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Ti and Zr bidentate bis-phosphinimide complexes

Emily Hollink, Jeffrey C. Stewart, Pingrong Wei and Douglas W. Stephan *
Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B3P4. E-mail: stephan@uwindsor.ca

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The diphosphines *m*-$C_6H_4(CH_2Pt\text{-}Bu_2)_2$ **1** and *m*-$C_6H_4(CH_2PCy_2)_2$ **2** were prepared and oxidized with Me_3SiN_3 to *m*-$C_6H_4(CH_2(t\text{-}Bu_2)PNSiMe_3)_2$ **3** and *m*-$C_6H_4(CH_2(Cy_2)PNSiMe_3)_2$ **4**, and subsequently converted to *m*-$C_6H_4(CH_2$-$(t\text{-}Bu)_2PNH)_2$ **5** and *m*-$C_6H_4(CH_2(Cy)_2PNH)_2$ **6**. Reaction of **5** and **6** with $Ti(NMe_2)_4$ afforded the yellow compounds *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Ti(NMe_2)_2$ **7** and *m*-$C_6H_4(CH_2(Cy)_2PN)_2Ti(NMe_2)_2$ **8**, and the low abundance by-product *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiBr(NMe_2)$ **9**. In a similar manner, the species *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Zr(NEt_2)_2$ **10** was prepared from $Zr(NEt_2)_4$. Compounds **8**, **9** and **10** were converted to $C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiBr_2$ **11**, *m*-$C_6H_4(CH_2$-$(Cy)_2PN)_2TiCl_2$ **13** and $C_6H_4(CH_2(t\text{-}Bu)_2PN)_2ZrCl_2$ **14** *via* reaction with Me_3SiX (X = Br, Cl). Alternatively, *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiCl_2$ **12** and **13** were prepared in low yield from reaction of **3** or **4** with $TiCl_4$. Alkylation of **11** with MeMgBr and $PhCH_2MgBr$ proceeded to give *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiMe_2$ **15** and *m*-$C_6H_4(CH_2$-$(t\text{-}Bu)_2PN)_2Ti(CH_2Ph)_2$ **16**, respectively. The species $(m\text{-}C_6H_4(CH_2(t\text{-}Bu)_2PN)_2)_2Zr$ **17** was prepared from $Zr(CH_2Ph)_4$. These synthetic routes are described and the implications for applications in olefin polymerization catalysis are considered. X-Ray structural data for compounds **1**, **3**, **4**, **5**, **8**, **9** and **16** are reported.

Introduction

A large number of phosphinimide ligand complexes have been prepared and characterized. Much of the earlier work has been reviewed by Dehnicke and co-workers.[1,2] In more recent work, we have reported a series of phosphinimide complexes of Ti and Zr in which the monodentate phosphinimide ligands act as steric equivalents to cyclopentadienyl groups.[3–6] Molecular orbital considerations also infer an electronic analogy.[1,2] This strategy has lead to the development of commercially viable ethylene polymerization catalyst precursors.[7] Thus, complexes of the form $CpTi(NPR_3)X_2$ and $(R_3PN)_2TiX_2$ exhibit similar reactivity to the corresponding metallocene systems. In an effort to further extend this analogy to include *ansa*-metallocene systems, it is logical to consider analogous chelating bis-phosphinimide ligands. Clearly one would envision synthetic routes to such complexes from bis-phosphines, a class of ligand that is well known. While commercially available bis-phosphines have been converted to bis-phosphinimines and further employed to prepare Group IV phosphinimide complexes by the research groups of Cavell[8–10] and Bochmann,[11] the resulting species are either bimetallic complexes, or have resulted in polymerization-inactive carbene derivatives. In contrast, it has only been very recently reported that complexes containing di-anionic, bis-phosphinimides as chelating ligands have been prepared.[12,13] In this manuscript, we address the paucity of chelating bis-phosphinimide ligands, in the development of synthetic routes to their corresponding Ti and Zr complexes.

Experimental

General considerations

The syntheses were performed employing an atmosphere of dry, oxygen-free nitrogen in a Vacuum Atmospheres inert atmosphere glove box or standard Schlenk techniques. ^1H NMR data were acquired on a Bruker Avance 500 MHz spectrometer, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data on a Bruker Avance 300 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are listed downfield from tetramethylsilane in parts per million, and were referenced to the residual proton or carbon peak of the solvent. ^{31}P NMR data were referenced using an external standard relative to 85% H_3PO_4. Spectra were reported in C_6D_6 unless otherwise noted. University of Windsor Analytical Services performed the combustion analyses. GPC analyses were performed employing a Waters 150C GPC using 1,2,4-trichlorobenzene as the mobile phase at 140 °C and were performed at NOVA Chemicals Corporation research facilities in Calgary. The samples were prepared by dissolving the polymer in the mobile phase solvent in an external oven at 0.1% (w/v) and were filtered before injection. Molecular weights are expressed as polyethylene equivalents with a relative standard deviation of 2.9% and 5.0% for M_n and M_w respectively. Reagent grade solvents and NEt_3 were purchased from Aldrich Chemical Co. Benzene, toluene and Et_2O were dried over Na/benzophenone, MeOH dried over Mg, and NEt_3 dried over KOH prior to distillation. C_6D_6 and CD_2Cl_2 were purchased from Canadian Isotopes Laboratories and degassed by at least 4 freeze/pump/thaw cycles before storing over 4 Å molecular sieves. The reagents MeMgBr, Me_3SiCl, Me_3SiBr, Me_3SiN_3, and α,α′-dibromo-*m*-xylene were purchased from Aldrich Chemical Co., $Zr(NEt_2)_4$, $HPt\text{-}Bu_2$, $HPCy_2$ and $Ti(NMe_2)_4$ were purchased from Strem Chemical Co.; all were used without further purification. $Zr(CH_2Ph)_4$ was prepared by a literature method.[14] MAO, t-*i*-BAl (Akzo Nobel) and $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were generously donated by NOVA Chemicals Corporation and were used as received. The phosphine *m*-$C_6H_4(CH_2Pt\text{-}Bu_2)_2$ **1** was prepared by known methods.[15]

Synthesis of *m*-$C_6H_4(CH_2PCy_2)_2$ 2. *Method 1.* α,α′-Dibromo-*m*-xylene (5.71 g, 21.6 mmol) was added to a Schlenk flask. MeOH was added *via* a cannula to generate a slurry, and $HPCy_2$ (9.43 g, 47.5 mmol) was added *via* a syringe at 25 °C. The mixture was stirred for 16 h during which time the solution became homogeneous. NEt_3 (4.80 g, 47.5 mmol) was added *via* a syringe, and the solution was cooled to −30 °C to afford the phosphine as fine, colourless needles (9.65g, 89%).

