Phosphinimide−Phosphinimide Ligands: New Bulky Ligands for Ethylene Polymerization Catalysts

Nancy L. S. Yue and Douglas W. Stephan*

School of Physical Sciences, Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada, N9P 3P4

Received February 13, 2001

The phosphinimide−phosphines $PPh_2(NPR_3)$ (R = *i*-Pr **1**, *t*-Bu **2**) were readily prepared in 80−98% yield. These species react with $AlMe_3$ or $B(C_6F_5)_3$ to form $Me_3AlPPh_2(NPR_3)$ (R = *i*-Pr **3**, *t*-Bu **4**) and $(C_6F_5)_3B(PPh_2(NPi\text{-}Pr_3))$ (**5**), respectively. Oxidation of compounds **1** and **2** with Me_3SiN_3 yields $Me_3SiNPPh_2(NPR_3)$ (R = *i*-Pr **6**, *t*-Bu **7**). These species react with $CpTiCl_3$ to give titanium(IV) complexes $CpTiCl_2(NPPh_2(NPR_3)$ (R = *i*-Pr **8**, *t*-Bu **9**) and subsequently the alkylated complexes $CpTiMe_2(NPPh_2(NPR_3))$ (R = *i*-Pr **10**, *t*-Bu **11**). Compounds **8**−**11** were tested for activity in ethylene polymerization. In the presence of excess methylalumoxane, the species **8** and **9** gave rise to active single-site catalysts, generating 299 and 34 gPE $mmol^{-1}$ h^{-1}, respectively. In contrast, activation of **10** and **11** by $[Ph_3C][B(C_6F_5)_4]$ showed negligible polymerization activity. Reaction of **11** with $B(C_6F_5)_3$ was shown to give numerous products, one of which was the dicationic species $[CpTi(\mu\text{-}Cl)(NPPh_2\text{-}(NPt\text{-}Bu_3)]_2[BC_6F_5)_4]_2$, **12**. The formation of this species and the implications of these results for catalyst and ancillary ligand design are considered and discussed. X-ray crystallographic data are reported for **1**, **3**, **4**, **8**, and **12**.

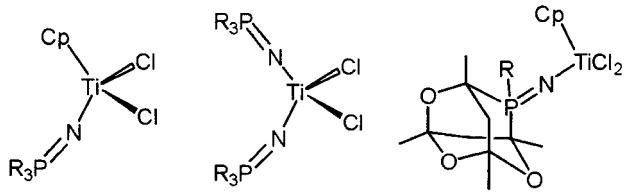
Introduction

The development of olefin polymerization catalysts continues to be a strong motivation for the development of the chemistry of a variety of the transition metals.[1−5] While the recent efforts focusing on the potential of late transition metal complexes have drawn much attention,[6−12] the implementation of group 4 metal catalysts in commercial practice continues to prompt study of new related systems. The introduction of new ancillary ligands offers one strategy for the discovery of new catalysts. In this regard, a variety of Ti and Zr species have been studied.[13−35] In our own efforts, we have recently published several studies of titanium phosphinimide complexes.[36−41] These works have shown that complexes of the form $CpTi(NPR_3)X_2$ and $(R_3PN)_2TiX_2$ are active single-site catalysts for the polymerization of ethylene.[40] In fact, the latter systems exhibit activity that exceeds that of the constrained geometry catalysts under specific commercially relevant conditions.[41] One advantage to this family of catalysts is the ability to effect facile modification of the steric and electronic properties of the ancillary phosphinimide ligands (Scheme 1). In exploring new derivatives, we have recently studied Ti complexes of phosphaadamantylphosphinimides.[42] (Scheme 1) While these ligands offer very sterically demanding ligands, the presence of the oxygen in the adamantyl cages prompts reaction with Lewis acids, leading to ligand−cage rupture and catalyst deactivation. In this article, we adopt an alternate

(1) Hlatky, G. G. *Coord. Chem. Rev.* **2000**, *199*, 235−329.
(2) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243−296.
(3) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *112*, 1354−1356.
(4) Kaminsky, W. *J. Chem. Soc. (D)* **1998**, *9*, 1413−1418.
(5) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285−289.
(6) Younkin, T. R.; Connor, E. F.; Henerson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462.
(7) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc. (D)* **1999**, *6*, 827−829.
(8) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049−4050.
(9) Mecking, S.; Johson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899.
(10) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, *7*, 849−850.
(11) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746−4764.
(12) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005−2007.
(13) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 8.
(14) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009.
(15) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241−5243.
(16) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415−4420.
(17) Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810−1812.
(18) Cloke, F. G. N.; Geldach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343−345.
(19) Repo, T.; Jany, G.; Salo, M.; Polamo, M.; Leskela, M. *J. Organomet. Chem.* **1997**, *541*, 363−366.
(20) Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303−3313.
(21) Bazan, G. C.; Donnelly, S. J.; Ridriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671−2672.
(22) Kowal, C. M.; Bazan, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 10317−10318.
(23) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489−4490.
(24) Sperry, C. K.; Cotter, W. D.; Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *121*, 7791−7805.
(25) Sperry, C. K.; Bazan, G. C.; Cotter, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 1513−1523.
(26) Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 3883−3888.
(27) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288−2290.
(28) Bazan, G. C.; Rodriguez, G. *Organometallics* **1997**, *16*, 2492−2494.
(29) Herberich, G. E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751−3757.

10.1021/om0101184 CCC: $20.00
Publication on Web 04/27/2001

Scheme 1



strategy to sterically demanding phosphinimide ligands. Herein we describe the synthesis of phosphinimide−phosphinimide ligands and the corresponding titanium complexes. The utility of these ligands and this strategy in the design of new polymerization catalysts is assessed, and the implications 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 a Grubb's type column system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker Avance-300 and/or 500. ^{1}H and ^{13}C NMR spectra are referenced to $SiMe_4$. ^{31}P NMR, ^{11}B NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H_3PO_4, $NaBH_4/H_2O$, and F_3CCOOH, respectively. Guelph Chemical Laboratories, Guelph, Ontario, performed combustion analyses.

