Synthesis, Structure, and Reactivity of the Phosphinimide Complexes (t-$Bu_3PN)_nMX_{4-n}$ (M = Ti, Zr)

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The phosphinimide complexes (t-$Bu_3PN)TiCl_3$ (**1**) and (t-$Bu_3PN)_2TiCl_2$ (**4**) are readily prepared in high yields from the stoichiometric reaction of t-$Bu_3PNSiMe_3$ and $TiCl_4$, while (t-$Bu_3PN)_3TiCl$ (**11**) is readily obtained from the reaction of t-Bu_3PNLi and $TiCl_4$. The analogous 1:1 or 2:1 reactions of $ZrCl_4$ and t-Bu_3PNLi afford mixtures of products, although in the 3:1 stoichiometric ratio (t-$Bu_3PN)_3ZrCl$ (**12**) is isolable. These complexes are readily alkylated with a variety of reagents to give (t-$Bu_3PN)TiMe_3$ (**2**), (t-$Bu_3PN)Ti(CH_2Ph)_3$ (**3**), (t-$Bu_3PN)_2TiMe_2$ (**5**), (t-$Bu_3PN)_2Ti(\eta^3$-$C_3H_5)_2$ (**6**), (t-$Bu_3PN)_2Ti(CH_2Ph)_2$ (**7**), (t-$Bu_3PN)_2TiPh_2$ (**8**), (t-$Bu_3PN)_2Ti(\eta^5$-Cp)Cl (**9**), (t-$Bu_3PN)_2Ti(\eta^5$-Cp)Me (**10**), (t-$Bu_3PN)_3TiMe$ (**13**), (t-$Bu_3PN)_3TiPh$ (**14**), (t-$Bu_3PN)_3ZrMe$ (**15**), (t-$Bu_3PN)_3Zr(CH_2Ph)$ (**16**), and (t-$Bu_3PN)_3Zr(\eta^5$-Cp) (**17**). Subsequent reactions of some of these alkyl derivatives with $[PhNMe_2H][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$, or $B(C_6F_5)_3$ are investigated. A number of zwitterionic and cationic species complexes have been characterized. These include [(t-$Bu_3PN)Ti(CH_2Ph)_2(PhCH_2)B(C_6F_5)_3$] (**18**), $[(t$-$Bu_3PN)_2TiMe(PMe_3)][B(C_6F_5)_4]$ (**19**), (t-$Bu_3PN)_2TiMe$ (μ-$MeB(C_6F_5)_3$) (**20**), (t-$Bu_3PN)_2Ti(\mu$-$MeB(C_6F_5)_3)_2$ (**21**), and (t-$Bu_3PN)_2Ti(C_6F_5)_2$ (**22**). The implications of this chemistry are considered. Structural data for **1**, **4**, **5**, **12**, **16**, **21**, and **22** are described.

Introduction

The reactivity of early transition metal chemistry has been dominated by systems with cyclopentadienyl ancillary ligands. Investigations of systems that incorporate lesser used ancillary ligands is a growing area of interest. Such systems may provide more reactive metal species as well as provide unforeseen reactivity patterns. One area of application that has spurred much of this interest is the use of novel ancillary ligands in early metal systems, with the target of new olefin polymerization catalyst systems.[1−9] In our own efforts, we have developed a strategy for alternative ancillary ligands for early metal systems based on the similarity of the steric characteristics of phosphinimide ligands to those of the cyclopentadienyl ligand.[10,11] This approach is based on the seminal work of Wolczanski et al. in 1984, in which they described the steric analogy between the cyclopentadienyl analogue and "tritox" R_3CO^-.[12] Although there are a number of structural studies of phosphinimide complexes,[13,14] there has been no systematic study of the chemistry of such compounds. In this article, we examine the ligand attributes via the study of the series of phosphinimide complexes (t-$Bu_3PN)_nTiX_{4-n}$ (n = 1−3, X = Cl, Me, Bz, allyl, Ph, Cp). Zwitterionic or cationic derivatives of several of these species are also described. The implications regarding the nature, utility, and anticipated effects on the chemistry of the phosphinimides complexes are considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing Grubb's type column systems manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. ^{31}P, ^{19}F, and ^{11}B NMR spectra were recorded on a Bruker Avance-300 spectrometer and are referenced to 85% H_3PO_4, CF_3CO_2H, and $NaBH_4$,

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respectively. All NMR spectra were recorded at 25 °C unless otherwise indicated. Guelph Chemical Laboratories Inc., Guelph, Ontario, performed combustion analyses. The ligand precursors *t*-Bu$_3$PNSiMe$_3$ and *t*-Bu$_3$PNLi were prepared as previously described.[13]

Synthesis of (*t*-Bu$_3$PN)TiCl$_3$, 1. Solid *t*-Bu$_3$PNSiMe$_3$ (5.000 g; 17.3 mmol) was added to a toluene solution (25 mL) of TiCl$_4$ (3.275 g; 17.3 mmol) at room temperature. The solution was refluxed for 12 h. The volatile products were removed under vacuum, and the residual solid was washed with hexane (3 × 20 mL). White solid **1** was isolated by filtration and dried under vacuum (6.210 g; 16.8 mmol; 97%). ^{1}H NMR: δ 1.03 (d, $^3J_{PH}$ = 14.0 Hz, 27H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: δ 56.8. ^{13}C{^{1}H} NMR: δ 42.10 (d, $^1J_{PC}$ = 44.0 Hz, P*C*Me$_3$), 29.10. Anal. Calcd for C$_{12}$H$_{27}$PNTiCl$_3$: C, 38.89; H, 7.34; N, 3.78. Found: C, 38.66; H, 7.23; N, 3.59.