Method 2. α,α′-Dibromo-*m*-xylene (130 mg, 0.49 mmol) was dissolved in THF (20 mL), and the solution was cooled to −78 °C. A clear solution of $LiPCy_2$ (210 mg, 1.03 mmol) in the same solvent (10 mL) was added dropwise, and the mixture was stirred for 4 h before it was gradually warmed to 25 °C. The solvent was removed *in vacuo*, and the product was extracted with hexanes. Following filtration through Hyflo Super Cel ®, the solution was concentrated, and the product was recrystallized to afford colourless needles (180 mg, 72%). The spectroscopic data were consistent with literature values. ^1H NMR δ: 7.51 (s, 1H, C_6H_4 (*o*′-H)), 7.18 (m, 2H, C_6H_4 (*o*-H)), 7.17 (m, 1H, C_6H_4 (*m*-H)), 2.77 (s, 4H, CH_2), 1.84–1.16 (m, 44H, Cy).

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$^{13}C\{^1H\}$ NMR δ: 140.8 (s, C_6H_4 (*ipso*-C)), 130.9 (s, C_6H_4 (*o*-C)), 128.5 (s, C_6H_4 (*o′*-C)), 127.0 (s, C_6H_4 (*m*-C)), 34.0 (d, $^1J_{P-C}$ = 24 Hz, *C*H_2), 30.3 (d, $^1J_{P-C}$ = 13 Hz, Cy (*ipso*-C)), 29.8 (d, $^2J_{P-C}$ = 10 Hz, Cy (*o*-C)), 27.7 (br s, Cy (*m*-C)), 26.9 (s, Cy (*p*-C)). $^{31}P\{^1H\}$ NMR δ: 1.9 (s).