Synthesis of $PPh_2(NPR_3)$ (R = *i*-Pr 1, *t*-Bu 2). Both compounds were prepared in a similar manner; thus one procedure is described. Ph_2PCl (2.44 g; 0.01 mol) was added dropwise to a clear orange benzene solution (100 mL) of *i*-Pr_3-PNLi (2.00 g; 0.01 mol). A white precipitate was formed. The solution became yellow after 4 h of stirring, and evaporation of the solvent under vacuum gave a pale yellow solid. The residue was extracted with 100 mL of hexane. Filtration and concentration of the solvent gave **1** in 80% yield. **1**: ^{31}P{^{1}H} NMR (C_6D_6): 42.4(d, *i*-Pr_3P, $|^2J_{P-P}|$ = 80 Hz), 38.9(d, PPh_2, $|^2J_{P-P}|$ = 80 Hz). ^{1}H NMR (C_6D_6): 8.02(m, 4H, *o*-Ar, $|J_{H-H}|$ = 7 Hz), 7.26(m, 4H, *m*-Ar, $|J_{H-H}|$ = 7 Hz), 7.08(m, 2H, *p*-Ar, $|J_{H-H}|$ = 7 Hz), 1.94(m, 3H, CH, $|J_{H-H}|$ = 4 Hz), 0.95(quart, 18H, CH_3, $|J_{H-H}|$ = 7 Hz). ^{13}C{^{1}H} NMR (C_6D_6): 151.2(d, *ipso*-Ar, $|J_{P-C}|$ = 27 Hz), 130.4(d, *o*-Ar, $|^2J_{P-C}|$ = 22 Hz), 128.1(d, *m*-Ar, $|^3J_{P-C}|$ = 6 Hz), 127.5(s, *p*-Ar), 25.5(d, CH, $|J_{P-C}|$ = 59 Hz), 17.2(s, CH_3). Anal. Calcd for $C_{21}H_{31}NP_2$: C, 70.17; H, 8.69; N, 3.90. Found: C, 69.63; H, 8.37; N, 3.68. **2**: Yield: 87% pale yellow crystalline solid. ^{31}P{^{1}H} NMR (C_6D_6): 47.9(d, *t*-Bu_3P, $|^2J_{P-P}|$ = 62 Hz), 40.8(d, PPh_2, $|^2J_{P-P}|$ = 62 Hz). ^{1}H NMR (C_6D_6): 8.01(m, 4H, *m*-Ar, $|J_{H-H}|$ = 7 Hz), 7.23(m, 4H, *o*-Ar, $|J_{H-H}|$ = 8 Hz), 7.05(m, 2H, *p*-Ar, $|J_{H-H}|$ = 7 Hz), 1.24(d, 27H, CH_3, $|J_{P-H}|$ = 13 Hz). ^{13}C{^{1}H} NMR (C_6D_6): 151.7(d, *ipso*-Ar, $|12J_{P-C}|$ = 20 Hz), 130.4(d, *o*-Ar, $|^2J_{P-C}|$ = 22 Hz), 128.4(d, *m*-Ar, $|^3J_{P-C}|$ = 7 Hz), 127.7(s, *p*-Ar), 41.6(d, C, $|J_{P-C}|$ = 49 Hz), 30.3(s, CH_3). Anal. Calcd for $C_{24}H_{37}NP_2$: C, 71.79; H, 9.29; N, 3.49. Found: C, 71.87; H, 9.37; N, 3.34.

Synthesis of $Me_3AlPPh_2(NPR_3)$ (R = *i*-Pr 3, *t*-Bu 4). Both compounds were prepared in a similar manner; thus one procedure is described. A 2.5 M hexane solution of $AlMe_3$ (0.42 mL; 0.84 mmol) was added to a clear benzene solution (6 mL) of **1** (100 mg; 0.28 mmol). The solution mixture was allowed to stir at room temperature overnight. Evaporation of the solvent gave a white solid. The solid was then washed with (2 × 2 mL) hexane and subsequently dried under vacuum. **3**: Yield: 90% white crystalline solid. ^{31}P{^{1}H} NMR (C_6D_6): 39.7, 26.3. ^{1}H NMR (C_6D_6): 7.77(m, 4H, *o*-Ar, $|J_{H-H}|$ = 8 Hz), 7.16-(m, 4H, *m*-Ar, $|J_{H-H}|$ = 7 Hz), 7.09(m, 2H, *p*-Ar, $|J_{H-H}|$ = 7 Hz), 1.80(m, 3H, CH, $|J_{H-H}|$ = 7 Hz), 0.86(quart, 18H, CH_3, $|J_{H-H}|$ = 7 Hz). ^{13}C{^{1}H} NMR (C_6D_6): 142.0(d, *ipso*-Ar, $|J_{P-C}|$ = 30 Hz), 132.5(d, *o*-Ar, $|^2J_{P-C}|$ = 14 Hz), 130.0(s, *p*-Ar), 128.5-(d, *m*-Ar, $|^3J_{P-C}|$ = 9 Hz), 26.3(d, CH, $|J_{P-C}|$ = 61 Hz), 17.4(s, CH_3), −6.4(s, CH_3). Anal. Calcd for $C_{24}H_{40}AlNP_2$: C, 63.78; H, 10.19; N, 3.54. Found: C, 63.24; H, 9.96; N, 3.12.

4: Yield: 98% white crystalline solid. ^{31}P{^{1}H} NMR (C_6D_6): 45.0(d, *t*-Bu_3P, $|^2J_{P-P}|$ = 26 Hz), 28.1(d, PPh_2, $|^2J_{P-P}|$ = 26 Hz). ^{1}H NMR (C_6D_6): 7.84(m, 4H, *o*-Ar, $|J_{H-H}|$ = 8 Hz), 7.16(m, 4H, *m*-Ar, $|J_{H-H}|$ = 6 Hz), 7.08(m, 2H, *p*-Ar, $|J_{H-H}|$ = 7 Hz), 1.06(m, 27H, CH, $|J_{H-H}|$ = 14 Hz), −0.15(s, 9H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): 141.9(d, *ipso*-Ar, $|J_{P-C}|$ = 29 Hz), 133.4-(d, *o*-Ar, $|^2J_{P-C}|$ = 14 Hz), 130.0(s, *p*-Ar), 128.4(d, *m*-Ar, $|^3J_{P-C}|$ = 8 Hz), 41.0 (d, C, $|J_{P-C}|$ = 51 Hz), 29.9 (s, CH_3), −5.9(s, CH_3). Anal. Calcd for $C_{27}H_{46}AlNP_2$: C, 68.47; H, 9.79; N, 2.96. Found: C, 68.80; H, 10.28; N, 2.99.