Synthesis of (*t*-Bu$_3$PN)TiMe$_3$, 2, and (*t*-Bu$_3$PN)Ti(CH$_2$Ph)$_3$, 3. These compounds were prepared in a similar manner using the appropriate Grignard reagent, and thus only a representative preparation is detailed. To a diethyl ether solution of complex **1** (0.500 g; 1.34 mmol) was added excess MeMgBr (1.5 mL; 3.0 M; 4.5 mmol). The solution was stirred at room temperature for 12 h. The solvent was removed under vacuum and the resulting gray solid extracted with hot hexane (3 × 10 mL). The volume of the solution was reduced to 5 mL. White crystalline solid **2** was obtained upon cooling to −30 °C for 10 h (0.325 g; 1.05 mmol; 78%). **2**: ^{1}H NMR δ 1.23 (d, $^3J_{PH}$ = 13.0 Hz, 27 H, PC*Me*$_3$), 1.15 (s, 9H, Ti*Me*). ^{31}P{^{1}H} NMR: δ 32.46. ^{13}C{^{1}H} δ 49.25 (Ti*Me*), 40.90 (d, $^1J_{PC}$ = 46.3 Hz, P*C*Me$_3$), 29.46. Anal. Calcd for C$_{15}$H$_{36}$PNTi: C, 58.24; H, 11.73; N, 4.53. Found: C, 58.12; H, 11.63; N, 4.22. **3**: Yield: 85%. ^{1}H NMR: δ 7.20 (t, 6H, Ph), 7.01 (d, 6H, Ph), 6.94 (t, 3H, Ph), 2.74 (s, 6H, C*H*$_2$Ph), 1.08 (d, $^3J_{PH}$ = 13.2 Hz, 27H, P*C*Me$_3$). ^{31}P{^{1}H} NMR: δ 37.24. ^{13}C{^{1}H} δ 147.42, 128.85, 121.89, 77.74 (Ti*C*H$_2$Ph), 40.90 (d, $^1J_{PC}$ = 45.4 Hz, P*C*Me$_3$), 29.36. Anal. Calcd for C$_{33}$H$_{48}$PNTi: C, 73.72; H, 9.00; N, 2.61. Found: C, 73.67; H, 8.88; N, 2.53.

Synthesis of (*t*-Bu$_3$PN)$_2$TiCl$_2$, 4. (i) A toluene solution (10 mL) of TiCl$_4$ (0.500 g; 2.636 mmol) was added to a toluene solution (50 mL) of *t*-Bu$_3$PNSiMe$_3$ (1.600 g; 5.526 mmol). The solution was refluxed to 110 °C for 12 h. The volatile products were removed under vacuum to give a white solid. The solid was washed with hexane (3 × 20 mL), isolated by filtration, and dried under vacuum (1.325 g; 2.403 mmol; 91%). (ii) Alternatively this compound can be prepared from the reaction of **1** with 1 equiv of *t*-Bu$_3$PNLi in toluene. ^{1}H NMR: δ 1.36 (d, $|J^3_{PH}|$ = 13.1 Hz, 54H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 41.36 (d, $|J^1_{PC}|$ = 46.1 Hz, P*C*Me$_3$), 29.73. ^{31}P{^{1}H} NMR: δ 35.37. Anal. Calcd for C$_{24}$H$_{54}$P$_2$N$_2$TiCl$_2$: C, 52.27; H, 9.87; N, 5.08. Found: C, 52.11; H, 9.59; N, 4.99.

Synthesis of (*t*-Bu$_3$PN)$_2$TiMe$_2$, 5, (*t*-Bu$_3$PN)$_2$Ti(η^3-C$_3$H$_5$)$_2$, 6, (*t*-Bu$_3$PN)$_2$Ti(CH$_2$Ph)$_2$, 7, (*t*-Bu$_3$PN)$_2$TiPh$_2$, 8, (*t*-Bu$_3$PN)$_2$Ti(η^5-Cp)Cl, 9, and (*t*-Bu$_3$PN)$_2$Ti(η^5-Cp)Me, 10. These compounds were prepared in a similar manner using the appropriate Grignard or alkylating reagent, and thus only a representative preparation is detailed. To a diethyl ether solution (10 mL) of **4** (0.500 g; 0.907 mmol) was added an excess of MeMgBr (0.9 mL; 3.0 M; 2.7 mmol). The solution was stirred at 25 °C for 12 h. The solvent was removed under vacuum to give a gray solid. The solid was extracted with hexane (3 × 20 mL). The volume of the solution was reduced to 5 mL and left to crystallize at 25 °C for 12 h. White crystalline **5** was isolated by filtration and dried under vacuum (0.380 g; 0.744 mmol; 82%). **5**: ^{1}H NMR δ 1.39 (d, $|J^3_{PH}|$ = 12.6 Hz, 54H, PC*Me*$_3$), 0.90 (s, 6H, Ti*Me*$_2$). ^{13}C{^{1}H} NMR: δ 40.81 (d, $|J^1_{PC}|$ = 47.2 Hz, P*C*Me$_3$), 36.27 (Ti*Me*$_2$), 29.87. ^{31}P{^{1}H} NMR: δ 25.72. Anal. Calcd for C$_{26}$H$_{60}$P$_2$N$_2$Ti: C, 61.16; H, 11.84; N, 5.49. Found: C, 60.99; H, 11.71; N, 5.39. **6**: Yield: 90%. ^{1}H NMR: δ 6.55 (q, $^3J_{HH}$ = 11.5 Hz, 2H, (CH$_2$)$_2$C*H*), 3.74 (d, $^3J_{HH}$ = 11.5 Hz, 8H, (C*H*$_2$)$_2$CH), 1.28 (d, $^3J_{PH}$ = 12.6 Hz, 54H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 142.95, 79.22, 40.90 (d, $^1J_{PC}$ = 46.8 Hz, P*C*Me$_3$), 29.87. ^{31}P{^{1}H} NMR: δ 26.29. Anal. Calcd for C$_{30}$H$_{64}$P$_2$N$_2$Ti: C, 64.04; H, 11.46; N, 4.98. Found: C, 63.87; H, 11.22; N, 4.56. **7**: Yield: 85%. ^{1}H NMR: δ 7.26 (d, 4H, Ph), 7.17 (t, 4H, Ph), 6.85 (t, 2H, Ph), 2.84 (s, 4H, TiC*H*$_2$Ph), 1.23 (d, $^3J_{PH}$ = 12.7 Hz, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR δ 29.12. ^{13}C{^{1}H} NMR: δ 152.45, 126.76, 119.79, 67.12, 40.60 (d, $^1J_{PC}$ = 46.9 Hz, P*C*Me$_3$), 29.80. Anal. Calcd for C$_{38}$H$_{68}$P$_2$N$_2$Ti: C, 68.86; H, 10.34; N, 4.23. Found: C, 68.56; H, 10.12; N, 4.01. **8**: Yield: 82%. ^{1}H NMR: δ 8.24 (d, 4H, Ph), 7.31 (t, 4H, Ph), 7.21 (d, 2H, Ph), 1.30 (d, $^3J_{PH}$ = 12.8 Hz, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: δ 28.58. ^{13}C{^{1}H} NMR: δ 188.74, 136.20, 126.29, 40.80 (d, $^1J_{PC}$ = 49.1 Hz, P*C*Me$_3$), 29.85. Anal. Calcd for C$_{36}$H$_{64}$P$_2$N$_2$Ti: C, 68.12; H, 10.16; N, 4.41. Found: C, 67.97; H, 10.01; N, 4.22. **9**: Yield: 83%. ^{1}H NMR: δ 6.56 (s, 5H, Cp), 1.35 (d, $^3J_{PH}$ = 12.7 Hz, 54 H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: δ 29.73. ^{13}C{^{1}H} NMR δ 111.24, 41.50 (d, $^1J_{PC}$ = 47.0 Hz, P*C*Me$_3$), 30.28. Anal. Calcd for C$_{29}$H$_{59}$ClP$_2$N$_2$Ti: C, 59.94; H, 10.23; N, 4.82. Found: C, 59.83; H, 10.04; N, 4.73. **10**: Yield: 73%. ^{1}H NMR: δ 6.35 (s, 5H, Cp), 1.32 (d, $^3J_{PH}$ = 12.4 Hz, 54 H, PC*Me*$_3$), 0.82 (s, 3H, Ti*Me*). ^{31}P{^{1}H} NMR: δ 24.46. ^{13}C{^{1}H} NMR: δ 109.08, 41.15 (d, $^1J_{PC}$ = 47.1 Hz, P*C*Me$_3$), 30.24, 29.88 (Ti*Me*). Anal. Calcd for C$_{30}$H$_{62}$P$_2$N$_2$Ti: C, 64.27; H, 11.15; N, 5.00. Found: C, 64.05; H, 10.99; N, 4.89.