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2)PNSiMe_3)_2$ 3 and *m*-C_6H_4-$(CH_2(Cy)_2)PNSiMe_3)_2$ 4. Solid **1** (2.06 g, 5.22 mmol) and Me_3SiN_3 (3.01 g, 26.10 mmol) were combined in a Schlenk flask to generate a slurry. The mixture was heated at reflux for 15 h, after which time the excess Me_3SiN_3 was removed *in vacuo*. The resulting beige solid was crushed with a mortar and pestle into a fine powder, washed with pentanes (3 × 5 mL), and dried for an additional 5 h. Yield of **3**: 2.30 g (94%). ^1H NMR δ: 7.53 (s, 1H, C_6H_4 (*o′*-H)), 7.32 (d, 2H, $^3J_{H-H}$ = 5 Hz, C_6H_4 (*o*-H)), 7.23 (d, 1H, $^3J_{H-H}$ = 5 Hz, C_6H_4 (*m*-H)), 2.93 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2), 1.09 (d, 36H, $^3J_{P-H}$ = 10 Hz, *t*-Bu), 0.36 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR δ: 135.3 (s, C_6H_4 (*ipso*-C)), 132.7 (s, C_6H_4 (*o*-C)), 128.8 (s, C_6H_4 (*o′*-C)), 127.6 (s, C_6H_4 (*m*-C)), 37.2 (d, $^1J_{P-C}$ = 60 Hz, *t*-Bu), 31.0 (d, $^1J_{P-C}$ = 56 Hz, CH_2P), 27.4 (s, *t*-Bu), 4.9 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR δ: 24.8 (s). Anal. Calcd for $C_{30}H_{62}N_2P_2Si_2$: C, 63.33; H, 10.98; N, 4.92. Found: C, 63.38; H, 10.89; N, 4.90%. Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. **4**: (2.30 g, 94%). ^1H NMR δ: 7.57 (s, 1H, C_6H_4 (*o′*-H)), 7.22 (br, 2H, C_6H_4 (*o*-H)), 7.16 (br, 1H, C_6H_4 (*m*-H)), 2.82 (d, 4H, $^2J_{P-H}$ = 12 Hz, CH_2P), 1.82–1.50 (m, 18H, PCy_2), 1.48–1.05 (m, 26H, PCy_2), 0.38 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR δ: 134.9 (s, C_6H_4 (*ipso*-C)), 132.3 (s, C_6H_4 (*o*-C)), 128.3 (s, C_6H_4 (*o′*-C)), 128.0 (s, C_6H_4 (*m*-C)), 37.8 (d, $^1J_{P-C}$ = 65 Hz PCy_2 (*ipso*-C)), 34.0 (d, $^1J_{P-C}$ = 60 Hz, CH_2P), 27.1 (br, PCy_2 (*o*-C)), 26.4 (s, PCy_2 (*m*-C)), 25.7 (s, PCy_2 (*p*-C)), 5.2 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR δ: 13.5 (s). Anal. Calcd for $C_{38}H_{70}N_2P_2Si_2$: C, 67.81; H, 10.48; N, 4.16. Found: C, 67.66; H, 10.60; N, 4.03%. Crystals suitable for X-ray diffraction were grown by slow evaporation from pentanes.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PNH)_2$ 5 and *m*-$C_6H_4(CH_2$-$(Cy)_2PNH)_2$ 6. Solid **3** (0.57 g, 1.2 mmol) and MeOH (30 mL) were heated at reflux for 16 h, after which time the volatile products were removed *in vacuo*. The oily residue was washed with hexanes (3 × 10mL) to afford a fine white powder (0.32g, 81%). **5**: ^1H NMR δ: 7.75 (s, 1H, C_6H_4 (*o*-H)), 7.29 (d, 2H, $^3J_{H-H}$ = 4 Hz, C_6H_4 (*o*-H)), 7.12 (br, 1H, C_6H_4 (*m*-H)), 2.86 (d, 4H, $^2J_{P-H}$ = 18 Hz, CH_2P), 1.11 (d, 36H, $^3J_{P-H}$ = 22 Hz, *t*-Bu). $^{13}C\{^1H\}$ NMR δ: 135.8 (s, C_6H_4 (*ipso*-C)), 132.6 (s, C_6H_4 (*o*-C)), 128.3 (s, C_6H_4 (*o′*-C)), 128.0 (s, C_6H_4 (*m*-C)), 36.2 (d, $^1J_{P-C}$ = 56 Hz, *t*-Bu), 30.1 (d, $^1J_{P-C}$ = 39 Hz, CH_2P), 27.9 (s, CMe_3). $^{31}P\{^1H\}$ NMR δ: 48.2 (s). Anal. Calcd for $C_{24}H_{46}N_2P_2$: C, 67.89; H, 10.92; N, 6.60. Found: C, 67.82; H, 10.93; N, 6.61%. **6**: (0.91 g, 96%). ^1H NMR (CD_2Cl_2) δ: 10.67 (br, 2H, N–H), 8.30 (s, 1H, C_6H_4 (*o′*-H)), 7.38 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 7.15 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 3.51 (d, 4H, $^2J_{P-H}$ = 12 Hz, CH_2P), 2.34–1.72 (m, 18H, PCy_2), 1.52–1.23 (m, 26H, PCy_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 140.8 (s, C_6H_4 (*ipso*-C)), 130.9 (s, C_6H_4 (*o*-C)), 128.5 (s, C_6H_4 (*o′*-C)), 127.0 (s, C_6H_4 (*m*-C)), 34.0 (d, $^1J_{P-C}$ = 24 Hz, CH_2P), 30.3 (d, $^1J_{P-C}$ = 13 Hz, PCy_2 (*ipso*-C)), 29.8 (br, PCy_2 (*o*-C)), 27.7 (s, PCy_2 (*m*-C)), 26.9 (s, PCy_2 (*p*-C)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 36.2 (s). Anal. Calcd for $C_{32}H_{54}N_2P_2$: C, 72.69; H, 10.29; N, 5.30. Found: C, 72.61; H, 10.13; N, 5.01%.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Ti(NMe_2)_2$ 7 and *m*-C_6H_4-$(CH_2(Cy)_2PN)_2Ti(NMe_2)_2$ 8. These compounds were prepared in a similar fashion and thus one preparation is detailed. $Ti(NMe_2)_4$ (0.25 mL, 1.08 mmol) was dissolved in PhH (40 mL), and a clear solution of **5** (460 mg, 1.08 mmol) in the same solvent (10 mL) was added dropwise at 25 °C. The clear yellow solution was stirred for 18 h, after which time the volatile products were removed *in vacuo*. The residue was extracted with pentanes (3 × 10 mL), filtered, and the solvent was removed *in vacuo* to afford a yellow solid (412 mg, 68%). **7**: ^1H NMR δ: 8.46 (s, 1H, C_6H_4 (*o′*-H)), 7.09 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 6.89 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 3.45 (s, 12H, NMe_2), 2.85 (d, 4H, $^2J_{P-H}$ = 9 Hz, CH_2P), 1.19 (d, 36H, $^3J_{P-H}$ = 13 Hz, *t*-Bu). $^{13}C\{^1H\}$ NMR δ: 134.9 (s, C_6H_4 (*o*-C)), 134.5 (s, C_6H_4 (*ipso*-C)), 127.4 (s, C_6H_4 (*o*-C)), 127.1 (s, C_6H_4 (*m*-C)), 47.3 (s, NMe_2), 37.1 (d, $^1J_{P-C}$ = 56 Hz, *t*-Bu), 30.0 (d, $^1J_{P-C}$ = 44 Hz, CH_2P), 27.7 (s, *t*-Bu). $^{31}P\{^1H\}$ NMR δ: 12.7 (s). Anal. Calcd for $C_{28}H_{56}N_4P_2Ti$: C, 60.21; H, 10.10; N, 10.03. Found: C, 60.61; H, 10.30; N, 9.93%. **8**: Yellow solid. Yield: 322 mg, 73%. ^1H NMR δ: 8.60 (s, 1H, C_6H_4 (*o*-H)), 7.11 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 7.86 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 3.57 (s, 12H, NMe_2), 2.69 (d, 4H, $^2J_{P-H}$ = 11 Hz, CH_2P), 1.95 (m, 4H, PCy_2), 1.60 (br, 12H, PCy_2), 1.44 (m, 4H, PCy_2), 1.35 (m, 8H, PCy_2), 1.32 (m, 4H, PCy_2), 1.11 (m, 12H, PCy_2). $^{13}C\{^1H\}$ NMR δ: 134.0 (s, C_6H_4 (*ipso*-C)), 133.9 (s, C_6H_4 (*o*-C)), 127.3 (s, C_6H_4 (*o*-C)), 127.1 (s, C_6H_4 (*m*-C)), 48.1 (s, NMe_2), 37.8 (d, $^1J_{P-C}$ = 62 Hz, PCy_2 (*ipso*-C)), 33.1 (d, $^1J_{P-C}$ = 48 Hz, CH_2P), 27.4 (d, $^2J_{P-C}$ = 12 Hz, PCy), 26.6 (s, PCy_2), 26.5 (s, PCy_2). $^{31}P\{^1H\}$ NMR δ: 1.6 (s). Anal. Calcd for $C_{36}H_{64}N_4P_2Ti$: C, 65.24; H, 9.73; N, 8.45. Found: C, 65.16; H, 9.91; N, 8.46%.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiBr(NMe_2)$ 9. This yellow solid was isolated as a by-product (minimal solubility in pentanes) from the above reaction; its presence was due to HBr salts that originated from the phosphine synthesis (typical yields ranged from 3–10%). ^1H NMR δ: 8.67 (s, 1H, C_6H_4 (*o′*-H)), 7.07 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 6.86 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 3.67 (s, 6H, NMe_2), 2.89 (d, 2H, $^2J_{P-H}$ = 14 Hz, CH_2P), 2.80 (d, 2H, $^2J_{P-H}$ = 14 Hz, CH_2P), 1.24 (d, 18H, $^3J_{P-H}$ = 14 Hz, CMe_3), 1.04 (d, 18H, $^3J_{P-H}$ = 14 Hz, CMe_3). $^{13}C\{^1H\}$ NMR δ: 174.9 (s, C_6H_4 (*ipso*-C)), 129.5 (s, C_6H_4 (*o*-C)), 128.3 (s, C_6H_4 (*o*-C)), 127.7 (s, C_6H_4 (*m*-C)), 48.6 (s, NMe_2), 38.2 (d, $^1J_{P-C}$ = 56 Hz, *t*-Bu), 36.2 (d, $^1J_{P-C}$ = 56 Hz, *t*-Bu), 29.2 (d, $^1J_{P-C}$ = 44 Hz, CH_2P), 27.3 (s, *t*-Bu), 27.2 (s, *t*-Bu). $^{31}P\{^1H\}$ NMR δ: 17.2 (s). Due to the presence of **7**, **9** could not be isolated cleanly for microanalyses, consequently repeated analyses gave high C and H values. Anal. Calcd for $C_{26}H_{50}BrN_3P_2Ti$: C, 52.54; H, 8.48; N, 7.07. Found: C, 55.04; H, 8.81; N, 7.11%. Recrystallization from benzene/pentanes afforded a few X-ray quality, pale yellow crystals of **9**.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Zr(NEt_2)_2$ 10. $Zr(NEt_2)_4$ (0.199 g, 0.53 mmol) was diluted in PhH (15 mL), and a clear solution of **5** (223 mg, 0.53 mmol) in the same solvent (10 mL) was added dropwise at 25 °C. The solution was stirred for 24 h, after which time the volatile products were removed *in vacuo* to afford an oily residue. Pentanes were added to precipitate a pale yellow solid, which was subsequently filtered off, washed with pentanes and dried. Yield: 302 mg, 87%. ^1H NMR δ: 8.20 (s, 1H, C_6H_4 (*o′*-H)), 7.09 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 6.88 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 3.59 (q, 8H, $^3J_{H-H}$ = 7 Hz, NCH_2), 2.83 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2P), 1.38 (t, 12H, $^3J_{H-H}$ = 7 Hz, CH_2Me), 1.17 (d, 36H, $^3J_{P-H}$ = 13 Hz, *t*-Bu). $^{13}C\{^1H\}$ NMR δ: 134.9 (d, $^3J_{P-C}$ = 9 Hz, C_6H_4 (*o*-C)), 133.7 (s, C_6H_4 (*ipso*-C)), 127.5 (s, C_6H_4 (*o*-C)), 127.4 (s, C_6H_4 (*m*-C)), 45.8 (s, NCH_2), 37.1 (d, $^1J_{P-C}$ = 56 Hz, *t*-Bu), 30.4 (d, $^1J_{P-C}$ = 44 Hz, CH_2P), 27.9 (s, *t*-Bu), 17.1 (s, CH_2Me). $^{31}P\{^1H\}$ NMR δ: 16.0 (s). Anal. Calcd for $C_{32}H_{64}N_4P_2Zr$: C, 58.41; H, 9.80; N, 8.51. Found: C, 58.66; H, 9.60; N, 8.33%.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiBr_2$ 11, *m*-$C_6H_4(CH_2$-$(Cy)_2PN)_2TiCl_2$ 13 and *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2ZrCl_2$ 14. These compounds were prepared in a similar fashion, with use of the appropriate silyl reagent Me_3SiX (X = Br, Cl), thus a representative experiment is described. A crude mixture of **7** and **9** (551 mg, *ca*. 1.1 mmol) was dissolved in PhH (40 mL) to give a clear yellow solution, and Me_3SiBr (0.30 mL, 2.2 mmol) was added dropwise at 25 °C. The solution was stirred for 20 h, during which time it became heterogeneous. The beige solid that precipitated was filtered off, washed with pentanes (3 × 5 mL) and