Synthesis of $(C_6F_5)_3B(PPh_2(NPi\text{-}Pr_3))$, 5. A benzene solution of $B(C_6F_5)_3$ (140 mg; 0.28 mmol) was added to a clear benzene solution (5 mL) of **1** (100 mg; 0.28 mmol). The solution mixture was allowed to stir at room temperature for 2 h. Evaporation of the solvent gave a white solid. The solid was then washed with (2 × 2 mL) hexane and subsequently dried under vacuum. **5**: Yield: 87% white solid. ^{31}P{^{1}H} NMR (C_6D_6): 39.8(d, *i*-Pr_3P, $^2|J_{P-P}|$ = 59 Hz), 33.2(v br, PPh_2). ^{1}H NMR (C_6D_6): 7.56(m, 4H, *o*-Ar, $|J_{H-H}|$ = 8 Hz), 6.97(m, 2H, *p*-Ar, $|J_{H-H}|$ = 8 Hz), 6.87(m, 4H, *m*-Ar, $|J_{H-H}|$ = 8 Hz), 1.59-(m, 3H, CH, $|J_{H-H}|$ = 7 Hz), 0.52(quart, 18H, CH_3, $|J_{H-H}|$ = 7 Hz). ^{11}B NMR (C_6D_6): 34.8. ^{19}F NMR (C_6D_6): −47.9(d, 6F, *o*-C_6F_5, $|J_{F-F}|$ = 22 Hz), −81.0(t, 6F, *m*-C_6F_5, $|J_{F-F}|$ = 21 Hz), −87.5(m, 3F, *p*-C_6F_5, $|J_{F-F}|$ = 23 Hz). ^{13}C{^{1}H} NMR (C_6D_6): 151.9, 142.0, 136.2, 135.5, 133.0, 131.2, 128.7(d, $|J_{P-C}|$ = 15 Hz), 127.8(d, $|J_{P-C}|$ = 15 Hz), 27.0(d, $|J_{P-C}|$ 12 = 61 Hz), 16.7. Anal. Calcd for $C_{39}H_{49}BF_{15}NP_2$: C, 53.75; H, 3.59; N, 1.61. Found: C, 53.21; H, 3.45; N, 1.42.

Synthesis of $Me_3SiNPPh_2(NPR_3)$ (R = *i*-Pr 6, *t*-Bu 7). Both compounds were prepared in a similar manner; thus one procedure is described. Me_3SiN_3 (129 mg; 1.12 mmol) was added dropwise to 335 mg (0.93 mmol) of white crystalline **1**. Gas evolution was observed. The mixture became an orange oil after refluxing overnight. The orange oil was extracted with (2 × 5 mL) hexane, and the hexane was filtered and removed under vacuum. **6**: Yield: 94% white solid. ^{31}P{^{1}H} NMR (C_6D_6): 41.4(d, *i*-Pr_3P, $|^2J_{P-P}|$ = 8 Hz), −6.1(d, PPh_2, $|^2J_{P-P}|$ = 9 Hz). ^{1}H NMR (C_6D_6): δ 8.10(m, 4H, *o*-Ar, $|J_{H-H}|$ = 8 Hz), 7.20(m, 4H, *m*-Ar, $|J_{H-H}|$ = 8 Hz), 7.08(m, 2H, *p*-Ar, $|J_{H-H}|$ = 7 Hz), 2.06(m, 3H, CH, $|J_{H-H}|$ = 7 Hz), 0.94(m, 18H, CH_3, $|J_{H-H}|$ = 8 Hz), 0.41(s, 9H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): 144.3-(d, *ipso*-Ar, $|J_{P-C}|$ = 128 Hz), 132.0(d, *o*-Ar, $|^2J_{P-C}|$ = 10 Hz), 129.4(*p*-Ar), 128.0(d, *m*-Ar, $|^3J_{P-C}|$ = 12 Hz), 25.5(d, CH, $|J_{P-C}|$

(30) Rogers, J. S.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 1288−1298.
(31) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152−2154.
(32) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308−321.
(33) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343−352.
(34) Sun, Y.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1997**, *16*, 2509−2513.
(35) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069−5072.
(36) Sung, R. C. W.; Courtenay, S.; McGarvey, B. R.; Stephan, D. W. *Inorg. Chem.* **2000**, *39*, 2542−2546.
(37) Kickham, J. E.; Guerin, F.; Stewart, J. C.; Stephan, D. W. *Angew. Chem.* **2000**, *112*, 1354−1356.
(38) Guérin, F.; Stewart, J. C.; Beddie, C.; Stephan, D. W. *Organometallics* **2000**.
(39) Guerin, F.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2000**, *39*, 1298−1301.
(40) Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *17*, 1116−1118.
(41) Stephan, D. W.; Guerin, F.; Spence, R. E. v.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *17*, 2046−2048.
(42) Carraz, C.; Stephan, D. W. *Organometallics* **2000**, *19*, 3791−3796.

= 60 Hz), 27.5(s, CH_3), 5.2(s, CH_3). **7**: Yield: 90% white solid. $^{31}P\{^1H\}$ NMR (C_6D_6): 46.5(d, *t*-Bu_3P, $^2J_{P-P}$ = 11 Hz), −8.4(d, PPh_2, $^2J_{P-P}$ = 11 Hz). ^1H NMR (C_6D_6): 8.07(m, 4H, *o*-Ar, J_{H-H} = 8 Hz), 7.20(m, 4H, *m*-Ar, J_{H-H} = 8 Hz), 7.08(m, 2H, *p*-Ar, J_{H-H} = 7 Hz), 1.21(d, 27H, CH_3, J_{H-H} = 13 Hz), 0.41-(s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 144.6(d, *ipso*-Ar, J_{P-C} = 130 Hz), 132.0(d, *o*-Ar, J_{P-C} = 10 Hz), 129.3(s, *p*-Ar), 128.0-(d, *m*-Ar, J_{P-C} = 12 Hz), 41.1(d, C, J_{P-C} = 51 Hz), 30.1(s, CH_3), 5.1(s, CH_3).