Synthesis of (*t*-Bu$_3$PN)$_3$TiCl, 11. To a benzene solution (20 mL) of **4** (0.500 g; 0.907 mmol) was added 1 equiv of *t*-Bu$_3$PNLi (0.205 g; 0.918 mmol). The solution was stirred at 25 °C for 12 h. The solvent was removed under vacuum and the residual white solid washed with hexane (3 × 10 mL). White crystalline **11** was isolated by filtration and dried under vacuum (0.627 g; 0.853 mmol; 95%). **11**: ^{1}H NMR: δ 1.49 (d, $^3J_{PH}$ = 12.5 Hz, 81H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 41.12 (d, $^1J_{PC}$ = 47.5 Hz, P*C*Me$_3$), 30.62. ^{31}P{^{1}H} NMR: δ 25.60. Anal. Calcd for C$_{36}$H$_{81}$ClP$_3$N$_3$Ti: C, 59.04; H, 11.15; N, 5.74. Found: C, 58.89; H, 11.01; N, 5.63.

Synthesis of (*t*-Bu$_3$P N)$_3$ZrCl, 12. To a benzene solution (20 mL) of ZrCl$_4$ (0.200 g; 0.859 mmol) was added 3 equiv of *t*-Bu$_3$PNLi (0.575 g; 2.577 mmol). The solution was stirred at room temperature for 12 h. The solvent was removed under vacuum and the residual white solid washed with hexane (3 × 10 mL). White crystalline **12** was isolated by filtration and dried under vacuum Yield: 0.620 g; 0.799 mmol; 93%. ^{1}H NMR: δ 1.42 (d, $|^3J_{PH}|$ = 12.2 Hz, 81H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 40.51 (d, $|^1J_{PC}|$ = 47.6 Hz, P*C*Me$_3$), 30.35. ^{31}P{^{1}H} NMR: δ 29.13. Anal. Calcd for C$_{36}$H$_{81}$ClP$_3$N$_3$Zr: C, 55.75; H, 10.53; N, 5.42. Found: C, 55.57; H, 10.34; N, 5.34.

Synthesis of (*t*-Bu$_3$PN)$_3$TiMe, 13, (*t*-Bu$_3$PN)$_3$TiPh, 14, (*t*-Bu$_3$PN)$_3$ZrMe, 15, (*t*-Bu$_3$PN)$_3$Zr(CH$_2$Ph), 16, and (*t*-Bu$_3$PN)$_3$Zr(η^5-Cp), 17. These compounds were prepared in a similar manner using the appropriate Grignard or alkylating reagent and metal complex precursor; thus only a representative preparation is detailed. To a diethyl ether solution of **11** (0.200 g; 0.272 mmol) was added MeMgBr (0.9 mL; 3.0 M; 0.3 mmol). The solution was stirred at 25 °C for 12 h. The solvent was removed under vacuum to give a gray solid. The solid was extracted with hexane (3 × 20 mL). The volume of the solution was reduced to 5 mL and left to crystallize at 25 °C for 12 h. This afforded white crystalline **13** (0.170 g; 0.238 mmol; 88%). ^{1}H NMR: δ 1.49 (d, $^3J_{PH}$ = 12.2 Hz, 81H, PC*Me*$_3$), 0.80 (s, 3H, Ti*Me*). ^{13}C{^{1}H} NMR: δ 41.00 (d, $|^1J_{PC}|$ = 46.9 Hz, P*C*Me$_3$), 28.95. ^{31}P{^{1}H} NMR: δ 21.44. Anal. Calcd for C$_{37}$H$_{84}$P$_3$N$_3$Ti: C, 62.42; H, 11.89; N, 5.90. Found: C, 62.33; H, 11.73; N, 5.66. **14**: Yield: 73%. ^{1}H NMR: δ 8.24 (d, 2H, Ph), 7.30 (t, 2H, Ph), 7.21 (d, 1H, Ph), 1.31 (d, $^3J_{PH}$ = 12.7 Hz, 81H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 188.74, 136.20, 126.28, 40.83 (d, $^1J_{PC}$ = 46.7 Hz, P*C*Me$_3$), 29.85. ^{31}P{^{1}H} NMR: δ 28.57. Anal. Calcd for C$_{42}$H$_{86}$P$_3$N$_3$Ti: C, 65.18; H, 11.20; N, 5.43. Found: C, 64.97; H, 11.03; N, 5.35. **15**: Yield: 88%. ^{1}H NMR: δ 1.44 (d, $|^3J_{PH}|$ = 12.1 Hz, 81H, PC*Me*$_3$), 0.39 (s, 3H, Zr*Me*). ^{13}C{^{1}H} NMR: δ 40.41 (d, $|^1J_{PC}|$ = 47.2 Hz, P*C*Me$_3$), 30.31, 18.56. ^{31}P{^{1}H} NMR: δ 26.75. Anal. Calcd for C$_{37}$H$_{84}$P$_3$N$_3$Zr: C, 58.84; H,

