Di-*tert*-butylbiphenylphosphinimide Titanium and Zirconium Complexes: Pendant Arene−Metal Interactions

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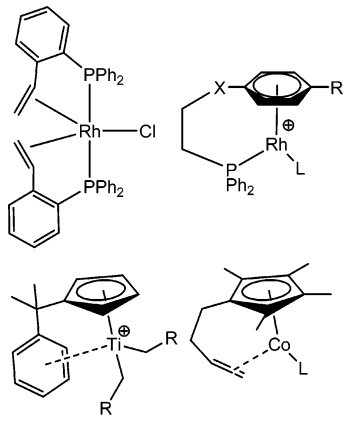
Received June 28, 2006

Reaction of *t*-Bu_2(2-C_6H_4Ph)PN$SiMe_3$ (**1**), with $TiCl_4$ affords the product *t*-Bu_2(2-C_6H_4Ph)PN$TiCl_3$ (**4**). This species is readily alkylated with MeMgBr to give *t*-Bu_2(2-C_6H_4Ph)PN$TiMe_3$ (**5**). X-ray crystallographic studies reveal that both **4** and **5** adopt conformations in which the biphenyl substituent is oriented toward the metal center. In contrast, the species derived from alkylation or amination and subsequent chemistry including *t*-Bu_2(2-C_6H_4Ph)PN$Ti(CH_2Ph)_3$ (**6**), *t*-Bu_2(2-C_6H_4Ph)PN$Ti(NMe_2)_3$ (**7**), *t*-Bu_2(2-C_6H_4Ph)PN$Ti(NMe_2)_2Cl$ (**8**), and *t*-Bu_2(2-C_6H_4Ph)PN$Ti(CH_2Ph)(NMe_2)_2$ (**9**) exist in solution as two isomers in which the biphenyl fragment is oriented toward and away from the metal center. The barriers to interconversion of these isomers were determined by variable-temperature NMR studies to be ca. 92 kJ/mol. The analogous Zr complexes *t*-Bu_2(2-C_6H_4Ph)PN$Zr(NEt_2)_3$ (**10**), *t*-Bu_2(2-C_6H_4Ph)PN$ZrCl_3$ (**11**), and *t*-Bu_2(2-C_6H_4Ph)PN$ZrMe_3$ (**12**) showed behavior similar to **6**−**9**. Reduction of **4** with Mg powder prompted disproportionation, affording [*t*-Bu_2(2-C_6H_4Ph)PN]$_2TiCl_2$ (**13**). This species also exists as two isomers: in the minor isomer one of the biphenyl substituents is oriented toward and the other away from the Ti center, while in the major isomer both biphenyl units are oriented away from the metal center. A similar observation was made for [*t*-Bu_2(2-C_6H_4Ph)PN]$_2TiMe_2$ (**14**) and [*t*-Bu_2(2-C_6H_4Ph)-PN]$_2ZrMe_2$ (**15**). The latter species was formed in a second-order ligand redistribution reaction from **12** with a rate constant of 4×10^{-4} s^{-1} at 333 K and $\Delta H^{\ddagger} = 69(2)$ kJ/mol and $\Delta S^{\ddagger} = -108(6)$ J/(mol K). Reaction of **5** with $B(C_6F_5)_3$ generates [*t*-Bu_2(2-C_6H_4Ph)PN$TiMe_2$][$MeB(C_6F_5)_3$] (**16**). **16** is a remarkably stable salt in which the Ti-cation is arene-stablized, although the arene is readily displaced by THF to give [*t*-Bu_2(2-C_6H_4Ph)PN$TiMe_2$(THF)][$MeB(C_6F_5)_3$] (**18**). In a similar fashion two isomers of [(*t*-Bu_2(2-C_6H_4Ph)PN)$_2$TiMe][$MeB(C_6F_5)_3$] (**19**) are formed. The biphenyl substituents of the major isomer of **19** are oriented in opposing directions, while in the minor isomer both biphenyl substituents are oriented toward the Ti center. In the latter isomer the arene rings are involved in an intramolecular exchange process ($\Delta H^{\ddagger} = 69(2)$ kJ/mol, $\Delta S^{\ddagger} = 60(2)$ J/(mol K)).

Introduction

An area of organometallic chemistry that has drawn recent attention involves the use of hemilabile ligands.[1] Such ligands combine a strong donor group with a fragment that weakly interacts with a metal center. Such systems have been developed to exploit the chelate effect to stabilize a reactive metal center in the absence of other reagents, but at the same time the weak donor group is readily displaced by substrate, allowing reactions to go forward. Examples of such hemilabile ligand systems that have been studied include phosphine−ether, phosphine−thioether, phosphine−arene, cyclopentadienyl−alkene, and cyclopentadienyl−arene ligands (Scheme 1).[1] Of particular interest to our group have been the latter two systems, in which pendant groups on cyclopentadienyl ligands have been used to stabilize cationic early metal complexes. In particular, Hessen and coworkers[2] recently exploited CpTi complexes with a pendant arene fragment to stabilize cationic Ti species that effect the specific catalytic trimerization of ethylene. In our own work, we have previously established that the steric analogy between cyclopentadienyl and phosphinimide ligands is a concept that can be used to develop highly effective olefin polymerization catalysts.[3−6] In extending our chemistry to systems incorporating hemilabile ligands, we have previously reported complexes

Scheme 1. Hemilabile Complexes



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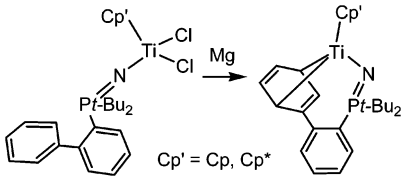
10.1021/om060569u CCC: $33.50
Publication on Web 09/02/2006

Scheme 2. Reduction of Cp′(*t*-Bu$_2$(2-C$_6$H$_4$Ph)PN)TiCl$_2$ to Give Cp′(*t*-Bu$_2$(2-C$_6$H$_4$Ph)PN)Ti



incorporating the di-*tert*-butylbiphenylphosphinimide ligand.[7] The pendant arene fragment of the biphenyl has been shown to oxidatively add to Ti upon reduction of the precursor Ti−dichloride complex, affording the species Cp′(*t*-Bu$_2$(2-C$_6$H$_4$Ph)-PN)Ti (Cp′ = Cp, Cp*) (Scheme 2).[7] While these complexes are best formulated as Ti(IV) species in which a formally Ti-(II) center has oxidatively added to the arene ring, this result suggests the potential of the di-*tert*-butylbiphenylphosphinimide ligand to act as a hemilabile ligand. In this paper we probe the chemistry of such phosphinimide complexes further. Herein, we report the synthesis and characterization of a series of Ti and Zr complexes bearing the di-*tert*-butylbiphenylphosphinimide ligand and explore the nature of the resulting hemilabile ligand complexes.

Experimental Section

General Procedures. All operations were performed under nitrogen atmosphere using glovebox or Schlenk line techniques. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. Deuterated solvents d_8-toluene (C_7D_8) and d_6-benzene (C_6D_6) were dried and distilled from sodium/benzophenone ketyl, while d_5-bromobenzene (C_6D_5Br), d_3-chloroform, and d_2-dichloromethane were dried and distilled from CaH_2. ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H}, ^{19}F, ^{7}Li, and ^{31}P{^{1}H} NMR experiments were performed on Bruker Avance 300 and 500 MHz spectrometers. Data are given in ppm relative to residual solvent signals for ^{1}H and ^{13}C spectra. Spectra were recorded at 25 °C unless otherwise noted. ^{11}B, ^{19}F, ^{7}Li, and ^{31}P spectra were referenced to external BF_3·OEt_2, CCl_3F, LiCl(aq), and 85% H_3PO_4, respectively. Elemental analyses were performed in the microanalytical laboratory of the Department of Chemistry (University of Windsor). *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNSiMe$_3$ (**1**) was prepared as previously reported.[7]