Synthesis of $CpTiCl_2(NPPh_2(NPR_3)$ (R = *i*-Pr 8, *t*-Bu 9). Both compounds were prepared in a similar manner; thus one procedure is described. (i) To a clear orange toluene solution (80 mL) of $CpTiCl_3$ (420 mg; 2.00 mmol) was added a toluene solution (10 mL) of **6** (940 mg; 2.10 mmol). The solution mixture was stirred at room temperature overnight. Evaporation of toluene under vacuum gave an orange oil. The oil was extracted with benzene (2 × 50 mL) and filtered, and the solvent was removed under vacuum. The resulting orange oil was washed with (3 × 5 mL) diethyl ether and dried under vacuum. **8**: Yield: 70% yellow solid. **9**: Yield: 91% orange solid. (ii) To a clear orange benzene solution (50 mL) of $CpTiCl_3$ (307 mg; 1.39 mmol) was added Me_3SiN_3 (256 mg; 2.23 mmol). (*Caution!* Although no problems were encountered with this preparation, metal azides may be explosive.) The solution mixture was stirred at room temperature overnight, and a benzene solution (30 mL) of **1** (500 mg; 1.39 mmol) was added. The solution became deep red-orange with gas evolution and was stirred at room temperature overnight. Evaporation of benzene gave a yellow solid, which was then washed with (3 × 10 mL) hexane. **8**: Yield: 84% yellow solid. $^{31}P\{^1H\}$ NMR (C_6D_6): 48.7(d, *i*-Pr_3P, $^2J_{P-P}$ = 8 Hz), −4.87(s, PPh_2). ^1H NMR (C_6D_6): 8.07(m, 4H, *o*-Ar, J_{H-H} = 7 Hz), 7.15(m, 4H, *m*-Ar, J_{H-H} = 8 Hz), 7.07(m, 2H, *p*-Ar, J_{H-H} = 8 Hz), 6.24, 2.24(d, 3H, CH, J_{P-H} = 7 Hz), 1.03(quart, 18H, CH_3, J_{H-H} = 7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): 138.2(d, *ipso*-Ar, J_{P-C} = 129 Hz), 132.3-(d, *o*-Ar, $^3J_{P-C}$ = 11 Hz), 131.4(s, *p*-Ar), 128.7(d, *m*-Ar, $^2J_{P-C}$ = 13 Hz), 114.9(s, Cp), 25.4(d, CH, J_{P-C} = 59 Hz), 17.2. Anal. Calcd for $C_{26}H_{36}Cl_2N_2P_2Ti$: C, 56.03; H, 6.51; N, 5.03. Found: C, 56.99; H, 6.71; N, 5.04. **9**: Yield: 96%. $^{31}P\{^1H\}$ NMR (C_6D_6): 52.3(d, *t*-Bu_3P, $^2J_{P-P}$ = 12 Hz), −11.5(d, PPh_2, $^2J_{P-P}$ = 10 Hz). ^1H NMR (C_6D_6): 8.11(m, 4H, *m*-Ar, J_{H-H} = 8 Hz), 7.14(m, 4H, *o*-Ar, J_{H-H} = 8 Hz), 7.06(m, 2H, *p*-Ar, J_{H-H} = 7 Hz), 6.29(s, 5H, Cp), 1.13(d, 27H, CH_3, J_{P-H} = 14 Hz). $^{13}C-\{^1H\}$ NMR (C_6D_6): 138.5(d, *ipso*-Ar, J_{P-C} = 132 Hz), 132.5-(d, *o*-Ar, $^3J_{P-C}$ = 11 Hz), 131.2(s, *p*-Ar), 128.7(d, *m*-Ar, $^2J_{P-C}$ = 13 Hz), 115.0(s, Cp), 40.9(d, C, J_{P-C} = 50 Hz), 29.8(CH_3). Anal. Calcd for $C_{30}H_{45}Cl_2N_2P_2Ti$: C, 58.64; H, 7.38; N, 4.56. Found: C, 58.31; H, 7.43; N, 4.88.

Synthesis of $CpTiMe_2(NPPh_2(NPR_3))$ (R = *i*-Pr 10, *t*-Bu 11). Both compounds were prepared in a similar manner; thus one procedure is described. To a clear orange toluene solution (10 mL) of **8** (150 mg; 0.27 mmol) was added a 3.0 M diethyl ether solution of CH_3MgBr (0.20 mL; 0.59 mmol). The solution mixture became orange-brown after 30 min of stirring. The solution was allowed to stir at room temperature overnight. Evaporation of toluene gave an orange-brown solid. The solid was extracted with (2 × 5 mL) benzene/hexane (3:1) and filtered, and the solvent was removed under vacuum. **10**: Yield: 91% yellow solid. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.9(d, *i*-Pr_3P, J^2_{P-P} = 7 Hz), −12.1(s, PPh_2). ^1H NMR (C_6D_6): δ 8.11(m, 4H, *m*-Ar, J_{H-H} = 7 Hz), 7.19(m, 4H, *o*-Ar, J_{H-H} = 7 Hz), 7.08-(m, 2H, *p*-Ar, J_{H-H} = 7 Hz), 6.09(s, 5H, Cp), 2.20(m, 3H, CH, J_{H-H} = 7 Hz), 0.97(q, 18H, CH_3, J_{H-H} = 7 Hz), 0.76(s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 141.7(d, *ipso*-Ar, J_{P-C} = 126 Hz), 132.0(d, *o*-Ar, $^3J_{P-C}$ = 10 Hz), 130.2(s, *p*-Ar), 128.3(d, *m*-Ar, $^2J_{P-C}$= 12 Hz), 111.0(s, Cp), 39.7(s, CH_3), 25.5(d, CH, J_{P-C} = 60 Hz), 17.3(s, CH_3). **11**: Yield: 88% yellow solid. $^{31}P\{^1H\}$ NMR (C_6D_6): 49.0(d, *t*-Bu_3P, $^2J_{P-P}$ = 11 Hz), −17.1(d, PPh_2, $^2J_{P-P}$ = 10 Hz). ^1H NMR (C_6D_6): 8.15(m, 4H, *m*-Ar, J_{H-H} = 8 Hz), 7.18(m, 4H, *o*-Ar, J_{H-H} = 7 Hz), 7.07(m, 2H, *p*-Ar, J_{H-H} = 7 Hz), 6.11(s, 5H, Cp), 1.20(d, 27H, CH_3, J_{P-H} = 14 Hz), 0.82(s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 142.1(d, *ipso*-Ar, J_{P-C} = 129 Hz), 132.2(d, *o*-Ar, $^3J_{P-C}$ = 10 Hz), 130.1(s, *p*-Ar), 128.2(d, *m*-Ar, $^2J_{P-C}$ = 12 Hz), 111.1(s, Cp), 41.0(d, C, J_{P-C} = 50 Hz), 40.5(s, CH_3), 29.9(s, CH_3).