Table 1. Crystallographic Parameters[a]

	1	4	5	12	16	21	22
formula	$C_{12}H_{27}Cl_3NPTi$	$C_{24}H_{54}Cl_2N_2P_2Ti$	$C_{26}H_{60}N_2P_2Ti$	$C_{36}H_{81}ClN_3P_3Zr$	$C_{43}H_{88}N_3NP_3Zr$	$C_{64}H_{64}B_2Cl_4F_{30}N_2P_2Ti$	$C_{39}H_{57}F_{10}N_2P_2Ti$
fw	370.57	551.43	510.60	775.62	831.29	1704.43	853.70
a, Å	29.497(6)	13.091(2)	13.1885(3)	21.744(7)	17.027(6)	23.417(9)	13.747(3)
b, Å	9.6471(19)	16.233(3)	16.4592(4)	12.801(2)	20.226(8)	14.776(6)	20.311(5)
c, Å	13.356(3)	15.413(4)	15.5549(3)	17.053(2)	14.319(7)	22.678(8)	17.027(4)
β, deg		107.04(2)	106.5890(10)	108.83(3)		109.98(3)	113.015(15)
V, Å^3	3800.4(13)	3131.4(10)	3235.99(12)	4492.8(16)	4931(4)	7374(5)	4375.5(16)
space group	$Pca2_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$Pnma$	$C2/c$	$P2_1/n$
d(calc), g cm^{-1}	1.295	1.170	1.048	1.147	1.120	1.535	1.296
Z	8	4	4	4	4	4	4
μ, mm^{-1}	0.943	0.560	0.378	0.436	0.349	0.421	0.340
no. of data collected	3415	5429	15936	22423	3755	15967	7636
no. of data used	2973	5427	5619	7801	2018	5661	5651
variables	325	280	280	397	207	483	481
R, %	0.0724	0.0606	0.0512	0.0387	0.0826	0.0824	0.0485
R_w, %	0.2137	0.1466	0.1438	0.1323	0.2237	0.1409	0.1409
goodness of fit	1.543	0.743	1.062	1.136	1.822	1.003	1.054

[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.71069$ Å), $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^2)^2]]^{0.5}$.

11.21; N, 5.56. Found: C, 58.58; H, 11.01; N, 5.26. **16**: Yield: 84%. ^{1}H NMR: δ 7.49 (t, 1H, Ph), 7.30 (t, 2H, Ph), 6.78 (d, 2H, Ph), 2.75 (s, 2H, C*H*$_2$Ph), 1.47 (d, $|^3J_{PH}| = 12.2$ Hz, 81H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 154.15, 130.02, 127.07, 118.34, 49.25, 40.32 (d, $^1J_{PC} = 47.5$ Hz, P*C*Me$_3$), 30.29. ^{31}P{^{1}H} NMR: δ 27.60. Anal. Calcd for $C_{43}H_{88}P_3N_3Zr$: C, 62.13; H, 10.67; N, 5.05. Found: C, 61.99; H, 10.51; N, 4.98. **17**: Yield: 67%. ^{1}H NMR: δ 6.57 (+s, 5H, Cp), 1.49 (d, $|^3J_{PH}| = 12.5$ Hz, 81H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 104.65, 41.2 (d, $|^1J_{PC}| = 47.4$ Hz, P*C*Me$_3$), 30.61. ^{31}P{^{1}H} NMR: δ 25.63. Anal. Calcd for $C_{41}H_{86}P_3N_3Zr$: C, 61.15; H, 10.76; N, 5.22. Found: C, 61.00; H, 10.61; N, 5.01.

Generation of [(*t*-Bu$_3$PN)Ti(CH$_2$Ph)$_2$(PhCH$_2$)B(C$_6$F$_5$)$_3$], 18. To a benzene solution of 10 mL of complex **3** (0.050 g; 0.093 mmol) was added a benzene (5 mL) solution of B(C$_6$F$_5$)$_3$ (0.052 g; 0.100 mmol). The orange solution turned dark red within seconds. A red oil separated from solution after 30 min. The benzene solution was decanted from the red oil, and the oil was washed with hexane (3 × 10 mL) and dried under vacuum (0.072 g; 0.069 mmol; 69%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.13 (t, 4H, Ph), 6.91 (t, 2H, Ph), 6.66 (d, 4H, Ph), 6.52 (br s, 2H, Ph), 6.36 (br s, 2H, Ph), 6.18 (br s, 1H, Ph), 3.25 (s, 2H, C*H*$_2$Ph), 2.50 (br, 4H, C*H*$_2$Ph), 1.02 (d, $^3J_{PH} = 13.4$ Hz, PC*Me*$_3$). ^{31}P{^{1}H} NMR: δ 51.32. ^{19}F NMR: δ −53.13, −84.08, −88.01.

Generation of [(*t*-Bu$_3$PN)$_2$TiMe(PMe$_3$)][B(C$_6$F$_5$)$_4$], 19. A methylene chloride solution (5 mL) of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.080 g; 0.100 mmol) was added to a CH_2Cl_2 solution of complex **5** (0.050 g; 0.098 mmol) and PMe_3 (0.050 g; 0.657 mmol). The solution was stirred at 25 °C for 30 min. The solvent was removed under vacuum, and the residual solid was washed with hexane (3 × 10 mL). The solid was highly sensitive and was characterized spectroscopically without further purification. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.55 (d, $|J^3_{PH}| = 12.4$ Hz, 9H, P*Me*$_3$), 1.51 (d, $|J^3_{PH}| = 13.2$ Hz, 54H, PC*Me*$_3$), 0.80 (s, 3H, Ti*Me*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 42.75, −22.78. ^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −55.63 (s), −86.36 (t, $|J_{FF}| = 20.6$ Hz), −90.19 (t, $|J_{FF}| = 16.9$ Hz). ^{11}B{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −16.98.