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNH, 2. Compound **1** (2.00 g, 5.19 mmol) was stirred in a mixture of toluene/methanol (20 mL/5 mL) for 20 h at 25 °C. The volatiles were removed, and the title compound was isolated as a white powder in quantitative yield. ^{1}H NMR ($CDCl_3$): −0.88 (s, br, 1H, NH), 1.25 (d, 18H, *t*-BuP, $^3J_{HP}$ = 13.7 Hz), 7.02−7.20, 7.31−7.38, 7.59−7.64 (m, 9H, 2-C$_6$H$_4$-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 28.16 (s, *t*-Bu), 37.15 (d, *t*-Bu, $^1J_{CP}$ = 61 Hz), 125.26 (d, $^2J_{CP}$ = 8 Hz), 126.92 (s), 127.07 (s), 129.23 (s), 129.28 (s), 131.11 (d, C$_{ipso}$, $^1J_{CP}$ = 48 Hz), 132.17 (d, $^3J_{CP}$ = 7 Hz), 133.23 (d, $^2J_{CP}$ = 8 Hz), 142.79 (s, C$_{ipso}$), 149.63 (d, C$_{ipso}$, $^3J_{CP}$ = 6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): 42.3 (s). Anal. Calcd for $C_{20}H_{28}NP$: C, 76.64; H, 9.00; N, 4.47. Found: C, 76.60; H, 9.28; N, 4.41.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNLi, 3. To a solution of **2** (272 mg, 0.87 mmol) in 5 mL of hexane was added *t*-BuLi (56 mg, 0.5 mL, 1.7 M in *n*-hexane) at 25 °C. The mixture was stirred for 16 h, and the resulting white precipitate filtered to yield 255 mg (92%) of the title compound. ^{1}H NMR (THF-d_8, 55 °C): 1.15 (d, br, 18H, *t*-BuP, $^3J_{HP}$ = 11.1 Hz), 6.89 (s, br, 2H, 2-C$_6$H$_4$Ph), 7.21−7.28 (m, 6H, 2-C$_6$H$_4$Ph), 7.81 (s, br, 1H, 2-C$_6$H$_4$Ph). ^{13}C{^{1}H} NMR (THF-d_8, 55 °C): 30.25 (s, *t*-Bu), 39.13 (d, *t*-Bu, $^1J_{CP}$ = 50 Hz), 125.31 (d, $^2J_{CP}$ = 8 Hz), 127.08 (s), 127.15 (s), 128.08 (s, br), 129.93 (s, br), 133.55 (s, br), 134.07 (br, C$_{ipso}$), 147.33 (s, br, C$_{ipso}$). ^{31}P{^{1}H} NMR (THF-d_8, 55 °C): 11.4 (s, br). ^{7}Li NMR (THF-d_8, 55 °C): −1.4 (s). Anal. Calcd for $C_{20}H_{27}NPLi$: C, 75.22; H, 8.52; N, 4.39. Found: C, 74.45; H, 8.13; N, 4.79.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTiCl$_3$, 4. To a solution of $TiCl_4$ (0.72 g, 3.78 mmol) in 20 mL of toluene at 0 °C was added **1** (1.46 g, 3.78 mmol) in 10 mL of toluene. The solution was refluxed for 16 h, the volatiles were removed under vacuum, and the residue was dissolved in CH_2Cl_2 and passed through a plug of Celite. Cooling the CH_2Cl_2 solution at −35 °C afforded 0.74 g (74%) of a light yellow crystalline solid. X-ray-quality crystals were obtained by the slow diffusion of pentane into a CH_2Cl_2 solution of the title compound. ^{1}H NMR ($CDCl_3$): 1.61 (d, 18H, *t*-BuP, $^3J_{HP}$ = 16 Hz), 7.28−7.61 (m, 9H, 2-C$_6$H$_4$Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): 28.48 (s, *t*-Bu), 41.43 (d, *t*-Bu, $^1J_{CP}$ = 48 Hz), 121.41 (d, C$_{ipso}$, $^1J_{CP}$ = 76 Hz), 126.15 (d, $^2J_{CP}$ = 12 Hz), 128.28 (s), 129.10 (s), 129.16 (s), 131.67 (d, $^2J_{CP}$ = 14 Hz), 131.94 (s), 135.59 (d, $^3J_{CP}$ = 9 Hz), 140.96 (s, C$_{ipso}$), 149.69 (s, C$_{ipso}$). ^{31}P{^{1}H} NMR (C_6D_6): 42.7 (s). Anal. Calcd for $C_{20}H_{27}Cl_3NPTi$: C, 51.48; H, 5.83; N, 3.00. Found: C, 51.66; H, 5.62; N, 3.30.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTiMe$_3$, 5. To a suspension of **4** (0.635 g, 1.36 mmol) in Et_2O (10 mL) was added MeMgBr (1.49 mL, 3.0 M, 4.48 mmol) at 25 °C. The mixture was stirred overnight, the solvent removed under vacuum, and the residue dissolved in toluene and filtered through Celite. The clear solution was cooled at −35 °C to give 452 mg (82%) of colorless crystals. ^{1}H NMR (C_6D_5Br): 0.72 (s, 9H, MeTi), 1.27 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz), 6.91−6.94 (m, 1H, 2-C$_6$H$_4$Ph), 7.10−7.19 (m, 5H, 2-C$_6$H$_4$Ph), 7.24−7.26 (m, 2H, 2-C$_6$H$_4$Ph), 7.49−7.53 (m, 1H, 2-C$_6$H$_4$Ph). ^{13}C-{^{1}H} NMR (C_6D_5Br, partial): 28.41 (s, *t*-Bu), 39.28 (d, *t*-Bu, $^1J_{CP}$ = 54 Hz), 53.25 (s, MeTi), 125.17 (d, $^2J_{CP}$ = 11 Hz), 126.76 (s), 127.33 (s), 129.13 (s), 129.97 (s), 131.84 (d, $^2J_{CP}$ = 12 Hz), 134.69 (d, $^3J_{CP}$ = 9 Hz), 142.70 (s, C$_{ipso}$), 149.55 (d, C$_{ipso}$, $^3J_{CP}$ = 5 Hz). ^{31}P{^{1}H} NMR (C_6D_6): 21.3 (s). Anal. Calcd for $C_{23}H_{36}NPTi$: C, 68.15; H, 8.95; N, 3.46. Found: C, 67.91; H, 8.30; N, 3.49.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTi(CH$_2$Ph)$_3$, 6. To a suspension of **4** (0.235 g, 0.50 mmol) in Et_2O (10 mL) was added $PhCH_2$-MgCl (1.67 mL, 1.0 M, 1.66 mmol) at room temperature. The mixture was stirred overnight, the solvent removed under vacuum, and the residue dissolved in toluene and filtered through Celite. The clear yellow solution was cooled to −35 °C to give 254 mg (76%) of the title compound as a 1:1.4 mixture of two isomers. ^{1}H NMR (toluene-d_8): 0.86 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, minor isomer), 0.99 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, major isomer), 2.41 (s, 6H, CH_2Ph, major isomer), 2.66 (s, 6H, CH_2Ph, major isomer), 6.73−7.24 (m, 2-C$_6$H$_4$Ph, major isomer and minor isomer), 9.00 (dd, 1H, 2-C$_6$H$_4$Ph, $^3J_{HH}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, minor isomer). ^{13}C{^{1}H} NMR (toluene-d_8) partial: 27.98 (s, *t*-Bu, minor isomer), 28.57 (s, *t*-Bu, major isomer), 38.31 (d, *t*-Bu, $^1J_{CP}$ = 52 Hz, minor isomer), 39.51 (d, *t*-Bu, $^1J_{CP}$ = 53 Hz, major isomer), 78.87 (s, CH_2Ph, minor isomer), 84.63 (s, CH_2Ph, major isomer), 121.70 (s), 121.99 (s), 127.26 (s), 127.45 (s), 127.78 (s), 129.81 (s), 130.31 (d, $^2J_{CP}$ = 11 Hz), 130.95 (s), 132.08 (d, $^2J_{CP}$ = 13 Hz), 133.16 (d, $^2J_{CP}$ = 9 Hz), 135.46 (d, $^3J_{CP}$ = 9 Hz), 139.37 (d, $^3J_{CP}$ = 9 Hz), 143.41 (s, C$_{ipso}$), 144.62 (s, C$_{ipso}$), 147.04 (s), 148.38 (s), 149.59 (s, C$_{ipso}$). ^{31}P{^{1}H} NMR (toluene-d_8): 25.5 (s, major isomer), 37.6 (s, minor isomer). Anal. Calcd for $C_{41}H_{48}NPTi$: C, 77.71; H, 7.64; N, 2.21. Found: C, 73.83; H, 8.13; N, 2.29.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTi(NMe$_2$)$_3$, 7. To a solution of Ti(NMe$_2$)$_4$ (0.385 g, 1.72 mmol) in toluene (10 mL) was added **2** (0.538 g, 1.72 mmol) at 25 °C. The mixture was stirred overnight at 70 °C, the volatiles were removed under vacuum, and the residue was dissolved in a minimum amount of toluene and cooled at −35 °C to give 0.82 g (97%) of orange crystals. Compound **7** exists as a 2.2:1 mixture of two isomers at 25 °C. Only the major isomer crystallizes and was characterized by X-ray diffraction. ^{1}H NMR

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(C_6D_6): 1.20 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15.1 Hz, minor isomer), 1.37 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, major isomer), 3.27 (s, 18H, NMe, major isomer), 3.53 (s, 18H, NMe, minor isomer), 7.05 (m, br, 3H, 2-C_6H_4Ph, minor isomer), 7.14 (m, br, 4H, 2-C_6H_4Ph, major isomer), 7.28 (m, 2H, 2-C_6H_4Ph, minor isomer), 7.31 (m, br, 3H, 2-C_6H_4Ph, major isomer), 7.50 (m, br, 1H, 2-C_6H_4Ph, minor isomer), 7.57 (m, 2H, 2-C_6H_4Ph, major isomer), 7.64 (m, 2H, 2-C_6H_4Ph, minor isomer), 9.72 (m, 1H, 2-C_6H_4Ph, minor isomer). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): 28.23 (s, *t*-Bu, minor isomer), 28.77 (s, *t*-Bu, major isomer), 36.96 (d, *t*-Bu, $^1J_{CP}$ = 55.4 Hz, minor isomer), 38.46 (d, *t*-Bu, $^1J_{CP}$ = 52.7 Hz, major isomer), 46.08 (s, MeNTi, minor isomer), 46.37 (s, MeNTi, major isomer), 124.68 (d, $^2J_{CP}$ = 11 Hz), 126.62 (s), 126.99 (s), 127.38 (s), 128.29 (s), 128.50 (s), 129.28 (s, C_{ipso}), 129.52 (s), 129.88 (s), 130.36 (s), 131.13 (s), 132.53 (d, $^2J_{CP}$ = 11 Hz), 132.90 (d, $^2J_{CP}$ = 9 Hz), 135.20 (d, $^2J_{CP}$ = 9 Hz), 139.21 (d, $^2J_{CP}$ = 7 Hz), 142.55 (s, C_{ipso}), 144.07 (d, C_{ipso}, $^3J_{CP}$ = 6 Hz), 145.47 (s, C_{ipso}), 150.17 (d, C_{ipso}, $^3J_{CP}$ = 5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): 20.6 (s, major isomer), 33.1 (s, minor isomer). Anal. Calcd for $C_{26}H_{45}N_4PTi$: C, 63.41; H, 9.21; N, 11.38. Found: C, 63.19; H, 9.60; N, 11.01.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTi(NMe$_2$)$_2$Cl, 8. To a solution of **7** (0.486 g, 0.98 mmol) in toluene (15 mL) was added Me_3SiCl (0.107 g, 0.98 mmol) in 5 mL of toluene at 25 °C. The mixture was stirred overnight, and the volatiles were removed under vacuum to give the title compound in quantitative yield as a 3.6:1 mixture of two isomers. ^1H NMR (C_6D_6): 1.18 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, minor isomer), 1.40 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, major isomer), 3.30 (s, 12H, NMe, major isomer), 3.50 (s, 12H, NMe, minor isomer), 7.00−7.29, 7.44−7.52 (m, 2-C_6H_4Ph, minor isomer and major isomer), 7.14 (dd, br, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 8 Hz, minor isomer). $^{13}C\{^1H\}$ NMR (C_6D_6): 27.79 (s, *t*-Bu, minor isomer), 28.79 (s, *t*-Bu, major isomer), 37.61 (d, *t*-Bu, $^1J_{CP}$ = 55 Hz, minor isomer), 39.30 (d, *t*-Bu, $^1J_{CP}$ = 53 Hz, major isomer), 45.87 (s, MeNTi, minor isomer), 46.33 (s, MeNTi, major isomer), 124.93 (d, $^2J_{CP}$ = 11 Hz), 126.65 (s), 127.28 (s), 129.69 (s), 129.93 (s), 130.86 (s, C_{ipso}), 132.19 (d, $^2J_{CP}$ = 12 Hz), 134.90 (d, $^3J_{CP}$ = 9 Hz), 142.19 (s, C_{ipso}), 149.92 (s, C_{ipso}). $^{31}P\{^1H\}$ NMR (C_6D_6): 21.9 (s, major isomer), 35.7 (s, minor isomer). Anal. Calcd for $C_{24}H_{39}N_3PClTi$: C, 59.57; H, 8.12; N, 8.68. Found: C, 59.39; H, 8.62; N, 8.60.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTi(CH$_2$Ph)(NMe$_2$)$_2$, 9. To a suspension of **7** (0.200 g, 0.41 mmol) in Et_2O (10 mL) was added $PhCH_2MgCl$ (0.4 mL, 1.0 M, 0.41 mmol) at room temperature. The mixture was stirred overnight, the solvent removed under vacuum, and the residue dissolved in toluene and filtered through Celite. The clear yellow solution was cooled at −35 °C to give 212 mg (95%) of the title compound as a 4:1 mixture of two isomers. ^1H NMR (C_6D_5Br): 1.01 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, minor isomer), 1.27 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, major isomer), 2.15 (s, 2H, CH_2Ph, major isomer), 2.51 (s, 2H, CH_2Ph, minor isomer), 2.92 (s, 12H, NMe, major isomer), 3.13 (s, 12H, NMe, minor isomer), 6.74−7.56 (m, 2-C_6H_4Ph, minor isomer and major isomer), 7.14 (dd, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, minor isomer). $^{13}C\{^1H\}$ NMR (C_6D_5Br): 26.75 (s, *t*-Bu, minor isomer), 27.78 (s, *t*-Bu, major isomer), 36.24 (d, *t*-Bu, $^1J_{CP}$ = 54 Hz, minor isomer), 38.07 (d, *t*-Bu, $^1J_{CP}$ = 54 Hz, major isomer), 44.06 (s, NMe, minor isomer), 44.44 (s, NMe, major isomer), 56.81 (s, CH_2-Ph, minor isomer), 58.99 (s, CH_2Ph, major isomer), 118.27 (s), 123.87 (d, $^2J_{CP}$ = 10 Hz), 124.33 (s), 124.58 (s), 124.78 (s), 125.11 (s), 125.64 (s), 126.43 (s), 126.71 (s), 127.21 (s), 128.01 (s), 128.12 (s), 128.51 (s), 130.91 (d, $^2J_{CP}$ = 11 Hz), 133.50 (d, $^3J_{CP}$ = 9 Hz), 136.42 (s), 141.10 (s), 148.39 (s), 150.58 (s). $^{31}P\{^1H\}$ NMR (C_6D_5-Br): 17.5 (s, major isomer), 33.1 (s, minor isomer). Anal. Calcd for $C_{31}H_{46}N_3PTi$: C, 69.01; H, 8.59; N, 7.79. Found: C, 70.67; H, 8.86; N, 6.99.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNZr(NEt$_2$)$_3$, 10. To a solution of $Zr(NEt_2)_4$ (1.01 g, 2.66 mmol) in toluene (20 mL) was added **2** (0.834 g, 2.66 mmol) at 25 °C. The mixture was stirred overnight, and the volatiles were removed under vacuum to give the title compound as a white solid in quantitative yield. The compound exists at room temperature as a 1.4:1 mixture of two isomers. The major isomer crystallizes from benzene and was characterized by X-ray diffraction. ^1H NMR (C_6D_6): 1.08 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, minor isomer), 1.18 (t, 18H, NCH_2Me, $^3J_{HH}$ = 7 Hz, major isomer), 1.25 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, major isomer), 1.31 (t, 18H, NCH_2Me, $^3J_{HH}$ = 7 Hz, minor isomer), 3.43 (q, 12H, NCH_2-Me, $^3J_{HH}$ = 7 Hz, major isomer), 3.62 (q, NCH_2Me, $^3J_{HH}$ = 7 Hz, minor isomer), 6.94−7.58 (m, 2-C_6H_4Ph, minor isomer and major isomer), 9.50 (dd, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, minor isomer). $^{13}C\{^1H\}$ NMR (C_6D_6): 15.61 (s, NCH_2Me, major isomer), 16.50 (s, NCH_2Me, minor isomer), 28.30 (s, *t*-Bu, minor isomer), 28.99 (s, *t*-Bu, major isomer), 36.85 (d, *t*-Bu, $^1J_{CP}$ = 57 Hz, minor isomer), 38.42 (d, *t*-Bu, $^1J_{CP}$ = 54 Hz, major isomer), 43.56 (s, NCH_2Me, major isomer), 44.36 (s, NCH_2Me, minor isomer), 124.66 (d, $^2J_{CP}$ = 11 Hz), 126.73 (d, $^2J_{CP}$ = 10 Hz), 126.92 (s), 127.26 (s), 127.36 (s), 129.37 (s), 129.94 (s), 130.61 (s), 131.17 (s), 132.60 (d, $^2J_{CP}$ = 11 Hz), 132.83 (d, $^2J_{CP}$ = 8 Hz), 133.16 (s, C_{ipso}), 133.62 (s, C_{ipso}), 135.08 (d, $^3J_{CP}$ = 8 Hz), 139.04 (d, $^3J_{CP}$ = 8 Hz), 142.79 (s, C_{ipso}), 143.97 (s, C_{ipso}), 145.67 (s, C_{ipso}), 149.97 (s, C_{ipso}). $^{31}P\{^1H\}$ NMR (C_6D_6): 21.4 (s, major isomer), 35.1 (s, minor isomer). Anal. Calcd for $C_{32}H_{57}N_4PZr$: C, 61.99; H, 9.27; N, 9.04. Found: C, 62.87; H, 9.18; N, 9.00.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNZrCl$_3$, 11. To a solution of **10** (562 mg, 0.90 mmol) in toluene (20 mL) was added Me_3SiCl (590 mg, 5.4 mmol) at 25 °C. The mixture was stirred for 3 days at 80 °C, the volatiles were removed under vacuum, and the residue was washed with $CHCl_3$. The compound is isolated as a white solid in 87% (402 mg) yield. ^1H NMR (THF-d_8): 1.22 (d, 18H, *t*-BuP, $^3J_{HP}$ = 16 Hz), 7.08−7.10, 7.35, 7.46−7.50, 7.52−7.54 (m, 2-C_6H_4-Ph), 9.37 (dd, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8): 25.60 (s, *t*-Bu), 37.09 (d, *t*-Bu, $^1J_{CP}$ = 53 Hz), 124.37 (d, $^2J_{CP}$ = 10 Hz), 125.53 (s), 125.94 (s), 126.82 (s, C_{ipso}), 127.97 (s), 128.72 (s), 130.76 (d, $^2J_{CP}$ = 10 Hz), 137.79 (d, $^3J_{CP}$ = 8 Hz), 142.33 (d, $^1J_{CP}$ = 8 Hz, C_{ipso}), 142.63 (s, C_{ipso}). $^{31}P\{^1H\}$ NMR (THF-d_8): 33.6 (s). Anal. Calcd for $C_{20}H_{27}NCl_3PZr$: C, 47.10; H, 5.34; N, 2.75. Found: C, 47.48; H, 5.86; N, 2.85.

Synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNZrMe$_3$, 12. To a suspension of **11** (1.6 g, 3.14 mmol) in Et_2O (20 mL) was added MeMgBr (3.36 mL, 3.0 M, 10.08 mmol) at 25 °C. The mixture was stirred for 4 h at 25 °C, the solvent removed under vacuum, and the residue dissolved in toluene and filtered through Celite. The clear solution was cooled at −35 °C to give 1.1 g (78%) of colorless crystals. ^1H NMR (C_6D_6): 0.49 (s, 9H, MeTi), 1.30 (d, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz), 7.05−7.43 (m, 2-C_6H_4Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): 28.40 (s, *t*-Bu), 38.61 (d, *t*-Bu, $^1J_{CP}$ = 55 Hz), 41.60 (s, MeTi), 125.20 (d, $^3J_{CP}$ = 11 Hz), 127.04 (s, C_{ipso}), 127.30 (s), 127.33 (s), 129.21 (s), 129.83 (d, $^3J_{CP}$ = 3 Hz, C_{ipso}), 132.06 (d, $^2J_{CP}$ = 11 Hz), 134.69 (d, $^3J_{CP}$ = 9 Hz), 143.06 (s, C_{ipso}), 149.97 (s, C_{ipso}). $^{31}P\{^1H\}$ NMR (C_6D_6): 20.5 (s). Anal. Calcd for $C_{23}H_{36}NPZr$: C, 61.56; H, 8.09; N, 3.12. Found: C, 60.65; H, 8.72; N, 3.02.

Synthesis of [*t*-Bu$_2$(2-C$_6$H$_4$Ph)PN]$_2$TiCl$_2$, 13. (a) To a solution of $TiCl_3$ (320 mg, 2.07 mmol) in 15 mL of THF was added **3** (660 mg, 2.07 mmol) in 10 mL of THF at −78 °C and the solution allowed to warm to 25 °C. Afterward the volatiles were removed, and the residue was dissolved in Et_2O and passed through a plug of Celite. Removal of Et_2O gave 353 mg (46%) of the title compound as a 2.2:1 mixture of two isomers. Crystals were grown by slow diffusion of hexanes into a solution of the title compound in Et_2O/C_6H_6. (b) To Mg powder (35 mg, 1.45 mmol) in 5 mL of Et_2O was added at room temperature 135 mg (0.29 mmol) of **4** in 10 mL of Et_2O. Afterward 1 mL of THF was added and the mixture stirred for 24 h at room temperature. The volatiles were removed under vacuum, and the residue was extracted in toluene and filtered through Celite. Removal of toluene gave 45 mg (42%) of the title

compound as a 2.2:1 mixture of two isomers. ^{1}H NMR ($CDCl_3$): 1.16 (d, br, 18H *t*-BuP, $^3J_{HP}$ = 18 Hz, minor isomer), 1.19 (d, 36H, *t*-BuP, $^3J_{HP}$ = 15 Hz, major isomer), 1.51 (d, br, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, minor isomer), 7.11−7.70 (m, 2-C_6H_4Ph, major isomer and minor isomer), 9.37 (dd, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 8 Hz, major isomer). ^{13}C{^{1}H} NMR ($CDCl_3$): 27.93 (s, Me_3CP, major isomer and minor isomer), 28.90 (s, *t*-Bu, minor isomer), 38.79 (d, *t*-Bu, $^1J_{CP}$ = 52 Hz, major isomer), 38.91 (d, *t*-Bu, $^1J_{CP}$ = 54 Hz, minor isomer), 40.03 (d, *t*-Bu, $^1J_{CP}$ = 52 Hz, minor isomer), 126.84 (d, $^2J_{CP}$ = 11 Hz), 127.47 (s), 127.72 (d, C_{ipso}, $^1J_{CP}$ = 24 Hz), 128.01 (s), 129.92 (s), 130.69 (s), 132.73 (d, $^3J_{CP}$ = 10 Hz), 139.26 (d, $^3J_{CP}$ = 7 Hz), 143.81 (d, C_{ipso}, $^2J_{CP}$ = 10 Hz), 144.23 (s, C_{ipso}). Only the aromatic carbons of the major isomer were detected. ^{31}P{^{1}H} NMR ($CDCl_3$): 23.7 (s, minor isomer), 36. 9 (s, minor isomer), 37.0 (s, major isomer). Anal. Calcd for $C_{40}H_{54}Cl_2N_2P_2Ti$: C, 64.61; H, 7.32; N, 3.77. Found: C, 64.64; H, 7.30; N, 3.46.

Synthesis of [*t*-Bu$_2$(2-C$_6$H$_4$Ph)PN]$_2$TiMe$_2$, 14. (a) To a solution of **5** (189 mg, 0.46 mmol) in 10 mL of toluene was added **2** (146 mg, 0.46 mmol) in 10 mL of toluene at 25 °C, and the mixture was heated to 80 °C for 4 h. Thereafter the volatiles were removed to give the title compound as a 2.4:1 mixture of two isomers in quantitative yield (by NMR). (b) To a solution of **13** (360 mg, 0.48 mmol) in Et_2O (10 mL) was added MeMgBr (0.33 mL, 3.0 M, 0.96 mmol) at 25 °C. The mixture was stirred overnight, the solvent removed under vacuum, and the residue dissolved in toluene and filtered through Celite. The clear yellow solution was cooled at −35 °C to give 292 mg (86%) of the title compound as a white solid. ^{1}H NMR (C_6D_5Br): 0.27 (s, 6H, Ti-Me, major isomer), 0.67 (s, 6H, Ti-Me, minor isomer), 1.02 (d, 36H, *t*-BuP, $^3J_{HP}$ = 15 Hz, major isomer), 1.05 (d, br, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, minor isomer), 1.27 (d, br, 18H, *t*-BuP, $^3J_{HP}$ = 14 Hz, major isomer), 6.80−7.55 (m, 2-C_6H_4Ph, minor isomer and major isomer), 9.39−9.55 (m, 2-C_6H_4Ph, minor isomer and major isomer). ^{13}C{^{1}H} NMR (C_6D_5Br): 28.11 (s, *t*-Bu, major isomer and minor isomer), 28.95 (s, *t*-Bu, minor isomer), 37.87 (d, *t*-Bu, $^1J_{CP}$ = 55 Hz, minor isomer), 38.06 (d, *t*-Bu, $^1J_{CP}$ = 56 Hz, minor isomer), 38.19 (s, Ti-Me), 39.26 (d, Me_3CP, $^1J_{CP}$ = 54 Hz, major isomer), 41.87 (s, TiMe), 124.66 (d, $^2J_{CP}$ = 10 Hz), 126.08 (d, $^2J_{CP}$ = 9 Hz), 126.56 (m), 127.66 (s), 127.70 (s), 129.25 (s, br), 129.62 (s), 129.79 (s), 130.84 (s), 131.37 (s), 132.33 (d, $^3J_{CP}$ = 8 Hz), 132.44 (d, $^2J_{CP}$ = 11 Hz), 134.73 (d, $^3J_{CP}$ = 9 Hz), 139.44 (d, $^3J_{CP}$ = 8 Hz), 139.72 (s), 139.83 (s), 142.83 (s, C_{ipso}), 143.58 (d, C_{ipso}, $^2J_{CP}$ = 8.8 Hz), 145.07 (d, C_{ipso}, $^2J_{CP}$ = 6.0 Hz), 149.94 (s, C_{ipso}). ^{31}P{^{1}H} NMR (C_6D_5Br): 13.8 (s, major isomer), 26.5 (s, major isomer), 27.1 (s, minor isomer). Anal. Calcd for $C_{42}H_{60}N_2P_2Ti$: C, 71.78; H, 8.61; N, 3.99. Found: C, 70.97; H, 9.09; N, 3.93.