dried *in vacuo*. Yield: 522 mg (*ca.* 76%). **11**: ^{1}H NMR (CD_2Cl_2) δ: 8.70 (s, 1H, C_6H_4 (*o*-H)), 7.19 (t, 1H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*m*-H)), 7.12 (d, 2H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*o*-H)), 3.27 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2P), 1.34 (d, 36H, $^3J_{P-H}$ = 14 Hz, *t*-Bu). ^{1}H NMR δ: 8.92 (s, 1H, C_6H_4 (*o′*-H)), 7.04 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 6.80 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 2.78 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2P), 1.10 (d, 36H, $^3J_{P-H}$ = 14 Hz, *t*-Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 135.4 (s, C_6H_4 (*o′*-C)), 133.0 (d, $^2J_{P-C}$ = 8 Hz, C_6H_4 (*ipso*-C)), 128.6 (s, C_6H_4 (*o*-C)), 128.2 (s, C_6H_4 (*m*-C)), 39.1 (d, $^1J_{P-C}$ = 54 Hz, *t*-Bu), 29.4 (d, $^1J_{P-C}$ = 45 Hz, CH_2P), 27.8 (s, *t*-Bu). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 24.7 (s). ^{31}P{^{1}H} NMR δ: 22.4. Anal. Calcd for $C_{24}H_{44}Br_2N_2P_2Ti$: C, 45.74; H, 7.04; N, 4.44. Found: C, 45.31; H, 7.11; N, 4.25%. Preliminary X-ray data: *C*2/*c*, *Z* = 8; *a* = 24.20(1) Å, *b* = 15.02(1) Å, *c* = 19.79(1) Å, β = 94.89(1)°. **13**: White solid (342 mg, 73%). ^{1}H NMR δ: 8.94 (s, 1H, C_6H_4 (*o′*-H)), 7.09 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 6.83 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 2.64 (d, 4H, $^2J_{P-H}$ = 11 Hz, CH_2), 2.10–0.99 (m, 44H, Cy). ^{13}C{^{1}H} NMR δ: 135.1 (s, C_6H_4 (*ipso*-C)), 132.4 (s, C_6H_4 (*o*-C)), 128.1 (s, C_6H_4 (*o′*-C)), 128.0 (s, C_6H_4 (*m*-C)), 37.3 (d, $^1J_{P-C}$ = 62 Hz, Cy (*ipso*-C)), 31.4 (d, $^1J_{P-C}$ = 49 Hz, CH_2), 26.9 (d, $^2J_{P-C}$ = 8 Hz, Cy (*o*-C)), 26.7 (d, $^2J_{P-C}$ = 6 Hz, Cy (*o*-C)), 26.2 (br s, Cy (*m*-C)), 26.1 (br s, Cy (*m*-C)), 25.9 (s, Cy, (*p*-C)). ^{31}P{^{1}H} NMR δ: 8.8 (s). Anal. Calcd for $C_{32}H_{52}Cl_2N_2P_2Ti$: C, 59.54; H, 8.12; N, 4.34. Found: C, 59.92; H, 8.45; N, 4.43%. Colourless crystals suitable for X-ray diffraction were grown by slow evaporation from benzene/pentanes. **14**: Yield: 120 mg, 75%. ^{1}H NMR δ: 7.56 (s, 1H, C_6H_4 (*o*-H)), 7.31 (d, 2H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*o*-H)), 7.23 (t, 1H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*m*-H)), 2.92 (d, 4H, $^2J_{P-H}$ = 11 Hz, CH_2), 1.05 (d, 36H, $^3J_{P-H}$ = 13 Hz, *t*-Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 129.3 (s, C_6H_4 (*o′*-C)), 135.0 (s, C_6H_4 (*ipso*-C)), 127.1 (s, C_6H_4 (*o*-C)), 125.6 (s, C_6H_4 (*m*-C)), 37.2 (d, $^1J_{P-C}$ = 60 Hz, *t*-Bu), 31.0 (d, $^1J_{P-C}$ = 56 Hz, CH_2), 27.6 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 24.5. Anal. Calcd for $C_{24}H_{44}Cl_2N_2P_2Zr$: C, 49.30; H, 7.59; N, 4.79. Found: C, 49.31; H, 7.11; N, 4.25%.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiCl_2$ 12 and *m*-$C_6H_4(CH_2(Cy)_2PN)_2TiCl_2$ 13. These compounds were prepared in a similar manner and thus one preparation is detailed. $TiCl_4$ (0.252 mL, 2.3 mmol) was diluted in PhMe (50 mL), and a clear solution of **4** (1.546 g, 2.3 mmol) in the same solvent (30 mL) was added dropwise at 25 °C. The solution became dark brown and heterogeneous immediately, and was then heated at refluxing temperature for 12 h. Upon cooling, the solution was filtered through Hyflo Super Cel ®, and the solvent was removed *in vacuo*. The crude mixture was purified by recrystallization in PhMe/hexanes at −35 °C to afford colourless crystals. **12**: Yield 244 mg, 30%. ^{1}H NMR δ: 9.05 (s, 1H, C_6H_4 (*o′*-H)), 7.04 (t, 1H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*m*-H)), 6.79 (d, 2H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*o*-H)), 2.76 (d, 4H, $^2J_{P-H}$ = 9 Hz, CH_2P), 1.07 (d, 36H, $^3J_{P-H}$ = 14 Hz, *t*-Bu). ^{13}C{^{1}H} NMR δ: 134.2 (s, C_6H_4 (*ipso*-C)), 127.9 (s, C_6H_4 (*o*-C)), 127.9 (s, C_6H_4 (*o′*-C)), 127.3 (s, C_6H_4 (*m*-C)), 37.8 (d, $^1J_{P-C}$ = 57 Hz, *t*-Bu), 29.9 (d, $^1J_{P-C}$ = 44 Hz, CH_2P), 27.5 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 20.7 (s). Anal. Calcd for $C_{24}H_{44}Cl_2N_2P_2Ti$: C, 53.24; H, 8.21; N, 5.17. Found: C, 53.41; H, 8.35; N, 5.20%. Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. Preliminary X-ray data: $P2_1/c$, *Z* = 8; *a* = 23.5658(2) Å, *b* = 14.7449(2) Å, *c* = 18.6175(2) Å, β = 113.267(1)°. **13**: Yield: 235 mg, 16%. NMR as described above.