Generation of (*t*-Bu$_3$PN)$_2$TiMe(*μ*-MeB(C$_6$F$_5$)$_3$), 20. To a benzene solution of complex **5** (0.050 g; 0.098 mmol) was added a benzene solution of B(C$_6$F$_5$)$_3$ (0.051 g; 0.100 mmol). The solution was stirred for 30 min at 25 °C. The solvent was removed under vacuum. The resulting solid was washed with hexane and dried under vacuum. The solid was highly sensitive and was characterized spectroscopically without further purification. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.44 (d, $|J^3_{PH}| = 13.1$ Hz, 54H, PC*Me*$_3$), 0.54 (s, 3H, Ti*Me*), 0.47 (br s, 3H *Me*B). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 49.75. ^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −55.78 (d, $|J_{FF}| = 21.5$ Hz), −88.07 (t, $|J_{FF}| = 19.9$ Hz), −90.58 (t, $|J_{FF}| = 18.7$ Hz). ^{11}B{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −15.27.

Synthesis of (*t*-Bu$_3$PN)$_2$Ti(*μ*-MeB(C$_6$F$_5$)$_3$)$_2$, 21. A methylene chloride solution (2 mL) of complex **5** (0.200 g; 0.392 mmol) was added to a CH_2Cl_2 solution (2 mL) of B(C$_6$F$_5$)$_3$ (0.421 g; 0.822 mmol). The solution turned bright yellow within seconds. The solution was stirred for 30 min at room temperature. The solvent was removed under vacuum to yield light yellow complex **21** (0.570 g; 0.371 mmol; 95%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.52 (d, $|J^3_{PH}| = 14.6$ Hz, 52 H, PC*Me*$_3$), 0.49 (s, 6H, *Me*B). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 60.57. ^{11}B{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −15.22. ^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −55.80 (d, $|J_{FF}| = 22.0$ Hz), −87.87 d, $|J_{FF}| = 20.6$ Hz, −90.44 d, $|J_{FF}| = 21.0$ Hz). EA Calcd for $C_{62}H_{60}B_2F_{30}N_2P_2Ti$: C, 47.06; H, 3.82; N, 1.77. Found: C, 46.86; H, 3.69; N, 1.73.

Synthesis of (*t*-Bu$_3$PN)$_2$Ti(C$_6$F$_5$)$_2$, 22. To a benzene solution (10 mL) of B(C$_6$F$_5$)$_3$ (0.036 g; 0.070 mmol) was added a benzene solution (5 mL) of complex **13** (0.050 g; 0.070 mmol). The solution was stirred for 30 min at room temperature. The solvent was removed under vacuum to yield an oily yellow solid. The solid was washed with hexane (3 × 10 mL) and dried under vacuum. Recrystalization from benzene afforded white crystalline **22** (0.045 g; 0.055 mmol; 79%). ^{1}H NMR: δ 1.41 (d, $^3J_{PH} = 13.2$ Hz, 54H, PC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 147.55 (m), 143.46 (m), 138.78 (m), 136.16 (m), 40.94 (d, $^1J_{PC} = 45.8$ Hz, P*C*Me$_3$), 29.65. ^{31}P{^{1}H} NMR: δ 38.42. ^{19}F{^{1}H} NMR: δ −38.14 (br s), −81.05 (t), −86.77 (t). Anal. Calcd for $C_{36}H_{54}F_{10}P_2N_2Ti$: C, 53.08; H, 6.68; N, 3.44. Found: C, 52.95; H, 6.43; N, 3.32.

X-ray Data Collection and Reduction. X-ray quality crystals of **1**, **4**, **5**, **12**, **16**, **21**, and **22** were obtained directly from the preparation as described above. The 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 collecting a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5° < 2*θ* < 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 package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on either an SGI Indy or Pentium computer. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature

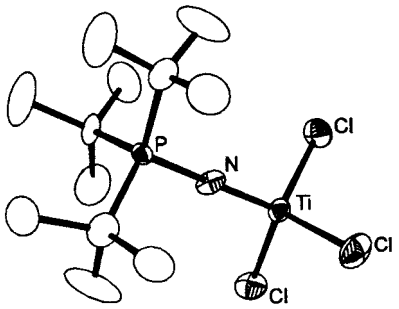

Figure 1. ORTEP drawings of **1**. 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti−N 1.714(6) Å, 1.705(7) Å, Ti−Cl 2.207(6) Å, 2.249(3) Å, 2.261(4) Å, 2.235(3) Å, 2.237(6) Å, 2.246(6) Å, P−N 1.628(6) Å, 1.631(7) Å, N−Ti−Cl 111.8(6)°, 107.4(2)°, 108.4(5)°, 109.6(3)°, 108.6(6)°, 108.2(5)°, Cl−Ti−Cl 108.6(3)°, 110.82(13)°, 109.9(3)°, 109.2(3)°, 112.2(3)°, 108.84(15)°, P−N−Ti 178.9(9)°, 179.4(12)°.

tabulations.[15] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routines. 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. Carbon-bound hydrogen 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. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. 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. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

Neutral Phosphinimide Complexes. The compound (t-Bu_3PN)$TiCl_3$ (**1**) is readily prepared from the stoichiometric reaction of t-$Bu_3PNSiMe_3$ and $TiCl_4$ in refluxing toluene. The resulting white crystalline product is obtained in 97% yield. ^1H, ^{13}C, and ^{31}P NMR spectroscopic data are consistent with the formulation of **1**. Crystallographic study of **1** confirms the monometallic nature and pseudo-tetrahedral geometry of the Ti coordination sphere (Figure 1). In the two molecules in the asymmetric unit, the average Ti−N and Ti−Cl distances were found to be 1.709(6) and 2.239(6) Å, respectively, while P−N−Ti angles were essentially linear, averaging 179.1(10)°. This geometry of the phosphinimide ligand on Ti is similar to that previously reported for (t-$Bu_3PN)_2TiCl_2$. Complex **1** is readily alkylated with the appropriate Grignard reagent to give the species (t-Bu_3PN)$TiMe_3$ (**2**) and (t-Bu_3PN)Ti-$(CH_2Ph)_3$ (**3**) in 78 and 85% respectively (Scheme 1). In the latter case, NMR data are consistent with η^1-binding of the benzyl ligands even on cooling to −80 °C.