Synthesis of [*t*-Bu$_2$(2-C$_6$H$_4$Ph)PN]$_2$ZrMe$_2$, 15. To a solution of **12** (120 mg, 0.26 mmol) in 2 mL of toluene was added **2** (84 mg, 0.26 mmol) in 2 mL of toluene at 25 °C, and the mixture was stirred for 1 h. Thereafter the volatiles were removed under vacuum to give the title compound as a 24:1 mixture of two isomers in quantitative yield (by NMR). ^{1}H NMR (C_6D_6): 0.38 (s, 6H, Zr-Me, major isomer), 0.76 (s, 6H, ZrMe, minor isomer), 1.27 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, major isomer), 1.48 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz, major isomer), 7.07−7.73 (m, 2-C_6H_4Ph, minor isomer and major isomer), 9.07 (m, 1H, 2-C_6H_4Ph, major isomer), 9.86 (m, 2H, 2-C_6H_4Ph, minor isomer). ^{13}C{^{1}H} NMR (C_6D_6): 28.07 (s, *t*-Bu, major isomer), 28.78 (s, *t*-Bu, major isomer), 31.56 (s, ZrMe), 37.39 (d, *t*-Bu, $^1J_{CP}$ = 56 Hz, major isomer), 38.54 (d, *t*-Bu, $^1J_{CP}$ = 55 Hz, major isomer), 124.53 (d, $^2J_{CP}$ = 10 Hz), 126.16 (d, $^2J_{CP}$ = 10 Hz), 127.00 (s), 127.22 (s), 127.44 (s), 128.08 (s), 129.13 (s), 129.49 (s), 129.94 (s), 130.94 (s), 132.28 (d, $^2J_{CP}$ = 11.0 Hz), 132.41 (d, $^3J_{CP}$ = 8 Hz), 134.54 (d, $^3J_{CP}$ = 7 Hz), 139.46 (d, $^3J_{CP}$ = 7 Hz), 143.09 (s), 143.81 (d, $^2J_{CP}$ = 6 Hz), 145.53 (s), 150.24 (s). Signals for the minor isomer were not detected. ^{31}P{^{1}H} NMR (C_6D_6): 20.3 (s, major isomer), 34.7 (s, major isomer), 35.2 (s, minor isomer). Anal. Calcd for $C_{42}H_{60}N_2P_2Zr$: C, 67.61; H, 8.11; N, 3.75. Found: C, 67.26; H, 9.01; N, 3.51.

Synthesis of [*t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTiMe$_2$][MeB(C$_6$F$_5$)$_3$], 16. A solution of $B(C_6F_5)_3$ (25 mg, 0.049 mmol) in C_6D_5Br (0.3 mL) was added via syringe to a frozen (liquid N_2) solution of **5** (20 mg, 0.049 mmol) in C_6D_5Br (0.3 mL). The mixture was warmed to 25 °C with vigorous shaking. ^{1}H NMR (C_6D_5Br): 0.80 (s, 6H, MeTi), 1.22 (d, 18H, *t*-BuP, $^3J_{HP}$ = 16 Hz), 1.25 (s, br, 3H, Me-B), 6.64 (m, 2H, 2-C_6H_4Ph), 7.09−7.13 (m, 2H, 2-C_6H_4Ph), 7.49−7.60 (m, 3H, 2-C_6H_4Ph), 7.70−7.82 (m, 2H, 2-C_6H_4Ph). ^{13}C{^{1}H} NMR (C_6D_5Br): 11.21 (s, br, Me-B), 27.16 (s, *t*-Bu), 38.49 (d, *t*-Bu, $^1J_{CP}$ = 52 Hz), 54.46 (s, MeTi). ^{31}P{^{1}H} NMR (C_6D_5Br): 34.1 (s). ^{11}B-{^{1}H} NMR (C_6D_5Br): −15.0 (s). ^{19}F NMR (C_6D_5Br): −166.8 (m, *m*-C_6F_5), −164.2 (t, *p*-C_6F_5), −132.2 (d, *o*-C_6F_5). Anal. Calcd for $C_{41}H_{36}BF_{15}NPTi$: C, 53.68; H, 3.96; N, 1.53. Found: C, 51.48; H, 4.11; N, 1.19.

Synthesis of [*t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTi(NMe$_2$)$_2$][PhCH$_2$B(C$_6$F$_5$)$_3$], 17. A solution of $B(C_6F_5)_3$ (98 mg, 0.19 mmol) in C_6D_5Br (0.4 mL) was added via syringe to a frozen (liquid N_2) solution of **9** (103 mg, 0.19 mmol) in C_6D_5Br (0.3 mL). The mixture was warmed to 25 °C with vigorous shaking. ^{1}H NMR (C_6D_5Br): 1.01 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz), 2.91 (s, 12H, NMe), 3.28 (s, br, 2H, $PhCH_2$−B), 6.66−7.37 (m, 14H, 2-C_6H_4Ph, $C_6H_5CH_2$). ^{13}C{^{1}H} NMR (C_6D_5Br): 27.62 (s, *t*-Bu), 32.26 (s, br, CH_2−B), 37.91 (d, *t*-Bu, $^1J_{CP}$ = 50.5 Hz), 48.75 (s, MeNTi). ^{31}P{^{1}H} NMR (C_6D_5Br): 28.9 (s). ^{11}B{^{1}H} NMR (C_6D_5Br): −15.0 (s). ^{19}F NMR (C_6D_5Br): −163.8 (dd, *m*-C_6F_5, $^3J_{FF}$ = 23 Hz), −161.06 (t, *p*-C_6F_5, $^3J_{FF}$ = 23 Hz), −127.55 (d, *o*-C_6F_5, $^3J_{FF}$ = 23 Hz). Anal. Calcd for $C_{49}H_{46}BF_{15}N_3PTi$: C, 55.97; H, 4.41; N, 4.00. Found: C, 54.67; H, 4.75; N, 3.46.

Generation of [*t*-Bu$_2$(2-C$_6$H$_4$Ph)PNTiMe$_2$(THF)][MeB(C$_6$F$_5$)$_3$], 18. This species was generated by the addition of THF (0.1 mL) to a C_6D_5Br solution of **16**. ^{1}H NMR (C_6D_5Br): 0.99 (s, 6H, MeTi), 1.26 (s, br, 3H, MeB), 1.34 (d, 18H, *t*-BuP, $^3J_{HP}$ = 15 Hz), 6.71−7.27 (m, 9H, 2-C_6H_4Ph). ^{31}P{^{1}H} NMR (C_6D_5Br): 36.4 (s). ^{11}B-{^{1}H} NMR (C_6D_5Br): −15.00 (s).

Synthesis of [(*t*-Bu$_2$(2-C$_6$H$_4$Ph)PN)$_2$TiMe][MeB(C$_6$F$_5$)$_3$], 19. A solution of $B(C_6F_5)_3$ (17.5 mg, 0.034 mmol) in C_6D_5Br (0.3 mL) was added via syringe to a frozen (liquid N_2) solution of **14** (24 mg, 0.034 mmol) in C_6D_5Br (0.3 mL). The mixture was warmed to 25 °C with vigorous shaking. The NMR spectra show the formation of two isomers in 2:1 ratio at 25 °C and 1:1 ratio at −20 °C. ^{1}H NMR (C_6D_5Br): 0.29 (s, 3H, TiMe, minor isomer), 0.45 (s, 3H, TiMe, major isomer), 0.91 (d, 9H, *t*-BuP, $^3J_{HP}$ = 15 Hz), 0.95 (d, 9H, *t*-BuP, $^3J_{HP}$ = 16 Hz), 1.00 (d, 9H, *t*-BuP, $^3J_{HP}$ = 15 Hz), 1.10 (d, 9H, *t*-BuP, $^3J_{HP}$ = 14 Hz), 1.11 (s, br, 6H, Me-B), 6.81−7.58 (m, 35H, 2-C_6H_4Ph major isomer and minor isomer), 8.95 (dd, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, major isomer). ^{31}P{^{1}H} NMR (C_6D_5Br): 27.6 (s, major isomer), 29.0 (s, br, minor isomer), 39.7 (s, major isomer). ^{11}B{^{1}H} NMR (C_6D_5Br): −14.0 (s). ^{19}F NMR (C_6D_5Br): −167.63 (m, *m*-C_6F_5), −165.21 (t, *p*-C_6F_5, $^3J_{FF}$ = 23 Hz), −132.84 (d, *o*-C_6F_5, $^3J_{FF}$ = 23 Hz). ^{1}H NMR (C_6D_5Br, −20 °C): 0.31 (s, 3H, TiMe), 0.43 (s, 3H, TiMe), 0.86−1.29 (m, *t*-BuP, Me-B), 6.10 (s, br, 1H, 2-C_6H_4Ph), 6.66 (d, 2H, 2-C_6H_4-Ph, $^3J_{HH}$ = 7.3 Hz), 6.88−7.47 (m, 32H, 2-C_6H_4Ph), 9.00 (dd, 1H, 2-C_6H_4Ph, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 9 Hz). ^{31}P{^{1}H} NMR (C_6D_5Br, −20 °C): 27.0 (s), 27.6 (s, br), 28.6 (s, br), 38.5 (s). ^{11}B{^{1}H} NMR (C_6D_5Br): −14.1 (s). ^{19}F NMR (C_6D_5Br, −20 °C): −166.38 (m, *m*-C_6F_5), −163.86 (t, *p*-C_6F_5, $^3J_{FF}$ = 23 Hz), −132.27 (d, *o*-C_6F_5, $^3J_{FF}$ = 23 Hz). Anal. Calcd for $C_{60}H_{60}BF_{15}N_2P_2Ti$: C, 59.33; H, 4.98; N, 2.31. Found: C, 56.65; H, 4.82; N, 2.17.