Synthesis of *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiMe_2$ 15 and *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Ti(CH_2Ph)_2$ 16. These compounds were prepared in a similar manner using the appropriate Grignard reagent, thus one preparation is detailed. MeMgBr (3.0 M solution in Et_2O, 0.17 mL, 0.50 mmol) was added dropwise to a heterogeneous solution of **11** (153 mg, 0.24 mmol) in Et_2O (30 mL). The solution was stirred for 12 h, after which time the solvent was removed *in vacuo*. The product was extracted with pentanes (3 × 10 mL), and the extracts were filtered through Hyflo Super Cel ®. The solvent was removed *in vacuo* to afford a white solid 75 mg (62%). **15**: ^{1}H NMR δ: 8.48 (s, 1H, C_6H_4 (*o′*-H)), 7.05 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*m*-H)), 6.84 (d, 2H, $^3J_{H-H}$ = 8 Hz, C_6H_4 (*o*-H)), 2.84 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2P), 1.17 (d, 36H, $^3J_{P-H}$ = 14 Hz, *t*-Bu), 0.88 (s, 6H, TiMe). ^{13}C{^{1}H} NMR δ: 134.0 (s, C_6H_4 (*ipso*-C)), 128.2 (s, C_6H_4 (*o*-C)), 127.8 (s, C_6H_4 (*o*-C)), 127.2 (s, C_6H_4 (*m*-C)), 37.9 (d, $^1J_{P-C}$ = 57 Hz, *t*-Bu), 36.9 (s, TiMe), 29.7 (d, $^1J_{P-C}$ = 44 Hz, CH_2P), 27.6 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 12.4 (s). Anal. Calcd for $C_{26}H_{50}N_2P_2Ti$: C, 62.37; H, 10.08; N, 5.60. Found: C, 62.59; H, 10.06; N, 5.22%. **16**: Yield: 62 mg, 74%. ^{1}H NMR δ: 8.20 (s, 1H, C_6H_4 (*o*-H)), 7.28 (m, 8H, CH_2Ph (*o,m*-H)), 7.04 (t, 1H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*m*-H)), 6.89 (t, 2H, $^3J_{H-H}$ = 7 Hz, CH_2Ph (*p*-H)), 6.82 (d, 2H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*o*-H)), 2.86 (s, 4H, CH_2Ph), 2.75 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2P), 1.02 (d, 36H, $^3J_{P-H}$ = 13 Hz, *t*-Bu). ^{13}C{^{1}H} NMR δ: 151.9, 134.0, 133.6, 128.9, 128.2, 127.4, 127.0, 120.1, 67.5 (s, CH_2Ph), 37.4 (d, $^1J_{P-C}$ = 55 Hz, *t*-Bu), 29.7 (d, $^1J_{P-C}$ = 43 Hz, CH_2P), 27.7 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 15.4 (s). Anal. Calcd for $C_{38}H_{58}N_2P_2Ti$: C, 69.92; H, 8.96; N, 4.29. Found: C, 69.59; H, 8.76; N, 4.22%.

Synthesis of (m-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2)_2Zr$ 17. Solid $Zr(CH_2Ph)_4$ (100 mg, 0.22 mmol) was added at RT to a clear solution of **5** (191 mg, 0.45 mmol) in PhH (20 mL). The slurry became dark brown and homogeneous upon stirring for 16 h. Following filtration through Hyflo Super Cel ®, the solvent was removed *in vacuo*, affording a yellow solid. It was washed with pentanes (3 × 5 mL) and dried *in vacuo*. Yield: 96 mg, 47%. ^{1}H NMR δ: 8.34 (s, 1H, C_6H_4 (*o′*-H)), 7.12 (t, 1H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*p*-H)), 6.97 (d, 2H, $^3J_{H-H}$ = 7 Hz, C_6H_4 (*o*-H)), 3.00 (d, 4H, $^2J_{P-H}$ = 10 Hz, CH_2P), 1.28 (d, 36H, $^3J_{P-H}$ = 13 Hz, *t*-Bu). ^{13}C{^{1}H} NMR δ: 135.7 (s, C_6H_4 (*ipso*-C)), 133.4 (s, C_6H_4 (*o*-C)), 127.3 (s, C_6H_4 (*o*-C)), 126.9 (s, C_6H_4 (*m*-C)), 37.4 (d, $^1J_{P-C}$ = 56 Hz, *t*-Bu), 31.9 (d, $^1J_{P-C}$ = 44 Hz, CH_2P), 28.7 (s, *t*-Bu). ^{31}P{^{1}H} NMR δ: 11.7 (s). Anal. Calcd for $C_{48}H_{88}N_4P_4Zr$: C, 61.57; H, 9.47; N, 5.98. Found: C, 61.82; H, 9.93; N, 5.61%.

Polymerization protocols

Ethylene was purchased from BOC Gas Co., and was dried over alumina and 3 Å molecular sieves. A dried 1 L Büchi autoclave was charged with PhMe (50 mL) and MAO (1000 eq, 10% in PhMe) or t-*i*-BAl (20 eq, 25% in heptanes) and the solution was presaturated with the monomer by briefly venting/backfilling (×4) and then stirring under an atmosphere of C_2H_4 for 5 min. The temperature was controlled at 30 °C (to *ca.* +2 °C), the pressure of C_2H_4 set to 12 psig, and the solvent stirred at a rate of 1000 rpm. A solution of the catalyst precursor (PhMe, 350 μmol L^{-1}) was injected, and the mixture was stirred at 25 °C for 10 min. The reaction was quenched with 1 M HCl in MeOH, and the precipitated polymer was washed with HCl, HCl/MeOH and PhMe before drying at 50 °C for at least 48 h prior to weighing.