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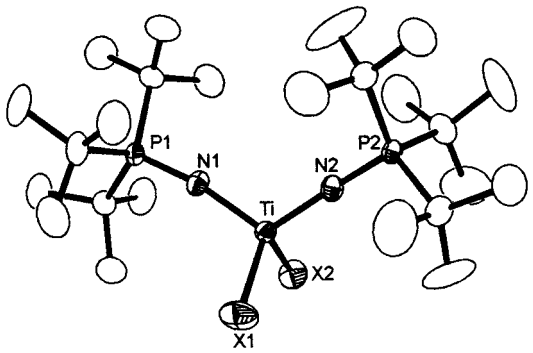
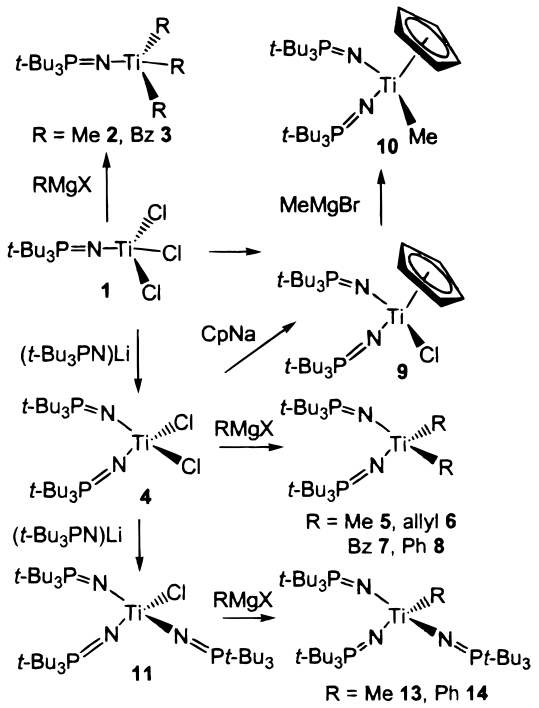


Figure 2. ORTEP drawings of **4** (**5**). 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. **4**: X = Cl, Ti−N 1.789(4) Å, 1.792(4) Å, Ti−Cl 2.288(2) Å, 2.292(2) Å, N−Ti−N 112.9(2)°, N−Ti−Cl(1) 109.34(14)°, 109.43(13)°, 109.51(13)°, 108.54(13)°, Cl−Ti−Cl 106.93(7)°. **5**: X = CH_3, Ti−N 1.824(2) Å, 1.830(2) Å, Ti−C 2.121(3) Å, 2.129(3) Å, N−Ti−N 117.24(11)°, N−Ti−C 109.99(13)°, 108.01(13)°, 108.59(14)°, 109.25(15)°, C−Ti−C 102.79(15)°.

Scheme 1



The bis-ligand complex (t-$Bu_3PN)_2TiCl_2$ (**4**) is prepared in a manner similar to that described for **1** with the appropriate alteration of the stoichiometry. Thus, reaction of 2 equiv of t-$Bu_3PNSiMe_3$ with $TiCl_4$ in refluxing toluene solution for 12 h affords **4** in 91% yield. Alternatively, **4** can be prepared from the reaction of **1** with 1 equiv of t-Bu_3PNLi in toluene. Alkylation of **4** with methylmagnesium bromide affords the corresponding dimethyl species, (t-$Bu_3PN)_2TiMe_2$ (**5**), in high yield (Scheme 1). Spectroscopic data support these formulations. X-ray crystallographic data confirming these formulations of **4** and **5** (Figure 2) have been previously communicated.[11] The metric parameters about Ti in **4** and **5** are similar to those presented above for **1**. The geometry about nitrogen in **1**, **4**, and **5** supports the notion of Ti−N multiple bonding, as the P−N bonds are lengthened significantly (**1**, 1.628(6) Å; **4**, 1.579(4) Å;

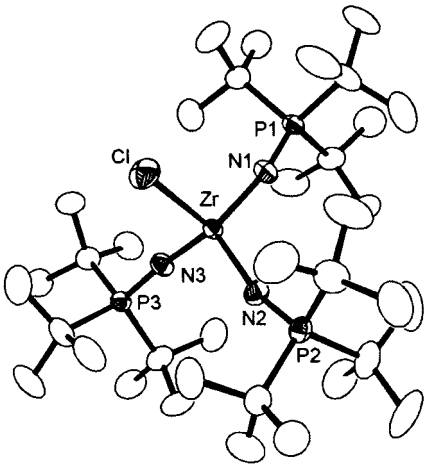


Figure 3. ORTEP drawings of **12**. 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Zr−N 1.989(2) Å, 1.988(3) Å, 1.993(2) Å, Zr−Cl 2.4601(10) Å, P−N 1.558(3) Å, 1.560(3) Å, 1.556(2) Å, N−Zr−N 111.38(11)°, 110.80(11)°, 113.32(12)°, N−Zr−Cl 106.30(8)°, 107.68(8)°, 106.96(8)°, P−N−Zr 167.7(2)°, 164.2(2)°, 164.8(2)°.

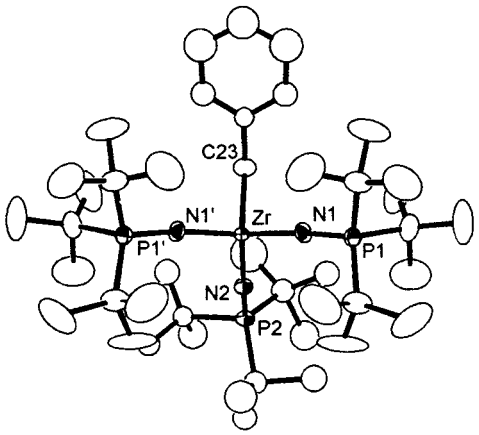


Figure 4. ORTEP drawings of **16**. 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Zr−N 1.997(6) Å, 2.016(12) Å, Zr−C23 2.30(2) Å, P−N 1.548(6) Å, 1.527(12) Å, N−Zr−N 114.2(5)°, 113.1(3)°, N−Zr−C 107.1(3)°, 100.9(7)°, P− N−Zr 174.1(5)°, 172.5(9)°.

5, 1.561(3) Å) compared to those seen in free phosphinimines (1.487 Å).

In a similar manner other alkyl derivatives of **4** can be prepared via treatment with the appropriate alkylating reagent. Reaction of **4** with allyl-Grignard affords the complex (*t*-$Bu_3PN)_2Ti(\eta^3$-$C_3H_5)_2$ (**6**) in 90% yield. The ^{1}H NMR data are consistent with η^3-binding of the allyl fragments, as a methylene and methine resonances are observed as a doublet and a quintet at 6.55 and 3.74 ppm, respectively. Alkylation of **4** with $PhCH_2MgBr$ affords (*t*-$Bu_3PN)_2Ti(CH_2Ph)_2$ (**7**) in 85% isolated yield, while treatment with PhLi gives (*t*-$Bu_3PN)_2TiPh_2$ (**8**) in 82% yield. Reaction of **4** with 1 equiv of NaCp affords an 83% yield of (*t*-$Bu_3PN)_2Ti(\eta^5$-Cp)Cl (**9**) (Scheme 1). The η^5-binding mode of the cyclopentadienyl ligand is confirmed by the observation of the ^{1}H NMR singlet at 6.56 ppm. Subsequent methylation of **9** with an equivalent of MeMgBr affords the white crystalline species (*t*-$Bu_3PN)_2Ti(\eta^5$-Cp)Me (**10**).