X-ray Data Collection. 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

Table 1. Crystallographic Data

	2	3	4	7	10	12	13
formula	$C_{20}H_{28}NP$	$C_{20}H_{27}Cl_3NPTi$	$C_{23}H_{36}NPTi$	$C_{26}H_{45}N_4PTi$	$C_{32}H_{54}N_4PZr$	$C_{23}H_{36}NPZr$	$C_{46}H_{60}Cl_2N_2P_2Ti$
fw	313.40	466.65	405.40	492.53	616.98	448.72	821.70
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	7.5461(8)	9.8980(16)	10.1625(18)	36.987(7)	11.705(11)	15.766(4)	10.176(2)
b (Å)	18.4617(19)	18.636(3)	23.486(4)	8.9097(17)	16.532(15)	10.345(3)	32.413(8)
c (Å)	13.6904(14)	12.627(2)	11.204(2)	20.268(4)	18.632(17)	15.789(4)	14.192(3)
α (deg)					89.866(10)		
β (deg)	100.0490(10)	92.086(2)	115.851(2)	120.594(2)	89.743(9)	105.277(2)	102.166(3)
γ (deg)					84.667(10)		
V (Å^3)	1878.0(3)	2327.5(6)	2406.5(7)	5749.4(19)	3590(6)	2484.1(10)	4575.7(19)
Z	4	4	4	8	4	4	4
d(calc) (g cm^{-1})	1.108	1.332	1.119	1.138	1.142	1.200	1.193
abs coeff, μ (cm^{-1})	0.144	0.785	0.428	0.372	0.374	0.513	0.406
no. of data collected	17 699	22 021	22 876	26 865	34 371	13 665	43 725
no. of data $F_o^2 > 3\sigma(F_o^2)$	3287	4090	4221	5068	12 543	2825	8061
no. of variables	203	235	235	289	685	235	478
R	0.0446	0.0371	0.0471	0.0589	0.0477	0.0379	0.0518
R_w	0.1191	0.1002	0.1467	0.1573	0.1285	0.0863	0.1195
GOF	1.014	1.034	0.743	1.007	1.014	0.728	0.995

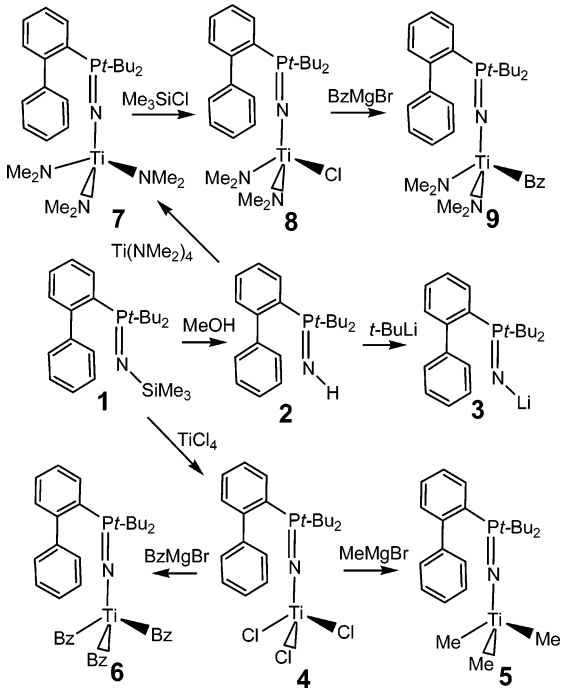
the space groups in each case. The data sets were collected (4.5° < 2θ < 45−50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. 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.[8] 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 Table 1 and are deposited as supplementary data.

Results and Discussion

Mono-phosphinimide Complexes. We have previously reported the synthesis of *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNSiMe$_3$ (**1**).[7] Following typical phosphinimine chemistry, compound **1** is readily converted to the white solid *t*-Bu$_2$(2-C$_6$H$_4$Ph)PNH (**2**) in quantitative yield via treatment with methanol in toluene followed by subsequent isolation (Scheme 3). The ^{31}P{^{1}H} NMR for **2** shows a significant downfield chemical shift at 42.3 ppm in comparison to **1**, which is observed at 22.3 ppm. A resonance

Scheme 3. Synthesis of Compounds 2−9



at −0.88 ppm in the ^{1}H NMR spectrum is attributable to the single NH proton. Moreover the ^{1}H NMR data were consistent with only a single conformation in solution. An X-ray crystallographic study of **2** confirmed the formulation and revealed a geometry in which the biphenyl unit is oriented toward the PNH fragment (Figure 1). A similar orientation was previously observed for **1**, and this was presumed to be a result of the minimization of steric conflicts between the biphenyl and *tert*-butyl groups. The P−N bond distance in **2** was found to be 1.5557(18) Å, typical of phosphinimines.[5,7] Compound **2** serves as the precursor to the phosphinimide salt *t*-Bu$_2$(2-C$_6$H$_4$Ph)-PNLi (**3**), as treatment with *t*-BuLi readily effects deprotonation. The air- and moisture-sensitive species **3** was isolated as a white solid in 92% yield (Scheme 3). The relatively poor solubility of **3** dictated that the NMR spectra were recorded in THF-d_8, at 55 °C. The ^{31}P{^{1}H} and ^{7}Li NMR spectra showed resonances at 11.4 and −1.4 ppm, respectively, reflecting the anionic nature of the phosphinimide unit.

(8) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; 1974; Vol. 4, pp 71−147.

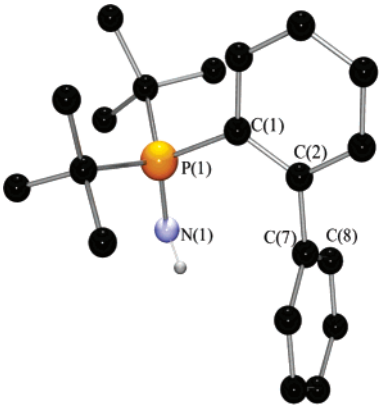


Figure 1. POV-ray representation of **2**. C: black, N: blue, P: orange, H: gray. Hydrogen atoms, except for the NH atom, are omitted for clarity. P(1)−N(1) = 1.5557(18) Å.

The phosphinimine **1** reacts with $TiCl_4$ in refluxing toluene. Subsequent workup affords the product **4** in 74% yield. Ti coordination by phosphinimide is inferred by the downfield shift of the $^{31}P\{^1H\}$ NMR resonance to 42.7 ppm, suggesting the formulation of **4** as *t*-Bu_2(2-C_6H_4Ph)PN$TiCl_3$ (Scheme 3). Recrystallization from CH_2Cl_2/pentane gave yellow crystals, which were confirmed by X-ray crystallographic study to be **4** (Figure 2a). This molecule is pseudo-tetrahedral at Ti with a Ti−N distance of 1.7311(19) Å, which is significantly shorter than the Ti−N distances reported for Cp′(*t*-Bu_2(2-C_6H_4Ph)PN)-$TiCl_2$ (Cp′ = Cp, Cp*) of 1.759(3) and 1.791(3) Å, respectively.[7] In contrast, the P−N distance in **4** of 1.6132(19) Å is similar to those seen in the Cp′ derivatives, where the P−N distances are 1.619(3) and 1.609(3) Å, respectively. [7] Similarly, the Ti−Cl distances in **4** ranging from 2.2262(8) to 2.2385(9) Å are significantly shorter than the Ti−Cl distances of 2.3087(17) and 2.3139(16) Å found in Cp(*t*-Bu_2(2-C_6H_4Ph)PN)$TiCl_2$. The P−N−Ti angle in **4** of 167.53(13)° approaches linearity, as is the case with the majority of Ti−phosphinimide complexes. The biphenyl substituent is oriented proximal to the metal center. The closest approach of a biphenyl C atom to Ti is 3.695 Å, while the distance of Ti to the mean plane of C_6H_5 ring is 3.6973 Å. This approach gives rise to a distortion in the biphenyl fragment as the C(1)−C(2)−C(7) angle of 127.5(1)° deviates from that expected for an sp^2 carbon. The angle between the planes of the phenyl rings in the biphenyl substituent is 58.1°. It is noteworthy that this approach of Ti to the pendant arene is significantly longer than that seen in the species [Ti(η^6-biphenyl)$_2$]$^-$ (Ti−ring plane: 1.78 Å).[9]

Alkylation of the Ti center proceeds via treatment of **4** with MeMgBr (Scheme 3). The product **5** exhibits a ^1H NMR resonances at 0.72 ppm attributable to the Ti-bound methyl groups, while the $^{31}P\{^1H\}$ NMR resonance was observed at 21.3 ppm, consistent with the formulation of **5** as *t*-Bu_2(2-C_6H_4Ph)-PN$TiMe_3$. A single-crystal X-ray study of **5** (Figure 2b) revealed that the average Ti−C distance is 2.097(5) Å, which is typical of L$TiMe_3$ complexes. The Ti−N distance of 1.791(2) Å is longer and the P−N distance of 1.576(2) Å is shorter than the corresponding distances in **4**. These observations are consistent with the increased electron density at Ti in **5** as a result of the electron-donating methyl substituents. The P−N−Ti angle of 166.33(16)° in **5** is similar to that seen in **4**. In addition the biphenyl substituent in **5** is oriented in a fashion similar to that seen in **4**, with the closest approach of a biphenyl C atom to Ti being 3.976 Å and the distance between Ti and the mean plane of the C_6H_5 ring of 3.757 Å. This slightly longer approach is consistent with the greater angle of 74.3° between the plane of the phenyl rings of the biphenyl substituent.

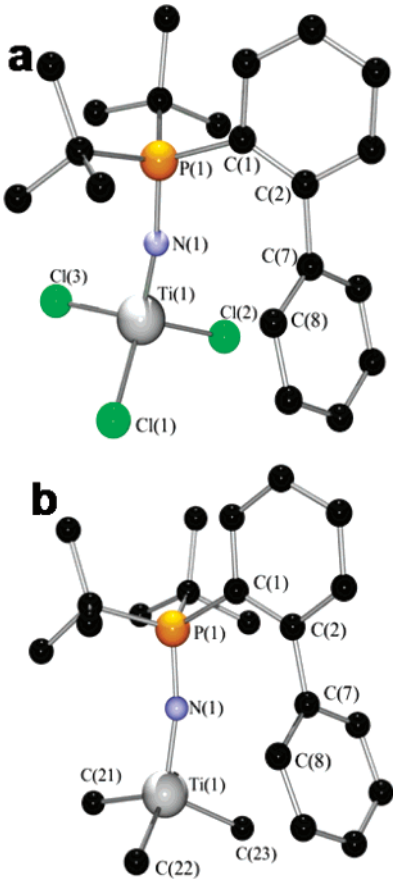
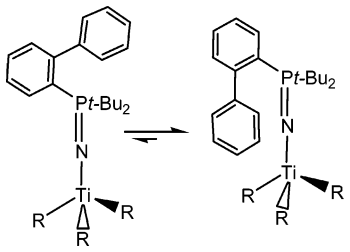


Figure 2. POV-ray representation of (a) **4** and (b) **5**. C: black, N: blue, P: orange, Ti: gray, Cl: green. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): **4**: Ti(1)−N(1) 1.7311(19), Ti(1)−Cl(2) 2.2262(8), Ti(1)−Cl(1) 2.2382(8), Ti(1)−Cl(3) 2.2385(9), P(1)−N(1) 1.6132(19), N(1)−Ti(1)−Cl-(1) 112.55(7), Cl(2)−Ti(1)−Cl(1) 112.72(4), N(1)−Ti(1)−Cl(3) 110.60(7), Cl(2)−Ti(1)−Cl(3) 105.09(4), Cl(1)−Ti(1)−Cl(3) 105.57-(4), P(1)−N(1)−Ti(1) 167.53(13). **5**: Ti(1)−N(1) 1.791(2), Ti(1)−C(23) 2.088(4), Ti(1)−C(21) 2.098(4), Ti(1)−C(22) 2.104(4), P(1)−N(1) 1.576(2), N(1)−Ti(1)−C(23) 111.48(14), N(1)−Ti(1)−C(21) 113.11(16), C(23)−Ti(1)−C(21) 104.7(2), N(1)−Ti(1)−C(22) 112.13(14), C(23)−Ti(1)−C(22) 111.77(16), C(21)−Ti(1)−C(22) 103.1(2), P(1)−N(1)−Ti(1) 166.33(16), C(1)−C(2)−C(7) 127.5(1).