X-Ray crystallography

Data collection and reduction. Crystals were manipulated and mounted in capillaries in a glove box, 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 second exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45–50.0°$). 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.[16] An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the

SHELXTL[16] solution package operating on a Pentium computer.

Structure solution and refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[17] 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 $\omega(|F_o| - |F_c|)^2$ 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 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. In the case of compounds **9** and **16** the geometry of the benzene of crystallization was constrained such that the C–C bonds were 1.39 Å. Similarly, for **8**, the geometry of the disordered cyclohexyl groups were constrained with C–C bond lengths of 1.54 Å. 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. Crystallographic data are reported in Table 1.

CCDC reference numbers 215279–215286.

See http://www.rsc.org/suppdata/dt/b3/b308114a/ for crystallographic data in CIF or other electronic format.

Results and discussion

We have previously described the synthesis and structure of bis-phosphinimide titanium complexes. In $(R_3PN)_2TiX_2$, as in related complexes of the form $Cp(R_3PN)TiX_2$, the Ti–N–P angle approaches linearity, ranging from 160–180°.[3,4,6] Thus, in order to construct a chelating bis-phosphinimide ligand and preclude bridging phosphinimide fragments, the link between the phosphorus atoms must be long enough to tolerate this linearity at N. To this end, we have employed a linkage derived from the α,α′-*m*-xylene fragment. Preliminary molecular mechanics computations supported the view that such a linkage would be flexible enough to permit chelation and yet not deform the nature of the approximately linear P–N–Ti linkage. The diphosphines *m*-$C_6H_4(CH_2P$*t*-$Bu_2)_2$ **1** and *m*-$C_6H_4(CH_2PCy_2)_2$ **2** were prepared according to literature methods.[15] Subsequent oxidation with Me_3SiN_3 afforded *m*-$C_6H_4(CH_2$-(*t*-Bu_2)$PNSiMe_3)_2$ **3** and *m*-$C_6H_4(CH_2(Cy_2)PNSiMe_3)_2$ **4** in 94% yield. The formulations of these species were consistent with the observed NMR spectral data. Treatment of **3** and **4** with methanol resulted in cleavage of the N–Si bonds to generate *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PNH)_2$ **5** and *m*-$C_6H_4(CH_2(Cy)_2PNH)_2$ **6** in 81% and 96% yield, respectively. In addition, compounds **1**, **3**, **4** and **5** were characterized crystallographically (Fig. 1). The structural data confirmed the formulation and the metric parameters were as expected. P–N bond lengths were ranged from 1.531(2) Å to 1.577(2) Å while the P–N–Si angles varied from 162.49(16)° to 175.12(17)°. This is typical of trimethylsilyl or parent phosphinimines.[2]

Reaction of the ligands **5** and **6** with $Ti(NMe_2)_4$ afforded the yellow compounds *m*-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Ti(NMe_2)_2$ **7** and *m*-$C_6H_4(CH_2(Cy)_2PN)_2Ti(NMe_2)_2$ **8** in yields of 68% and 73%, respectively (Scheme 1). In the case, of **8**, X-ray quality crystals were obtained (Fig. 2). The pseudo-tetrahedral coordination sphere about titanium comprised of four nitrogen atoms. The two Ti–N bond lengths for the phosphinimide scaffold were found to be 1.866(4) Å and 1.879(5) Å. These compare with the

Table 1 Crystallographic data

	1	**3**	**4**	**5**	**8**	**9**·$2C_6H_6$	**16**·C_6H_6
Formula	$C_{24}H_{44}P_2$	$C_{30}H_{62}N_2P_2Si_2$	$C_{38}H_{70}N_2P_2Si_2$	$C_{24}H_{46}N_2P_2$	$C_{36}H_{64}N_4P_2Ti$	$C_{38}H_{62}BrN_3P_2Ti$	$C_{44}H_{64}N_2P_2Ti$
M	394.53	568.94	673.08	424.57	662.75	750.66	730.81
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a/Å	25.554(13)	9.860(9)	10.541(6)	13.457(8)	8.726(5)	14.413(8)	9.799(3)
b/Å	8.449(5)	14.083(12)	15.118(8)	13.908(8)	12.389(8)	17.579(9)	14.917(6)
c/Å	12.046(6)	14.838(13)	15.328(9)	14.713(8)	18.381(11)	17.190(9)	29.534(9)
α/°	90.00	65.975(16)	67.282(9)	90.00	102.835(11)	90.00	90.00
β/°	93.013(10)	75.781(16)	71.043(9)	108.388(10)	93.060(12)	103.449(11)	90.00
γ/°	90.00	84.345(16)	75.162(10)	90.00	90.686(12)	90.00	90.00
V/Å^3	2597(2)	1824(3)	2107(2)	2613(3)	1934(2)	4236(4)	4317(2)
d_{calc}/g cm^{-1}	4	2	2	4	2	4	4
Z	1.009	1.036	1.061	1.079	1.138	1.177	1.124
μ/cm^{-1}	0.173	0.204	0.186	0.178	0.332	1.248	0.303
Data collected	5318	7834	8928	10896	8246	17553	8129
Data $F_o^2>3\sigma(F_o^2)$	1849	5226	6025	3714	5491	6034	5712
Variables	119	325	397	253	364	406	442
R	0.0453	0.0438	0.0449	0.0422	0.0766	0.0802	0.0877
Rw	0.1338	0.1177	0.1246	0.1236	0.2299	0.2391	0.1290
GOF	1.077	0.959	1.036	1.011	0.999	1.138	1.035