Synthesis of $[CpTi(\mu\text{-}Cl)(NPPh_2(NPt\text{-}Bu_3))]_2[BC_6F_5)_4]_2$, 12. To a CH_2Cl_2 solution (1.5 mL) of $B(C_6F_5)_3$ (70 mg; 0.136 mmol) was added dropwise a clear orange CH_2Cl_2 solution (1.5 mL) of **11** (0.200 g; 0.036 mmol). The solution was allowed to stir at room temperature for 2 weeks. A few deep red crystals were obtained upon standing. Yield: <10%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 58.0(d, $^2J_{P-P}$ = 10 Hz), 10.2(d, $^2J_{P-P}$ = 10 Hz). ^1H NMR (CD_2Cl_2): 7.81(m, 8H, *o*-Ar, J_{H-H} = 7 Hz), 7.68(m, 4H, *p*-Ar, J_{H-H} = 8 Hz), 7.57(m, 8H, *m*-Ar, J_{H-H} = 8 Hz), 6.63(s, 10H, Cp), 1.46(d, 54H, CH_3, J_{P-H} = 14 Hz). Anal. Calcd for $C_{56}H_{48}BClF_{20}N_2P_2Ti$: C, 52.34; H, 3.76; N, 2.18. Found: C, 52.01; H, 3.28; N, 2.09.

Ethylene Polymerization These experiments were done in one of two ways. Each is described below. (i) A solution of 6−10 μmol of catalyst precursor in 2.0 mL of dry toluene was added to a flask containing 2.0 mL of dry toluene. Five hundred equivalents of a 10 wt % toluene solution of methylaluminoxane (MAO) was added to the flask. Alternatively, a catalyst precursor was combined with $[Ph_3C][B(C_6F_5)_4]$ under an ethylene atmosphere. The flask was attached to a Schlenk line with cold trap, a stopwatch was started, and the flask was three times evacuated for 5 s and refilled with predried 99.9% ethylene gas. The solution was rapidly stirred under 1 atm of ethylene at room temperature. The polymerization was stopped by the injection of a 1.0 N HCl/methanol solution, total reaction time was noted, and the polymer was isolated. (ii) A 1 L autoclave was dried under vacuum (10^{-2} mmHg) for several hours. Dried toluene (500 mL) was transferred into the vessel under a positive pressure of N_2 and was heated to 30 °C. The temperature was controlled (to ca. ± 2 °C) with an external heating/cooling bath and was monitored by a thermocouple that extended into the polymerization vessel. Solutions of MAO (500 equiv) and catalyst precursor in toluene were sequentially injected. The mixture was stirred for 3 min at a rate of 150 rpm after each addition. The rate of stirring was increased to 1000 rpm, and the vessel was vented of N_2 and pressurized with ethylene (33 psi). Any exotherm was within the allowed temperature differential of the heating/cooling system. The solution was stirred for 1 h, after which time the reaction was quenched with 1 M HCl in MeOH. The precipitated polymer was subsequently washed with MeOH and dried at 100 °C for at least 24 h prior to weighing.

X-ray Data Collection and Reduction. X-ray quality crystals were obtained 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 either on a Rigaku AFC6 four-circle or a Siemens SMART System CCD diffractometer. In the latter case the data were collect in 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° < 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 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 a Pentium computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[43] The heavy atom positions were determined using

(43) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. A* **1968**, *A24*, 390.

Table 1. Crystallographic Parameters[a]

	1	3	4	8	12
formula	$C_{21}H_{31}NP_2$	$C_{24}H_{40}AlNP_2$	$C_{39}H_{32}BF_{15}NP_2$	$C_{26}H_{36}Cl_2N_2P_2Ti$	$C_{59}H_{48}BClF_{20}N_2P_2Ti$
fw	359.41	431.49	872.41	557.31	1321.09
a, Å	9.27450(10)	17.6217(2)	14.654(4)	10.479(5)	11.1052(4)
b, Å	14.67250(10)	15.2123(2)	13.954(8)	25.114(8)	15.3036(6)
c, Å	15.6324(2)	21.5862(3)	19.314(16)	10.932(2)	18.4595(8)
α, deg					93.7560(10)
β, deg	99.890(1)	113.6220(10)	104.11(5)	94.81(4)	106.3140(10)
γ, deg					95.5220(10)
V (Å^3)	2095.65(4)	5301.68(12)	3830(4)	2866.8(16)	2982.8(2)
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
d(calc), g cm^{-1}	1.139	1.081	1.513	1.291	1.471
Z	4	4	4	4	2
μ, mm^{-1}	0.210	0.207	0.218	0.613	0.345
no. of data collected	8907	25 603	18 407	3703	125 429
no. of data used	3647	9190	6628	2393	7643
no. of variables	217	505	523	288	724
R (%)	0.0691	0.0514	0.0732	0.0950	0.1038
R_w (%)	0.1571	0.1247	0.1496	0.2456	0.2960
goodness of fit	0.685	1.044	1.032	1.133	1.251