The corresponding alkylation of **4** with 3 equiv of $PhCH_2$-MgBr proceeds in a fashion similar to give a yellow solution of the product *t*-Bu_2(2-C_6H_4Ph)PN$Ti(CH_2Ph)_3$ (**6**), which was subsequently isolated in 76% yield (Scheme 3). In contrast to **4** and **5**, NMR data revealed that two isomers of **6** exist in solution at 25 °C in a 1.4:1 ratio. The major isomer exhibits a $^{31}P\{^1H\}$ NMR resonance at 25.5 ppm, while the minor isomer shows a signal at 37.6 ppm. Similarly, the ^1H NMR spectrum showed resonances at 0.99 and 0.86 ppm attributable to *tert*-butyl groups of the major and minor isomers, respectively. The corresponding resonances arising from the benzylic protons were seen at 2.66 and 2.41 ppm, respectively. A variable-temperature $^{31}P\{^1H\}$ NMR experiment over the temperature range 303−353 K revealed coalescence of the two signals at 343 K. These data were consistent with a rotational barrier to interconversion

(9) Blackburn, D. W.; Britton, D.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1495.

Scheme 4. Interconversion of Rotational Isomers



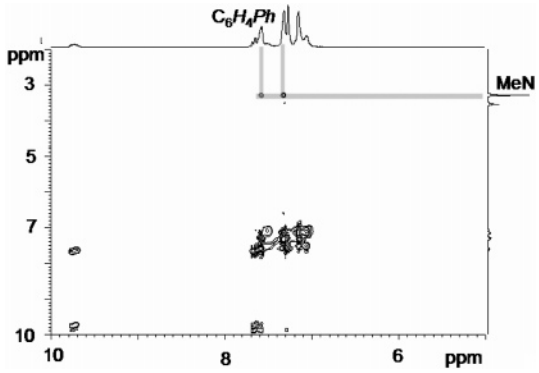


Figure 3. $^1H-^1H$ NOESY spectrum of **7**.

of the two isomers of **6**.[10] The activation barrier was calculated to be 92 kJ/mol (Scheme 4). On the basis of the similarity of the ^{31}P chemical shift to **5**, the more abundant isomer is thought to be the conformer in which the biphenyl group is oriented toward the metal center. A similar observation of two rotational isomers was reported for Cp′(*t*-Bu_2(2-C_6H_4Ph)PN)$TiCl_2$ (Cp′ = Cp, Cp*), although in those cases poor solubility precluded the determination of the barrier.[7] Subsequent data on related compounds in this paper support the present interpretation (vide infra). The upfield ^{31}P chemical shift of the more abundant isomer is attributed to shielding effects resulting from the proximity of the arene ring of the biphenyl fragment.

The direct synthesis of a related tris-amido derivative is achieved via the reaction of $Ti(NMe_2)_4$ with **2** (Scheme 3). The NMR data for the resulting product **7** are consistent with the formation of a 2.2:1 mixture of two isomers of *t*-Bu_2(2-C_6H_4-Ph)PN$Ti(NMe_2)_3$ at 25 °C. This product was isolated as orange crystals in 97% yield. As for **6**, the $^{31}P\{^1H\}$ NMR spectrum of **7** showed two resonances at 20.6 and 33.1 ppm for the major and minor isomers, respectively, and the corresponding ^1H NMR resonances for the *tert*-butyl groups gave rise to signals at 1.37 and 1.20 ppm. Similarly, the NMe groups gave distinct signals for the two isomers at 3.27 ppm (major isomer) and 3.53 ppm (minor isomer). Assignment of the aromatic regions to the two isomers was assisted by a 2D-NOESY spectrum (Figure 3), which revealed correlations of the resonances arising from the NMe groups in the major isomer to aromatic proton signals at 7.14, 7.31, and 7.57 ppm. These data support the proposition that the biphenyl group in the major isomer is oriented toward the amido substituents. This orientation of the biphenyl unit presumably shields the P−N fragment and accounts for the upfield $^{31}P\{^1H\}$ resonance for the major isomer. Nonetheless, it is surprising that the orientation of the biphenyl appears to have a larger impact on the $^{31}P\{^1H\}$ chemical shift than substitution on Ti. Variable-temperature ^1H (Figure 4) and $^{31}P\{^1H\}$ NMR spectra over the temperature range 303−353 K revealed a barrier to interconversion of the two isomers of 94-(1) kJ/mol, as coalescence was observed at 333 K (Scheme 4).[10] The proposed structure of the preferred isomer was subsequently confirmed, as this isomer afforded suitable crystals for X-ray diffraction studies (Figure 5). The overall complex geometry of **7** is similar to that seen in **4** and **5**, with a pseudo-tetrahedral Ti center and the biphenyl substituent oriented toward the metal center. The strong σ- and π-donation from the amido ligands results in $Ti-N_{amide}$ distances that range from 1.907(3) to 1.934-(3) Å and a $Ti-N_{phosphinimide}$ of 1.843(3) Å. This latter bond length is significantly longer than those seen in **4** or **5**. The P−N distance of 1.567(3) Å in **7** is slightly shorter and the P−N−Ti angle of 159.24(19)° is more distorted from linearity than the corresponding values in **5**. This is attributed to the greater steric demands and donor ability of the amide ligands over methyl. The approach of the biphenyl rings to Ti in **7** is slightly longer than in **4** or **5**, as the mean distance between the C_6H_5 plane and Ti is 3.8857 Å. This is consistent with the greater steric conflict between the biphenyl substituents and the amido ligands in **7**. This also accounts for the increase in the angle between the phenyl ring planes of the biphenyl substituent to 76.4°.

The isolation of **7** afforded further derivatization in a clean fashion. Treatment of **7** with Me_3SiCl afforded the quantitative isolation of *t*-Bu_2(2-C_6H_4Ph)PN$Ti(NMe_2)_2Cl$ (**8**) (Scheme 3).

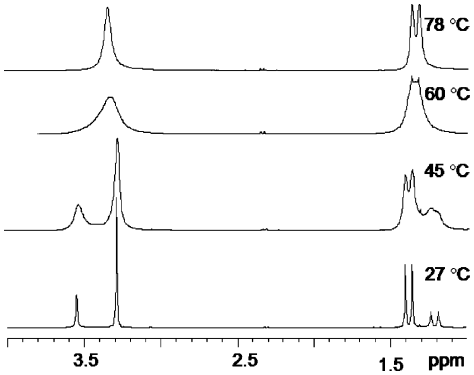


Figure 4. Portion of the variable-temperature ^1H NMR spectra of **7** showing methylene and methyl resonances.

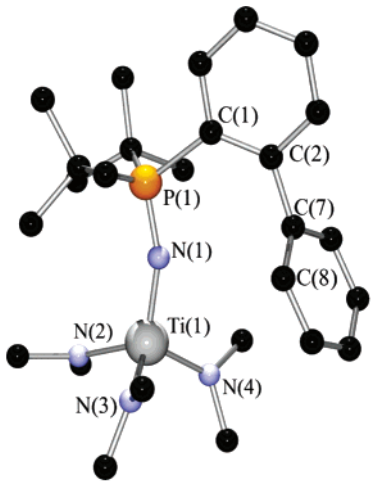


Figure 5. POV-ray representation of **7**. C: black, N: blue, P: orange, Ti: gray. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(1) 1.843(3), Ti(1)−N(4) 1.907(3), Ti(1)−N(3) 1.917(3), Ti(1)−N(2) 1.934(3), P(1)−N(1) 1.567(3), N(1)−Ti(1)−N(4) 114.12(14), N(1)−Ti(1)−N(3) 110.77-(14), N(4)−Ti(1)−N(3) 110.83(15), N(1)−Ti(1)−N(2) 115.48(13), N(4)−Ti(1)−N(2) 102.20(15), N(3)−Ti(1)−N(2) 102.61(16), P(1)−N(1)−Ti(1) 159.24(19).

(10) Reich, H. J. *WinDNMR: Dynamic NMR Spectra for Windows*, 3D2; J. Chem. Educ. Software: 1996.

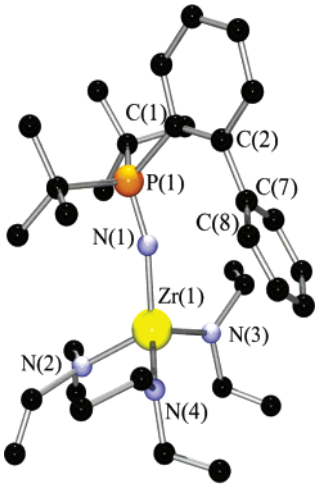


Figure 6. POV-ray representation of one of the two molecules of **10** in the asymmetric unit. C: black, N: blue, P: orange, Zr: yellow. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Zr(1)−N(1) 1.981(3), Zr(1)−N(2) 2.051(4), Zr(1)−N(4) 2.082(4), Zr(1)−N(3) 2.170(4), P(1)−N(1) 1.522(3), N(1)−Zr(1)−N(2) 117.19(14), N(1)−Zr(1)−N(4) 112.74(14), N(2)−Zr(1)−N(4) 93.03(15), N(1)−Zr(1)−N(3) 106.34(14), N(2)−Zr(1)−N(3) 105.54(16), N(4)−Zr(1)−N(3) 121.93(14), P(1)−N(1)−Zr(1) 165.24(18).

Two isomers of this product were also observed, as evidenced by the $^{31}P\{^1H\}$ NMR resonances at 21.9 and 35.7 ppm. The former resonance resulted from the more dominant isomer in the 3.6:1 mixture at 25 °C. On the basis of the chemical similarities, the dominant isomer was again ascribed to the isomer in which the C_6H_5 ring is oriented toward the metal center. The increase in the proportion of this isomer in solution is consistent with the reduced steric crowding at Ti. Compound **8** was readily alkylated with $PhCH_2MgCl$ to give the species *t*-Bu_2(2-C_6H_4Ph)PNTi(CH_2Ph)(NMe_2)$_2$ (**9**) in 95% yield (Scheme 3). This species exists as a mixture of two isomers in a 3:1 mixture in solution at 25 °C, giving rise to $^{31}P\{^1H\}$ NMR resonances at 17.5 and 33.1 ppm, respectively. In a similar sense to **6** and **7**, ^1H NMR resonances attributed to the *tert*-butyl groups, the benzylic protons, and the NMe groups of the major and minor isomers were seen at 1.27 and 1.01 ppm, 2.15 and 2.51 ppm, and 2.92 and 3.13 ppm, respectively.

In an analogous fashion, Zr complexes were synthesized. Reaction of Zr(NEt_2)$_4$ with **2** afforded the quantitative synthesis of *t*-Bu_2(2-C_6H_4Ph)PNZr(NEt_2)$_3$ (**10**). The $^{31}P\{^1H\}$ NMR resonances at 21.4 and 35.1 ppm revealed a 1.4:1 ratio of the two conformational isomers. ^1H and $^{13}C\{^1H\}$ NMR spectra showed similar evidence of isomerism. For example, the methylene groups of the amido ligands showed ^1H NMR resonances at 3.43 and 3.62 ppm and ^{13}C resonances at 43.56 and 44.36 ppm for the major and minor isomers, respectively. The major isomer of **10** crystallized, allowing an X-ray diffraction study (Figure 6). The overall geometry is similar to that seen in **7**. The Zr−N_{amide} bond lengths ranged from 2.051(4) to 2.170(4) Å, while the Zr−$N_{phosphinimide}$ averaged 1.984(4) Å. This latter distance is slightly longer than those seen in the species Cp*Zr(NP*t*-Bu_3)Cl_2 (1.923(2) Å) and Cp_2Zr(NP*t*-Bu_3)Cl (1.978(5) Å).[11] Similarly, the average P−N−Zr angle seen in **10**, 165.25(18)°, falls in the range of 163.49(12)° and 171.9(3)° seen for Cp*Zr(NP*t*-Bu_3)Cl_2 and Cp_2Zr(NP*t*-Bu_3)Cl, respectively.[11] The proximity of the biphenyl substituent to the metal is similar to that seen in **7**, as the distance between Zr and the plane of the C_6H_5 ring is 3.8441 Å and the angle between the phenyl rings of the biphenyl substituent is 71.9°.