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

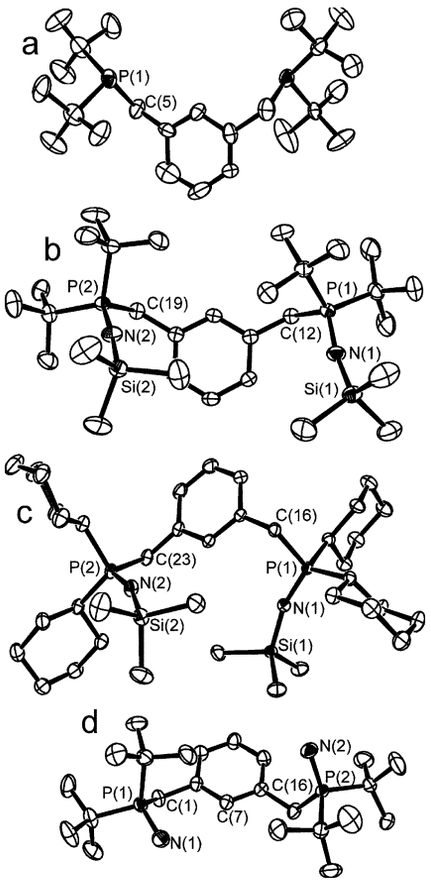
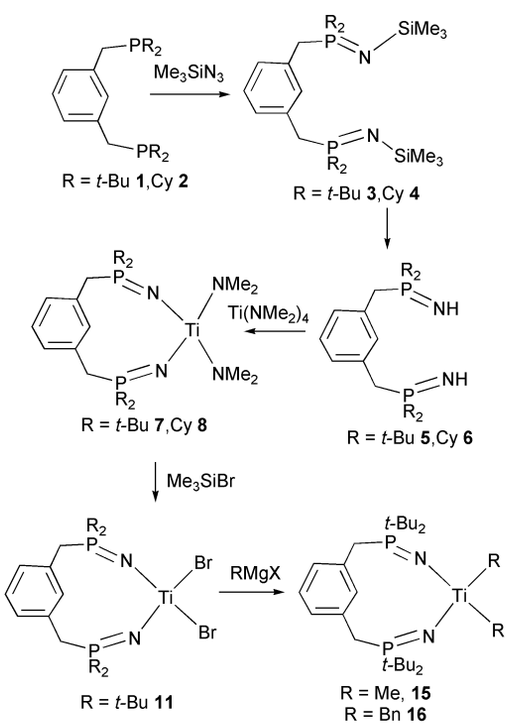


Fig. 1 ORTEP[16] drawings of (a) **1**, (b) **3**, (c) **4**, (d) **5**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): **3**: P(1)–N(1) 1.538(2), P(2)–N(2) 1.531(2), Si(1)–N(1) 1.663(3), Si(2)–N(2) 1.662(3); P(1)–N(1)–Si(1) 165.05(16), P(2)–N(2)–Si(2) 175.12(17). **4**: P(1)–N(1) 1.533(2), P(2)–N(2) 1.533(2), Si(1)–N(1) 1.664(2), Si(2)–N(2) 1.668(2); P(1)–N(1)–Si(1) 163.07(15), P(2)–N(2)–Si(2) 162.49(16). **5**: P(1)–N(1) 1.577(2), P(2)–N(2) 1.581(2).



Scheme 1

Ti–N bond lengths of 1.789(4) Å and 1.792(4) Å found in $(t\text{-Bu}_3\text{PN})_2\text{TiCl}_2$.[4] The amido-ligands gave rise to longer Ti–N bond distances of 1.902(4) Å and 1.926(5) Å, respectively. The

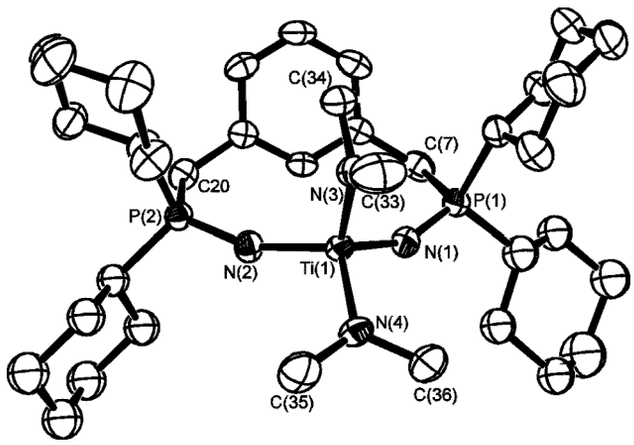


Fig. 2 ORTEP drawing of **8**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ti(1)–N(2) 1.866(4), Ti(1)–N(1) 1.879(5), Ti(1)–N(4) 1.902(4), Ti(1)–N(3) 1.926(5), P(1)–N(1) 1.553(4), P(2)–N(2) 1.567(4); N(2)–Ti(1)–N(1) 115.61(18), N(2)–Ti(1)–N(4) 109.68(18), N(1)–Ti(1)–N(4) 109.08(19), N(2)–Ti(1)–N(3) 109.65(19), N(1)–Ti(1)–N(3) 109.64(19), N(4)–Ti(1)–N(3) 102.3(2), P(1)–N(1)–Ti(1) 151.3(3), P(2)–N(2)–Ti(1) 157.7(3).

shorter titanium–phosphinimide bond lengths are consistent with the stronger donor character of the phosphinimide ligands. The bite angle of the 10-membered chelating ring of the bis-phosphinimide was found to be 115.61(18)°, which accommodated P–N–Ti angles at the phosphinimide nitrogen atoms of 151.3(3)° and 157.7(3)°. These angles are less than those seen in the related bulky bis-phosphinimide complex $(t\text{-Bu}_3\text{PN})_2\text{TiCl}_2$ (175.5(2)°)[4] as well as the related monodentate phosphinimide species $\text{CpTi(NPR}_2\text{CH}_2\text{Ph)Cl}_2$ (175.16(11)°).[18] The P–N bond distances are 1.553(4) Å and 1.567(4) Å, similar to those seen in $(t\text{-Bu}_3\text{PN})_2\text{TiX}_2$ (X = Cl 1579(4) Å, Me 1.561(3) Å).[4] The titanium-bound amido groups exhibit typical planar geometry at nitrogen, although it is interesting to note that the amido ligands are oriented such that the planes are orthogonal to one another.

A low abundance by-product, typically present in 3–10%, was also isolated from the reaction to prepare complex **7**. NMR data and X-ray data confirmed that this latter species was $m\text{-C}_6\text{H}_4(\text{CH}_2(t\text{-Bu})_2\text{PN})_2\text{TiBr(NMe}_2)$ **9** (Fig. 3). It was determined that this species formed as a result of the presence of a residual amount of HBr that was carried through as an impurity from the preparation of the original phosphine **1**. X-Ray data for **9** showed a pseudo-tetrahedral geometry about titanium, with a bidentate bis-phosphinimide ligand, a dimethylamido ligand and a bromide ligand completing the coordination sphere. Titanium–nitrogen bond distances of 1.818(4) Å and 1.827(4) Å were seen for the phosphinimide nitrogen atoms, while the Ti–amido distance was 1.905(5) Å. The increased titanium–nitrogen bond distance in the amido ligand, also observed in the structure of **8**, is consistent with the stronger donor character of the phosphinimide ligand. The chelate ring of the bis-phosphinimide is large enough to allow the angles at nitrogen to approach linearity, and as a result, the Ti–N–P angles are 170.9(3)° and 172.3(3)°. The larger Ti–N–P angles in **9** compared to **8** may be related to a more Lewis acidic titanium center due to the presence of only one ancillary amido ligand. In addition, the *t*-Bu substituted bis-phosphinimide chelating ligand may be a slightly better donor than the Cy-analog. The bite angle of the N–Ti–N in the chelating phosphinimide ligand is 117.1(2)°. In addition, the aromatic ring in the chelate backbone is canted with respect to the TiN_2 plane at an angle of 25.3°. This orients the nearest hydrogen atom on the arene ring 3.105 Å from the Ti center. The planar amido group and the Ti–Br distance of 2.5202(19) Å are typical of Group IV amido complexes.[19] In a similar fashion, related zirconium derivatives were prepared. Reaction of **5** with