Tris-ligand complexes are also accessible. The species (*t*-$Bu_3PN)_3TiCl$ (**11**) is obtained in 95% yield via the reaction of **4** with *t*-Bu_3PNLi in benzene at room temperature for 12 h. The analogous Zr species, (*t*-$Bu_3PN)_3ZrCl$ (**12**) is derived from the reaction of 3 equiv of *t*-Bu_3PNLi with $ZrCl_4$. The formulation of **12** was confirmed by crystallographic study. The Zr−N bond distances in **12** average 1.990(3) Å, significantly shorter than the Zr−N distance of 2.169(2) Å found in bispyrazolate derivative $Cp_2Zr(NC_4H_4)_2$.[16] The Zr−Cl distance 2.4601(10) Å is comparable to the range of Zr−Cl distances found in various substituted zirconocene derivatives. In addition, the N−Zr−N and N−Zr−Cl angles average 111.8(1)° and 107.0(1)°, respectively. The average P−N bond in **12** is 1.558(3) Å, while the Zr−N−P angles range from 164.2(2)° to 167.7(2)°. These minor distortions from linearity of the phosphinimide ligands are attributable to steric crowding within the coordination sphere of Zr.

Reactions of **11** and **12** with alkylating agents provide facile routes to (*t*-$Bu_3PN)_3TiMe$ (**13**) and (*t*-$Bu_3PN)_3TiPh$ (**14**) and (*t*-$Bu_3PN)_3ZrMe$ (**15**) and (*t*-$Bu_3PN)_3Zr(CH_2Ph)$ (**16**), respectively (Scheme 1). An X-ray study of **16** (Figure 4) confirmed the formulation and revealed Zr−N_{av} and Zr−C distances of 2.00(1) Å and Zr−C23 2.30(2) Å. The P−N distances (1.538(6) Å) and P−N−Zr angles (173.3(5)°, 172.5(9)°) are similar to those seen in **12**.

It is noteworthy that attempts to react **11** with NaCp failed to result in substitution. In contrast, the analogous reaction with **12** afforded (*t*-$Bu_3PN)_3Zr(\eta^5$-Cp) (**17**) in 67% isolated yield. This observation is consistent with the smaller nature of the coordination sphere of Ti relative to Zr.

Zwitterionic and Cationic Complexes. The characterization of zwitterionic and cationic derivatives of the above phosphinimide species was undertaken. In the case of the monophosphimide species **3**, reaction with $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ leads to highly unstable products that could not be characterized. In contrast, reaction of **3** with $B(C_6F_5)_3$ proceeds in benzene to give a dark red oil. This extremely sensitive species **18** is soluble in CD_2Cl_2. ^{1}H NMR data reveal resonances at 3.25 and 2.50 ppm in a ratio of 2:4 attributable to the benzylic protons, and the aromatic resonances are consistent with two types of phenyl-ring environments. Although the resonances are broad, cooling to −90 °C failed to lead to significant sharpening of the signals. The $^{31}P\{^1H\}$ resonance for **18** is shifted significantly downfield to 51.3 ppm. These data, in addition to the ^{19}F data, are consistent with the formulation of **18** as [(*t*-$Bu_3PN)Ti(CH_2Ph)_2(PhCH_2)B(C_6F_5)_3$] (Scheme 2). The NMR data suggest a zwitterionic formulation with a cationic Ti center stabilized by an η^6-interaction with the benzyl group of the borate, as has been previously observed.[17]

An authentic salt is derived from bisphosphinimide complexes. Reaction of **5** with $[PhNMe_2H][B(C_6F_5)_4]$ affords a mixture of products. These apparently cationic products may result from various modes of stabilization

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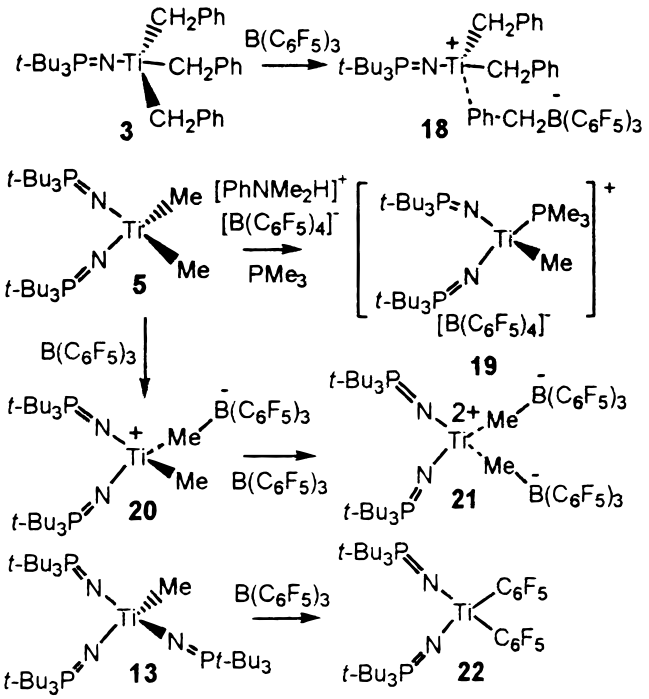
Scheme 2



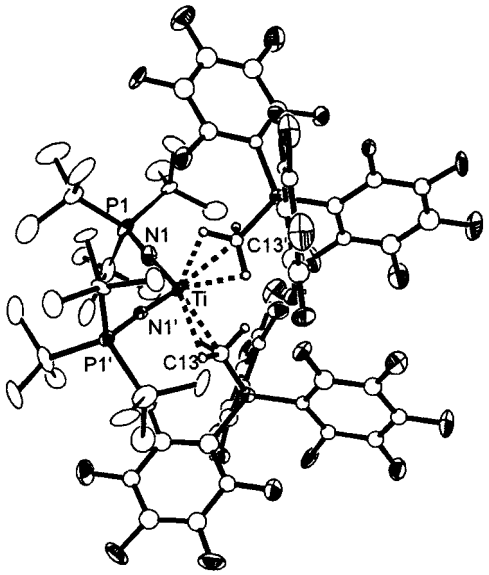


Figure 5. ORTEP drawings of **21**. 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Core of **3**: Ti−N 1.756(5) Å, Ti−C 2.333(7) Å, P−N 1.628(5) Å, N−Ti−N 115.4(3)°, N−Ti−C 109.0(2)°, C−Ti−C′ 104.5(4)°, P−N−Ti 176.3(3)°, B−C−Ti 174.9(5)°.