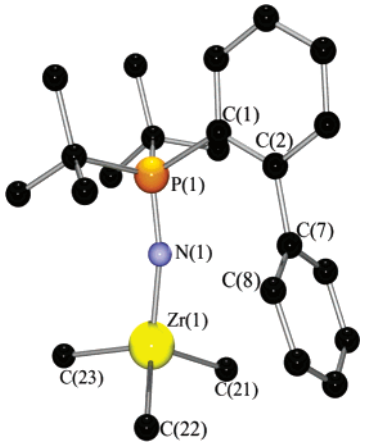


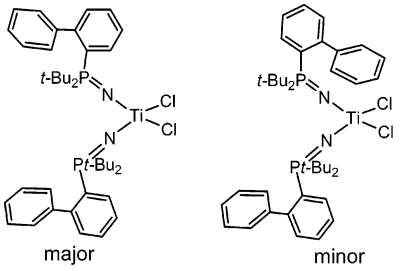
Figure 7. POV-ray representation of **12**. C: black,-N: blue, P: orange, Zr: yellow. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Zr(1)−N(1) 1.922(3), Zr(1)−C(23) 2.233(6), Zr(1)−C(21) 2.239(5), Zr(1)−C(22) 2.247(6), P(1)−N(1) 1.573(3), N(1)−Zr(1)−C(23) 110.34(19), N(1)−Zr(1)−C(21) 111.85(18), C(23)−Zr(1)−C(21) 105.3(3), N(1)−Zr(1)−C(22) 113.20(19), C(23)−Zr(1)−C(22) 105.7(3), C(21)−Zr(1)−C(22) 110.0(2), P(1)−N(1)−Zr(1) 164.2(2).

Treatment of **10** with excess Me_3SiCl provides a convenient route for the synthesis and subsequent isolation of *t*-Bu_2(2-C_6H_4-Ph)PNZrCl_3 (**11**) in 87% yield. Subsequent methylation of **11** afforded *t*-Bu_2(2-C_6H_4Ph)PNZrMe_3 (**12**) in 78% isolated yield. The observation of a single $^{31}P\{^1H\}$ NMR signal at 20.5 ppm suggests a geometry similar to that seen for **5**, where the biphenyl unit is oriented toward the metal center. Indeed this proposition was confirmed via a crystallographic study of **12** (Figure 7). The Zr−N and average Zr−C distances were found to be 1.922(3) and 2.240(7) Å, respectively. The Zr−N distance in **12** is significantly shorter than that seen in **10**. A similar result was described above for the related Ti species **7** and **4** and is attributed to the σ- and π-donor ability of amido ligands. The P−N−Zr angle remains approximately linear at 164.2(2)°. The methyl substitution on Zr in **11** appears to reduce the impact on the biphenyl substituent relative to that seen in the complexes above: the closest approach of Zr to the C_6H_5 ring is 4.033 Å, with the distance of Zr to the mean plane of this ring being 3.9097 Å, and the inter-phenyl ring angle is 88.4°. It is also noteworthy that the C(1)−C(2)−C(7) angle is 114.3°, which is significantly smaller than those reported above. Thus the biphenyl fragment appears unperturbed by the proximity to the $ZrMe_3$ unit. Nonetheless, the observation of a consistent preference for an orientation in which the biphenyl is disposed toward the metal suggests an electrostatic attraction between the electron-rich arene and the Lewis acidic metal centers. However, the role of steric conflict between biphenyl and *tert*-butyl substituents in the minor conformer cannot be dismissed.

Bis-phosphinimide Complexes. Efforts to stabilize a Ti(III) center with such pendant arene ligands prompted examination of the reduction of **3** with Mg powder in Et_2O. This resulted in isolation of the diamagnetic compound **13** in 42% yield. The $^{31}P\{^1H\}$ NMR spectrum of **13** shows three resonances attributable to the presence of two isomers in a 2.2:1 ratio. The minor isomer gives rise to two signals at 23.7 and 36.9 ppm, inferring the presence of two inequivalent P centers, while the major isomer shows one signal at 37.0 ppm. Similarly in the ^1H NMR spectrum, doublets at 1.16 and 1.51 ppm were attributed to the

(11) Hollink, E.; Wei, P.; Stephan, D. W. *Organometallics* **2004**, *23*, 1562−1569.

Scheme 5. Rotational Isomers of 13



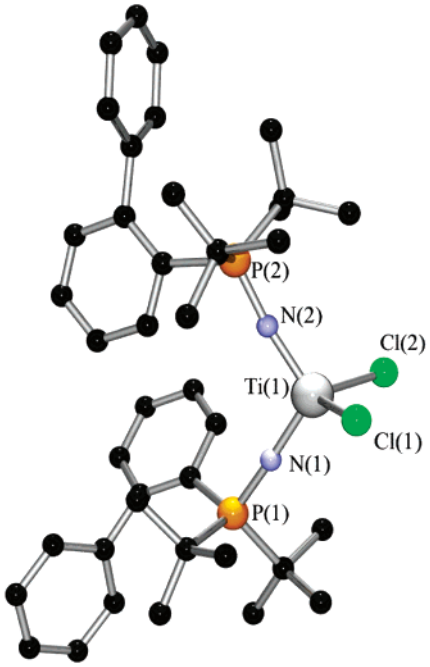
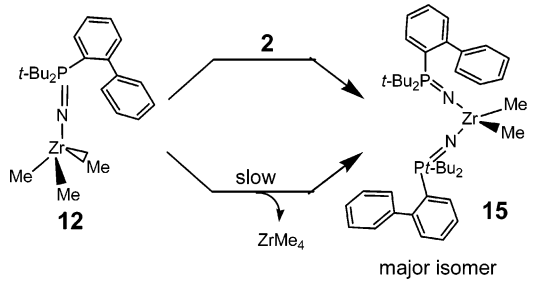


Figure 8. POV-ray representation of **13**. C: black,-N: blue, P: orange, Ti: gray, Cl: green. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ti(1)−N(2) 1.784(3), Ti(1)−N(1) 1.784(3), Ti(1)−Cl(1) 2.2920(12), Ti(1)−Cl(2) 2.2991(13), P(1)−N(1) 1.591(3), P(2)−N(2) 1.583(3), N(2)−Ti(1)−N(1) 112.04(13), N(2)−Ti(1)−Cl(1) 108.46(9), N(1)−Ti(1)−Cl(1) 110.45(10), N(2)−Ti(1)−Cl(2) 107.93(9), N(1)−Ti(1)−Cl(2) 108.47(10), Cl(1)−Ti(1)−Cl(2) 109.43(5), P(1)−N(1)−Ti(1) 176.5(2), P(2)−N(2)−Ti(1) 172.19(18).

tert-butyl resonances of the minor isomer, while the corresponding signal for the major isomer was seen at 1.19 ppm. These data suggest the formulation of **13** as two conformations of $[t\text{-Bu}_2(2\text{-C}_6\text{H}_4\text{Ph})\text{PN}]_2\text{TiCl}_2$. In the minor isomer, the two phosphorus centers are inequivalent: one of the biphenyl substituents oriented toward and the other away from the Ti center. On the other hand, the single downfield ^{31}P NMR resonance seen for the major isomer indicates that the two biphenyl units are equivalent and oriented away from the metal (Scheme 5). The reason for the preponderance of this isomer of **13** is not clear, although clearly steric congestion between the substituents on adjacent ligands is an issue.

The nature of the major isomer of **13** was confirmed unequivocally by X-ray diffraction (Figure 8).This crystallographic study of **13** revealed the pseudo-tetrahedral geometry about the Ti center with Ti−N bond lengths of 1.784(3) Å and Ti−Cl bond lengths of 2.2920(12) and 2.2991(13) Å. These compare with the corresponding distances of 1.791(4) and 2.290(2) Å found in $(t\text{-Bu}_3\text{PN})_2\text{TiCl}_2$.[4] Similarly, the N−Ti−N angle in **13** and $(t\text{-Bu}_3\text{PN})_2\text{TiCl}_2$ is in the same range, being 112.04(13)° and 112.9(2)°, respectively. The P−N distances in **13** were

Scheme 6. Formation of 15



determined to be 1.591(3) and 1.583(3) Å, while the P−N−Ti angles range from 172.19(18)° to 176.5(2)°. The Cl−Ti−Cl angle was found to be 109.43(5)°, slightly larger than that in $(t\text{-Bu}_3\text{PN})_2\text{TiCl}_2$ (106.93(7)°).

The mechanism of formation of **13** is unknown. However, an alternative and more direct synthesis of this mixture of isomers of **13** was found to involve the direct reaction of $TiCl_3$ with the Li salt **3**. In either synthesis it is thought that the Ti(III) species $t\text{-Bu}_2(2\text{-C}_6\text{H}_4\text{Ph})\text{PNTiCl}_2$ is generated. This species undergoes disproportionation to the Ti(IV) product **13** and $TiCl_2$. Although the latter product has not been unambiguously identified, the black, insoluble precipitate that is filtered from the solution may be this material or its degradation products. In related chemistry we have previously reported the analogous reduction of $\text{Cp}'(t\text{-Bu}_2(2\text{-C}_6\text{H}_4\text{Ph})\text{PN})\text{TiCl}_2$ (Cp′ = Cp, Cp*) with Mg.[7] In these cases, the reactions gave Ti(IV) species $\text{Cp}'(t\text{-Bu}_2(2\text{-C}_6\text{H}_4\text{Ph})\text{PN})\text{Ti}$ in which the pendant phenyl ring was reduced by the transient Ti(II) center (Scheme 2).[7]

Compound **13** is alkylated with MeMgBr to give $[t\text{-Bu}_2(2\text{-C}_6\text{H}_4\text{Ph})\text{PN}]_2\text{TiMe}_2$ **14** in 46% yield. In a similar fashion **14** is formed by the reaction of **5** with **2** in quantitative yield by NMR spectroscopy and could be isolated in 86% yield. NMR data showed that like **13**, **14** exists as two isomers in a 2.4:1 ratio. However in contrast to **13**, the major isomer of **14** gave rise to two $^{31}\text{P}\{^1\text{H}\}$ NMR resonances at 13.8 and 26.5 ppm, while the minor isomer gave a signal at 27.1 ppm. These data are consistent with the major isomer of **14** adopting a conformation in which one of the biphenyl substituents is oriented toward the metal while the other is oriented away from the metal center. Variable-temperature NMR experiments[10] revealed coalescence at 348 K and an activation barrier for the interconversion of these rotation isomers of 92 kJ/mol.

The analogous Zr complex $[t\text{-Bu}_2(2\text{-C}_6\text{H}_4\text{Ph})\text{PN}]_2\text{ZrMe}_2$ (**15**)- is accessible by a protolysis of a methyl group on **12** with **2** (Scheme 6). The product **15** exists in solution as two isomers in a 24:1 ratio. The major isomer exhibits two $^{31}\text{P}\{^1\text{H}\}$ NMR resonances at 20.3 and 34.7 ppm, while the minor isomer shows a resonance at 35.2 ppm. Like **14**, these data are consistent with the major isomer of **15**, in which the two biphenyl substituents are oriented toward and away from Zr.