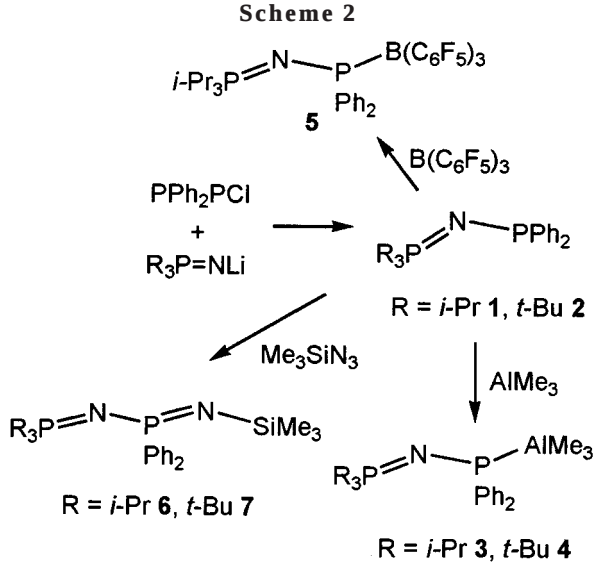
[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.71069$ Å), $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2|/\sum|F_o|^2]^{0.5}$.

Table 2. Ethylene Polymerization Data

catalyst presursor	cocatalyst[a]	time (min)	productivity (g mmol^{-1} h^{-1} atm^{-1})	M_w	M_w/M_n
8[c]	MAO	3.00	299	118 700	1.74
9[b]	MAO	60.00	34	1 083 000	2.24
10[c]	TB	3.00	*d*	*d*	*d*
11[c]	TB	3.00	*d*	*d*	*d*
Cp_2ZrCl_2[c]	MAO	2.00	895	11 600	2.82

[a] MAO = methylaluminoxane; TB = trityl tetrakis(pentafluorophenyl)borate. [b] 33 psi (ethylene), 60−65 °C. [c] 1 atm (ethylene), 25 °C. [d] Insufficient polymerization to report.

Scheme 2



direct methods employing either the SHELXTL or 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 ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. 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. For chiral space groups, the correct enantiomorphic was confirmed by data inversion and refinement. 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.

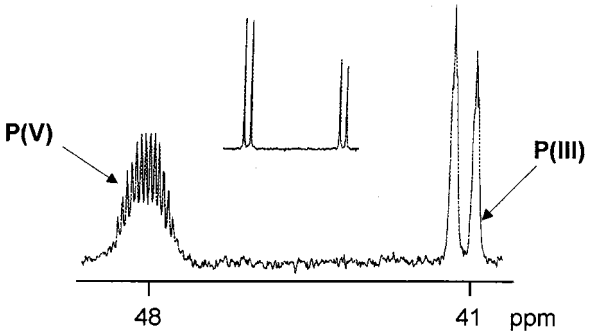


Figure 1. ^{31}P NMR and $^{31}P\{^1H\}$ NMR spectra (inset) of **2**.

Results and Discussion

Synthesis. The phosphinimide−phosphines $PPh_2(NPR_3)$ (R = *i*-Pr **1**, *t*-Bu **2**) were readily prepared in 80−98% yields by stoichiometric reaction of R_3PNLi and chlorodiphenylphosphine under mild conditions (Scheme 2). The presence of two phosphorus atoms was confirmed by the presence of the two doublets in the $^{31}P\{^1H\}$ NMR spectra. For compound **2**, the resonance at 47.9 ppm was attributed to a P(V) center, while the signal at 40.8 ppm was assigned to the P(III) atom. The P−P coupling constant is 62 Hz. In the ^{31}P NMR spectrum, the P(V) signal was split into a multiplet centered at 47.4 ppm, revealing coupling to the *tert*-butyl methyl protons of 12 Hz. On the other hand, only broadening of the P(III) doublet was observed (Figure 1). The structure of **1** was confirmed by X-ray crystallographic data (Figure 2). The P−N bond distances of 1.584(3) and 1.659(3) Å correspond to those expected for P−N double and single bonds, respectively.[44,45] The

(44) Dehnicke, K.; Kreiger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19−65.

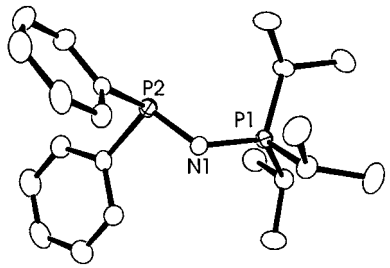


Figure 2. ORTEP drawing of **1**; 30% ellipsoids are shown, hydrogen atoms have been omitted for clarity. P(1)−N(1) 1.584(3) Å; P(2)−N(1) 1.659(3) Å; P(1)−N(1)−P(2) 126.55(19)°.

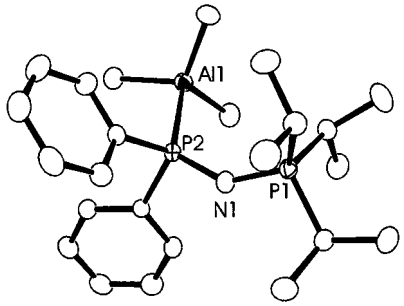


Figure 3. ORTEP drawing of one of the two molecules of **3** in the asymmetric unit; 30% ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles for the two molecules are listed: (a) Al(1)−P(2) 2.5190(11) Å; P(1)−N(1) 1.568(2) Å; P(2)−N(1) 1.627(2) Å; N(1)−P(2)−Al(1) 123.92(9)°; P(1)−N(1)−P(2) 141.52(16)°. (b) Al(2)−P(4) 2.5183(11) Å; P(3)−N(2) 1.567(2) Å; P(4)−N(2) 1.619(2) Å; N(2)−P(4)−Al(2) 124.72(10)°; P(3)−N(2)−P(4) 144.48(18)°.

P−N−P angle is bent as expected, forming an angle of 126.55(19)°.