of the cationic Ti center generated by protonolysis of one of the Ti−methyl fragments. However, addition of PMe_3 to this mixture results in the conversion to the single highly sensitive, cationic species formulated as [(*t*-$Bu_3PN)_2TiMe(PMe_3)][B(C_6F_5)_4]$ (**19**) based on the ^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, and $^{11}B\{^1H\}$ NMR data (Scheme 2). The cation of this salt is expected to be structurally similar to the analogous metallocene cations described by Jordan,[18,19] Marks,[20] and others.[21−24]

Formation of zwitterionic species derived from **5** produces a very interesting result. Stoichiometric 1:1 reaction of **5** with $B(C_6F_5)_3$ results in the formation of (*t*-$Bu_3PN)_2TiMe$ (*μ*-$MeB(C_6F_5)_3$) (**20**), as evidenced by the NMR data. The ^1H NMR spectrum of **20** shows a sharp resonance at 0.54 ppm attributable to the Ti−Me fragment and a broad singlet at 0.47 ppm attributable to the methyl group of the associated borate. Interestingly, addition of a second equivalent of $B(C_6F_5)_3$ results in further reaction affording the new species **21**, which is isolated as a light-yellow crystalline product in 95% yield (Scheme 2). This product **21** exhibits a single resonance at 0.49 ppm in the ^1H NMR spectrum attributable to the methyl groups of the borate groups, suggesting abstraction of both Ti−Me fragments and thus a formulation of **21** as (*t*-$Bu_3PN)_2Ti(\mu$-$MeB(C_6F_5)_3)_2$. This was confirmed with a crystallographic study (Figure 5). The details of the structure have been previously communicated.[25] It is noteworthy that attempts to prepare analogues of **20** and **21** via methyl abstraction using $[Ph_3C][B(C_6F_5)_4]$ resulted in decomposition. These observations lend support to the formulation of **20** and **21** as ion-paired species in solution. The formation of **21** is certainly the first structurally characterized zwitterionic dication species, although evidence for metallocene dications has recently appeared in the literature.[26,27] Presumably, the distal nature of the steric demands of the phosphinimide ligands in comparison with those of the cyclopentadienyl ligands in metallocenes permits the approach of two $B(C_6F_5)_3$ to the metal center. It is also noteworthy that while **20** has been shown to be an effective catalyst for ethylene polymerization, **21** is inactive. These data infer that $B(C_6F_5)_3$ can play the role of both activator and poison.[25]

Reaction of the trisphosphinimide complex **13** with $B(C_6F_5)_3$ proceeds to give a white crystalline product **22** in 79% yield. The ^1H NMR spectrum of isolated **22** shows only a doublet resonance at 1.41 ppm attributable to the phosphinimide ligand. $^{19}F\{^1H\}$ NMR data suggest the presence of fluorinated aryl rings, although ^{11}B NMR spectra show no signal. The formulation of **22** was delineated by X-ray crystallography, which shows **22** to be the species (*t*-$Bu_3PN)_2Ti(C_6F_5)_2$ (Figure 6). The Ti−N and Ti−C bond lengths in **22** average 1.792(3) Å and 2.204(4) Å, respectively, while the N−Ti−N and C−Ti−C angles were found to be 116.82(10)° and 111.20(11)°. It is noteworthy, however, that similar transfer of a single C_6F_5 group has been recently observed by McConville.[28]

The nature of the boron-containing byproduct(s) derived in the formation of **22** is (are) not known While

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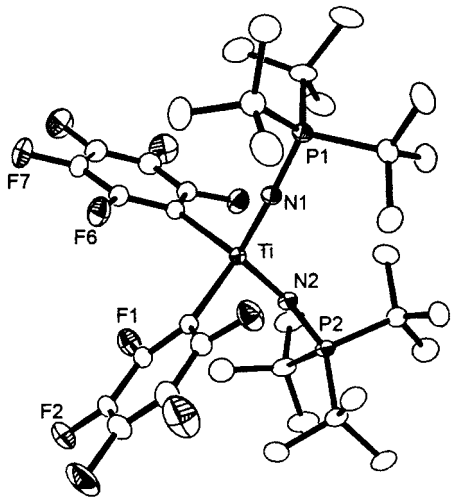

Figure 6. ORTEP drawings of **22**. 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Ti−N 1.788(2) Å, 1.795(2) Å, Ti−C 2.198(3) Å, 2.208(3) Å, P−N 1.592(2) Å, 1.590(2) Å, N−Ti−N 116.82(10)°, N−Ti−C 110.08(11)°, 104.10(10)°, 103.75(10)°, 111.04(11)°, 111.20(11)°, P−N−Ti 171.80(15)°, 169.76(14)°.

the mechanism of formation of **22** is also unknown, the initial step in the process is thought to involve abstraction of the methyl group of **13** by $B(C_6F_5)_3$, yielding an intermediate cation $[(t\text{-}Bu_3PN)_3Ti]^+$. Such a species could effect abstraction of a C_6F_5 fragment from boron. Subsequent phosphinimide ligand abstraction and B−C bond cleavage steps are required to achieve formation of **22**, but neither the sequence nor the nature of the intermediates is known. Nonetheless, the formation of **22** infers that an intermediate cation of the form $[(t\text{-}Bu_3PN)_3Ti]^+$ is highly electron deficient and thus Lewis acidic. Attempts to intervene in these reactions and stabilize such a cation with donor ligands have proved unsuccessful to date.

Summary. The synthesis and structure of a series of titanium and zirconium phosphinimide complexes of the form $(t\text{-}Bu_3PN)_nMCl_{4-n}$ are described. These complexes are readily alkylated with a variety of reagents. Reaction of these species with borane or borate reagents results in zwitterionic and cation derivatives. Some of these products prove to be highly unstable, undergoing further reactions, which clearly distinguish these systems from the analogous cyclopentadienyl compounds. Further unique aspects of the reactivity of such highly electron deficient, charged species are the subject of ongoing study.

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

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