2$ species with 2 equiv of $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ and 20 equiv of $Al(i\text{-}Bu)_3$ as a scavenger generally gave more consistently active catalysts. In general, higher activities were observed using $[Ph_3C][B(C_6F_5)_4]$ as the activator. A similar observation has been made for $CpTiMe_2(NPtBu_3)$.[27] In the case of **12** or **23** with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ the activities exceeded that observed with the standard $CpTiMe_2(NPtBu_3)$. Again single-site catalysis is indicated by the PDIs, which are about 2.0. The higher observed PDI of 3.77 in the case of **12/** $[Ph_3C][B(C_6F_5)_4]$ is consistent with a thermal spike that may be associated with the high activity. Molecular weights of the polyethylene produced range from 400 000 to 1 100 000 when they could be measured.

Summary. Synthetic pathways have been developed to prepare a series of Ti complexes in which a cyclopentadienyl fragment and a phosphinimide ligand are linked by an alkenyl chain. This methodology is based on olefin metathesis. These complexes provide active olefin polymerization catalysts. These observations suggest that elaboration of the cyclopentadienyl ligand may provide a new class of phosphinimide-based complexes that may be effective catalysts for stereoselective polymerization of α-olefins. Synthetic work toward this goal is underway, and the results will be reported in due course.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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