The Lewis basicity of **1** and **2** was probed. Upon reaction with $AlMe_3$, coordination of Al at the P(III) centers of **1** and **2** was inferred by the shift and the breadth of the upfield signals in the $^{31}P\{^1H\}$ NMR spectra. The formulation of these products as the alane adducts $Me_3AlPPh_2(NPR_3)$ (R = *i*-Pr **3**, *t*-Bu **4**) was confirmed by an X-ray crystallographic study of **3** (Figure 3). The Al−P distances in **3** average 2.5186(11) Å, while the P−N distances range from 1.567(2) to 1.627(2) Å. The Al−N−P and P−N−P angles average 124.82(10)° and 144.50(18)°, respectively, consistent with a sterically crowded pseudo-tetrahedral coordination geometry about phosphorus. In a similar manner, **1** reacts with $B(C_6F_5)_3$ in hydrocarbon solvents at room temperature, generating compound **5** in 87% yield. On the basis of the multinuclear NMR data, **5** is formulated as $(C_6F_5)_3B(PPh_2(NPi\text{-}Pr_3))$. The quadrupolar-broadened resonance in the $^{31}P\{^1H\}$ NMR spectrum is attributed to the boron-bound P(III) center. An X-ray structure of **5** (Figure 4) confirmed the formulation. The P−N bond lengths in **5** are 1.590(4) and 1.577(4) Å. The shortening of the P(III)−N bond is consistent with electron donation to B. The P−N−P bond angle in **5** of 157.1(3)° in considerably larger than that in **3**, presumably a result of the steric demands of both the phosphinimide−phosphine ligand and $B(C_6F_5)_3$.

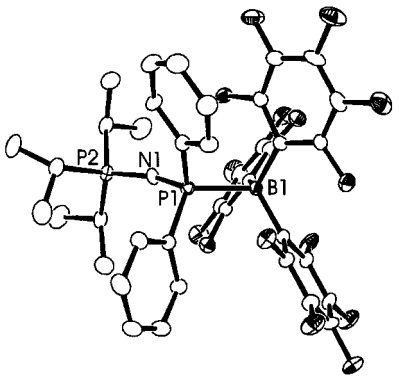
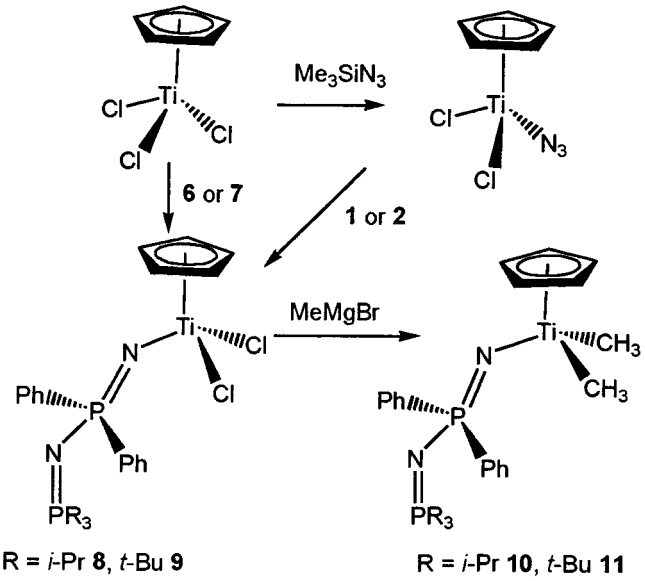


Figure 4. ORTEP drawing of **4**; 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. P(1)−N(1) 1.590(4) Å; P(1)−B(1) 2.135(5) Å; P(2)−N(1) 1.577(4) Å; N(1)−P(1)−B(1) 110.9(2)°; P(2)−N(1)−P(1) 157.1(3)°.

Scheme 3



Oxidation of compounds **1** and **2** via the Staudinger reaction[44,45] with 1 equiv of Me_3SiN_3 proceeds with the elimination of N_2 and the formation of the corresponding phosphinimide−phosphinimine ligands $Me_3SiNPPh_2(NPR_3)$ (R = *i*-Pr **6**, *t*-Bu **7**, respectively. In a standard manner,[40,41] these species react with $CpTiCl_3$ to give titanium(IV) complexes $CpTiCl_2(NPPh_2(NPR_3)$ (R = *i*-Pr **8**, *t*-Bu **9**, respectively) with loss of Me_3SiCl (Scheme 3). Alternatively, complexes **8** and **9** were also prepared via a one-pot reaction of $CpTiCl_3$ with Me_3SiN_3, followed by the addition of 1 equiv of the precursor phosphinimide−phosphine **1** or **2**. The $^{31}P\{^1H\}$ NMR spectra of **8** and **9** consist of the typical AX spin pattern similar to that seen for compounds **6** and **7**. The formulation of these titanium complexes was confirmed spectroscopically and by an X-ray crystallographic study of complex **8** (Figure 5). The Ti−N bond distance of 1.774(3) Å in complex **8** was within the range typically seen for Ti−phosphinimide derivatives.[38] It is interesting to note that the P(1)−N(1) bond distance, 1.612(3) Å, is slightly longer than the P(1)−N(2) and P(2)−N(2) distances of 1.598(4) and 1.593(4) Å. The P−N−Ti angle in **8** of 164.7(2)° approaches linearity, as is typical of Ti−phosphinimide derivatives.[36,38,40,41] Treatment of **8** and

(45) Dehnicke, K.; Weller, F. *Coord. Chem. Rev.* **1997**, *158*, 103−169.

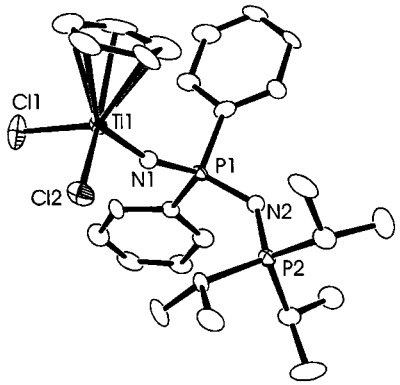


Figure 5. ORTEP drawing of **8**; 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Ti(1)−N(1) 1.774(3), Ti(1)−Cl(2) 2.3145(15) Å; Ti(1)−Cl(1) 2.3176(16), P(1)−N(2) 1.598(4) Å; P(1)−N(1) 1.612(3) Å; P(2)−N(2) 1.593(4) Å; N(1)−Ti(1)−Cl(2) 104.24(12)°; N(1)−Ti(1)−Cl(1) 102.07(12)°; Cl(2)−Ti(1)−Cl(1) 102.01(7)°; N(2)−P(1)−N(1) 118.16(18)°; P(1)−N(1)−Ti(1) 164.7(2)°; P(2)−N(2)−P(1) 134.9(2)°.