Compound **15** is also formed spontaneously from **12** on standing in toluene solution for several hours. Stoichiometry suggests that the formation of **15** is concurrent with liberation of $ZrMe_4$, although the instability of this byproduct precluded unambiguous confirmation of this proposition (Scheme 6). The kinetics of this transformation was monitored by NMR spectroscopy. The concentration dependence of the rate was consistent with second-order kinetics (Figure 9), suggesting an associative mechanism for ligand exchange affording **15** and $ZrMe_4$. The rate constant was determined to be 4×10^{-4} s^{-1} at 333 K. Eyring plots over a 40 K range (311−351 K) provide the activation parameters: $\Delta G^{\ddagger}(329\text{ K}) = 104(2)$ kJ/mol, $\Delta H^{\ddagger} = 69(2)$ kJ/mol, and $\Delta S^{\ddagger} = -108(6)$ J/(mol K) (Figure 10).

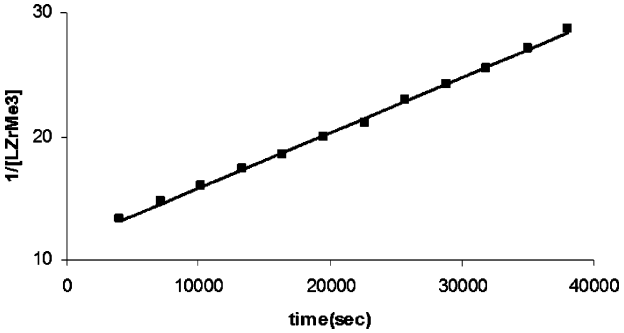


Figure 9. Typical kinetic data for the transformation of **12** to **15** ($[\mathbf{12}]_o = 0.0982$ M), $T = 329$ K.

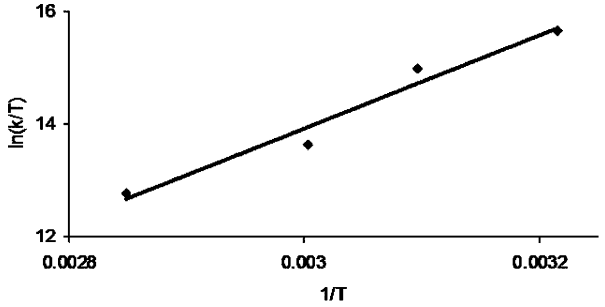
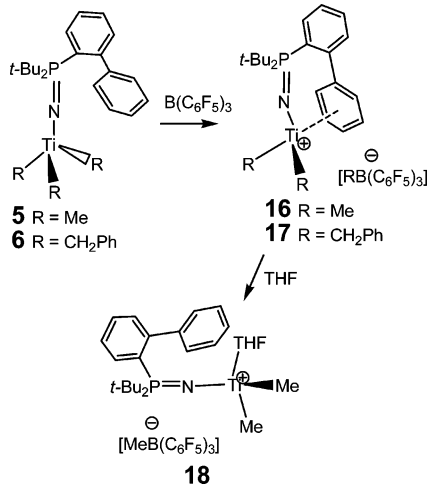


Figure 10. Eyring plot for the transformation of **12** to **15** over the temperature range 311−351 K.

Scheme 7. Formation of Cationic Ti Species 16−18



The negative entropy term is consistent with the proposition of a bimolecular ligand exchange process, while the enthalpic barrier to ligand exchange is accessible albeit endothermic.

Zwitterionic and Cationic Species. Given the propensity of the biphenyl substituent, in the absence of steric restrictions, to be oriented toward the metal center in the above compounds, the potential for a direct interaction with metal was probed. Compound **5** reacts with $B(C_6F_5)_3$ to generate a species formulated as [*t*-Bu_2(2-C_6H_4Ph)PNTiMe_2][Me$B(C_6F_5)_3$] (**16**). A similar situation was observed for the reaction of **9** with $B(C_6F_5)_3$. In this case abstraction of the benzyl group generates [*t*-Bu_2(2-C_6H_4Ph)PNTi$(NMe_2)_2$][Ph$CH_2B(C_6F_5)_3$] (**17**) (Scheme 7). In both cases, the observation of a ^{11}B NMR chemical shift at −15.00 ppm and the ^{19}F NMR data are consistent with uncoordinated borate anions, while the downfield shifts of the ^{31}P{^{1}H} NMR resonances are consistent with the generation of cationic Ti centers. In the case of **16**, the ^{1}H NMR spectrum shows a disperse aryl region with resonances at 6.64, 7.09−7.13, 7.49−7.60, and 7.70−7.82 ppm. These data support the formulation of **16** as a salt in which the Ti cation is arene-stablized (Scheme 7). Solutions of **16** in C_6H_5Br are stable for several days. This stands in marked contrast to stabilities of the products derived from *t*-Bu_3PNTiMe_3/$B(C_6F_5)_3$[12] or Cp-TiMe_3/$B(C_6F_5)_3$,[13] where the absence of a donor ligand results in prompt degradation of the transient products of methyl abstraction. The stability of the present cation **16** may be attributed to the chelate effect. As the molecular structure of the **16** was not determined, the hapticity of the arene−metal interaction is not unambiguously known; however it is noteworthy that an η^6-arene interaction was observed for the Hf cation [Cp*HfMe_2(η^6-toluene)][Me$B(C_6F_5)_3$].[14] While the barrier to arene dissociation could not be determined, the work of Casey *et al.* has shown that the barrier to alkene dissociation from the Zr cation in $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2SiMe_2CH_2CH{=}CH_2][B(C_6F_5)_4]$ is $\Delta G^{\ddagger}(245\text{ K}) = 53.3$ kJ/mol[15] and $\Delta G^{\ddagger} = 44.9$ and 44.6 kJ/mol for the diastereomers of $Cp^*_2Zr[\eta^1,\eta^2\text{-}CH_2CHMeCH_2CH{=}CH_2][B(C_6F_5)_4]$.[16] Thus it is suggested from the stability of **16** that the barrier to arene dissociation is significantly higher than these values.

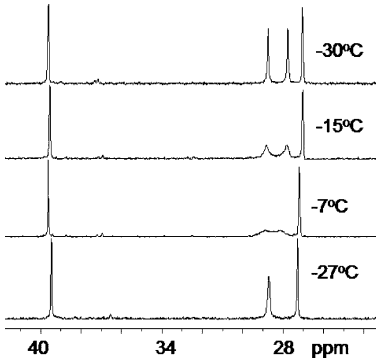
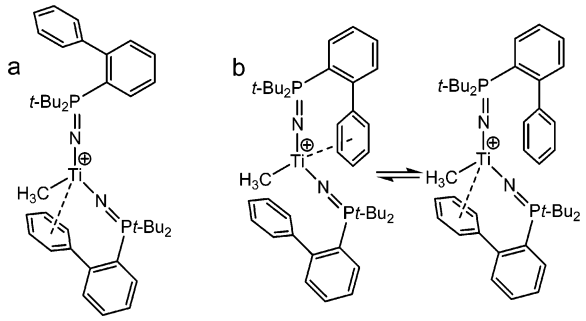


Figure 11. Variable-temperature ^{31}P{^{1}H} NMR spectra of **14**.

Scheme 8. Isomers of 19: (a) Major Isomer at 25 °C, (b) Arene Exchange in Minor Isomer at 25 °C



Addition of THF to solutions of **16** results in a new species, **18**. This species shows no change to the ^{11}B and ^{19}F NMR resonances; however the ^{1}H NMR spectrum exhibits signals consistent with THF coordination and the arene signals are grouped between 6.8 and 7.2 ppm. These data infer the formulation of **18** as [*t*-Bu_2(2-C_6H_4Ph)PNTiMe_2(THF)][MeB-$(C_6F_5)_3$]. A similar change was observed for the arene region

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(13) Gillis, D. J.; Tudoret, M. J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543−2545.
(14) Gillis, D. J.; Quyoum, R.; Tudoret, M.-J.; Wang, Q.; Jeremic, D.; Roszak, A. W.; Baird, M. C. *Organometallics* **1996**, *15*, 3600−3605.
(15) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *Organometallics* **2001**, *20*, 4262−4265.
(16) Casey, C. P.; Carpenetti, D. W., II. *Organometallics* **2000**, *19*, 3970−3977.

of the ^{1}H NMR spectra when THF was added to **17**, although these products could not be isolated in an analytically pure form.

In the similar reaction of **14** with $B(C_6F_5)_3$, the product [(*t*-Bu_2(2-C_6H_4Ph)PN)$_2$TiMe][MeB(C_6F_5)$_3$] (**19**) is formed. ^{11}B{^{1}H} and ^{19}F NMR data reflect the formation of free borate anion. ^{1}H and ^{31}P{^{1}H} NMR spectra show the formation of two isomers in 2:1 ratio at 25 °C. The ^{31}P{^{1}H} NMR spectrum of the major isomer shows resonances at 27.6 and 39.7 ppm, while the minor isomer shows a signal at 29.0 ppm (Figure 11). These data suggest that, like the precursor **14**, the biphenyl substituents of the major isomer of **19** are oriented in opposing directions, one being toward the metal and the other away from Ti (Scheme 8a). The ^{31}P chemical shift of the minor isomer suggests a conformation in which both biphenyl substituents are oriented toward the Ti center. As the temperature is decreased from 303 to 243 K, the relative proportion of the major and minor isomers of **14** becomes 1:1 at 243 K. In addition, the minor isomer is shown to give rise to an intramolecular process by variable-temperature ^{31}P{^{1}H} NMR data. As the temperature is reduced, the signal attributable to the minor isomer broadens, ultimately splitting into two well-resolved signals at 27.6 and 28.6 ppm. Line-shape analyses[10] of these spectra reveal the activation parameters as follows: $\Delta G^{\ddagger}$(268 K) = 52(2) kJ/mol, $\Delta H^{\ddagger}$ = 69(2) kJ/mol, $\Delta S^{\ddagger}$ 60(2) J/(mol K). The positive entropy term is consistent with an intramolecular process proposed to involve exchange of the arene rings in the coordination sphere of Ti (Scheme 8b). This process amounts to the inversion of chirality at the cationic Ti center. This barrier is comparable to that found for the site epimerization of the Zr center in Cp*$_2$Zr[η^1,η^2-CH_2-$CHMeCH_2CH{=}CH_2$][$B(C_6F_5)_4$] ($\Delta G^{\ddagger}$ = 60.5 kJ/mol) reported by Casey and co-workers.[16]

Summary

The synthesis and characterization of a series of Ti and Zr bis-*tert*-butylbiphenylphosphinimide complexes has been achieved. In the absence of steric conflicts with metal substituents, the preferred orientation of the biphenyl fragment appears to be one in which it is oriented toward the metal center. On the other hand, steric congestion as a result of other bulky ligands on Ti or Zr prompts rotational conformers which interconvert under thermal duress. Interactions of the pendant arene with the metal center act to stabilize cationic species. In bis-phosphinimide complex cations, such stabilization may be enhanced due to the possibility of intramolecular arene exchange. It is clear that the present work illustrates the potential of *tert*-butylbiphenylphosphinimide ligands to provide a stabilizing influence on otherwise highly reactive species. Current efforts are targeting exploitation of these findings for applications in catalysis.

Acknowledgment. Financial support from NSERC of Canada and NOVA Chemical Corporation is gratefully acknowledged.

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

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