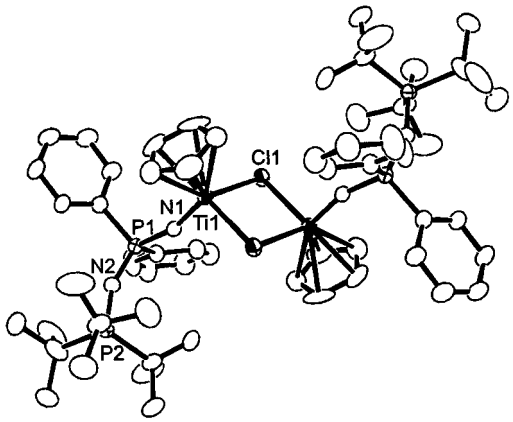


Figure 6. ORTEP drawing of the dication of **12**; 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Ti(1)−N(1) 1.755(5) Å; Ti(1)−Cl(1)′ 2.451(2) Å; Ti(1)−Cl(1) 2.455(2) Å; P(1)−N(2) 1.577(6) Å; P(1)−N(1) 1.666(5) Å; P(2)−N(2) 1.600(6) Å; N(1)−Ti(1)−Cl(1)′ 104.53(17)°; N(1)−Ti(1)−Cl(1) 104.11(17)°; Cl(1)′−Ti(1)−Cl(1) 89.12(6)°; Ti(1)′−Cl(1)−Ti(1) 90.88(6)°; N(2)−P(1)−N(1) 116.6(3)°; P(1)−N(1)−Ti(1) 162.4(3)°; P(1)−N(2)−P(2) 157.6(4)°.

9 with MeMgBr readily provides the alkylated complexes $CpTiMe_2(NPPh_2(NPR_3))$ (R = *i*-Pr **10**, *t*-Bu **11**) in high yields, as evidenced by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR data.

Ethylene Polymerization Compounds **8**−**11** were tested for activity in ethylene polymerization. Employing a large excess of MAO (500 equiv), the species **8** gave rise to an active catalyst. The initial rate of polyethylene production (3 min) in this case was 299 gPE $mmol^{-1}$ h^{-1} at 25 °C and 1 atm ethylene pressure. Employing **9** and MAO at higher temperature (60−65 °C) and pressure (33 psi) resulted in a catalyst that gave 34 gPE $mmol^{-1}$ h^{-1} atm^{-1} over a 1 h period. In both cases, the polydispersity and high molecular weights of the resulting polyethylene were consistent with single-site catalysis. While the activities are significant, they are substantially less than those derived from use of Cp_2ZrCl_2 or other simple Ti−phosphinimide complexes as catalyst precursors under similar conditions.[40,41] It is noteworthy that in contrast to Ti−phosphaadamantylphosphinimide complexes[42] or Ti−trialkylphosphinimide derivatives,[37] these systems are not attacked by excess $AlMe_3$. This tolerance augurs well for catalyst optimization efforts employing related phosphinimide−phosphinimide ligands.

In marked contrast to the above results, related tests at 1 atm ethylene employing the methyl derivatives **10** and **11** using $[Ph_3C][B(C_6F_5)_4]$ as the activator showed minimal polymerization activity. This is in sharp contrast to the analogous phosphinimide complexes $CpTi(NPR_3)Me_2$, where activation with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ leads to catalysts of varying activity depending on the phosphinimide substituents.[40] Stoichiometric reactions of phosphinimide complexes of the form $CpTi(NPR_3)Me_2$ with $B(C_6F_5)_3$ have been shown to lead cleanly to the zwitterionic species $CpTiMe(NPR_3)(\mu\text{-}MeB(C_6F_5)_3)$.[40] Efforts to probe similar reactions with **11** were undertaken in an effort to understand the surprisingly low activity of catalysts derived from **10** and **11**/$[Ph_3C][B(C_6F_5)_4]$. The reaction of **11** with excess $B(C_6F_5)_3$ was monitored by ^{31}P NMR spectroscopy, revealing the formation of a number of unidentified products. Upon standing for 2 weeks in CH_2Cl_2, one of the products crystallized from solution. Although the crystal quality was not the best, the X-ray crystallographic data did establish the formulation of **12** as $[CpTi(\mu\text{-}Cl)(NPPh_2(NPt\text{-}Bu_3))]_2[BC_6F_5)_4]_2$. This centrosymmetric dication of **12** is comprised of a chloro-bridged dimeric unit analogous to the previously reported Ti(III) dimer $[CpTi(\mu\text{-}Cl)(NPt\text{-}Bu_3)]_2$.[36] It is noteworthy that the Ti−Cl and Ti−N distances of 1.755(5) and 2.453(2) Å in **12** are significantly shorter than the corresponding distances of 1.820(2) and 2.4840(11) Å found in $[CpTi(\mu\text{-}Cl)(NPt\text{-}Bu_3)]_2$,[36] consistent with the dicationic charge. A pair of $[BC_6F_5)_4]$ anions provide the required charge balance.

While the mechanism of formation of **12** is the subject of speculation, its formation does permit some inferences to be made. Assuming the initial interaction of **11** with $B(C_6F_5)_3$ is the expected methyl abstraction, the resulting zwitterion is apparently highly reactive. Subsequent reactions are complex but clearly include borate-substituent redistribution as well as activation of the solvent CD_2Cl_2. In contrast, the analogous zwitterionic Ti species of the form $CpTiMe(NPR_3)(\mu\text{-}MeB(C_6F_5)_3)$ are stable.[40] This observation suggests that electron-withdrawing phosphinimide substituents on phosphinimide ligand complexes result in highly Lewis acidic and consequently reactive Ti centers. The activity of the catalysts derived from **8** or **9** and MAO suggests that interactions with MAO serve to stabilize the generated catalysts. Moreover, these results suggest that the steric bulk of these ligands preclude complex degradation by the Al activator as has been seen in related systems.[37,42]

Acknowledgment. Financial support from NSERC of Canada and NOVA Chemicals is gratefully acknowledged. Xiaoliang Gao of NOVA Chemicals is thanked for helpful discussions.

Supporting Information Available: Crystallographic tables and spectra data for **6**, **7**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0101184