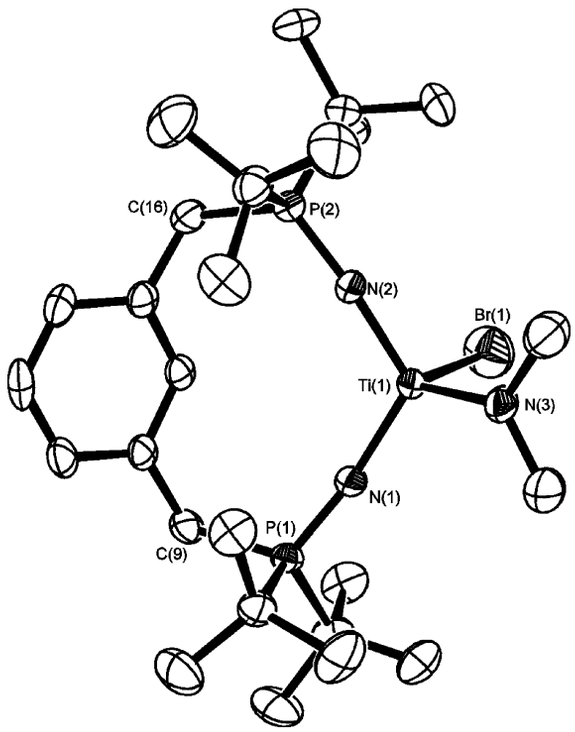


Fig. 3 ORTEP drawing of **9**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ti(1)–N(1) 1.818(4), Ti(1)–N(2) 1.827(4), Ti(1)–N(3) 1.905(5), Ti(1)–Br(1) 2.5202(19), N(1)–P(1) 1.578(5), N(2)–P(2) 1.570(5); N(1)–Ti(1)–N(2) 117.1(2), N(1)–Ti(1)–N(3) 108.9(2), N(2)–Ti(1)–N(3) 109.8(2), N(1)–Ti(1)–Br(1) 109.10(16), N(2)–Ti(1)–Br(1) 107.03(17), N(3)–Ti(1)–Br(1) 104.16(17), P(1)–N(1)–Ti(1) 170.9(3), P(2)–N(2)–Ti(1) 172.3(3), C(26)–N(3)–C(25) 109.6(5), C(26)–N(3)–Ti(1) 124.3(4), C(25)–N(3)–Ti(1) 125.8(4).

$Zr(NEt_2)_4$ gave the species m-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Zr(NEt_2)_2$ **10** in 87% yield.

Reaction of a crude mixture of **7** and **9** with Me_3SiBr resulted in selective cleavage of the titanium amido bonds, affording the species m-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiBr_2$ **11** in 76% yield. Preliminary X-ray data for **11** confirmed the connectivity, however the data were of too poor quality for detailed discussion. In a similar manner, treatment of **8** with Me_3SiCl gave m-$C_6H_4(CH_2(Cy)_2PN)_2TiCl_2$ **13** and m-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2ZrCl_2$ **14** in similarly good yields of 73–75%. Attempts to prepare the Ti–chloride species directly from $TiCl_4$ upon reaction with the trimethylsilyl phosphinimines **3** and **4** was also attempted. Despite the general utility of the Me_3SiCl elimination reaction in the preparation of compounds of the form $CpTi(NPR_3)Cl_2$,[6] this strategy was found to provide low (typically 10–20%) and unreliable yields of $C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiCl_2$ **12** and m-$C_6H_4(CH_2(Cy)_2PN)_2TiCl_2$ **13**. Nonetheless, crystalline samples of these colorless compounds were obtained from numerous attempts to optimize the reaction conditions. In the case of **12** and **13** several X-ray data sets were obtained. Although these data once again confirmed the connectivity, the solutions were of poor quality.

Alkylation of **11** with precise control of the stoichiometry of MeMgBr and $PhCH_2MgBr$ proceeded in a straightforward manner to prepare m-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2TiMe_2$ **15** and m-$C_6H_4(CH_2(t\text{-}Bu)_2PN)_2Ti(CH_2Ph)_2$ **16** in yields of 62% and 74%, respectively. X-Ray data for **16** (Fig. 4) revealed slightly longer titanium–nitrogen phosphinimide bond distances, averaging 1.818(7) Å. The titanium–carbon bond distances were found to be 2.129(8) Å and 2.172(8) Å. The bite angle of the chelating ligand was found to be 117.7(3)°, while the P–N–Ti angles approached linearity at 168.9(5)° and 175.2(5)°.

In a related strategy targeting the Zr analog of **16**, reaction of $Zr(CH_2Ph)_4$ with **5** resulted in the formation of (m-$C_6H_4(CH_2$-

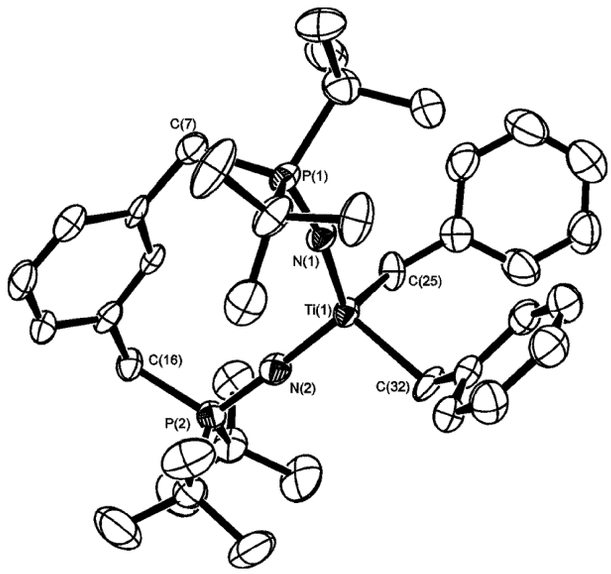
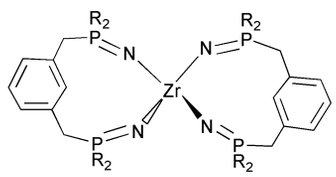


Fig. 4 ORTEP drawing of **16**, 30% ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ti(1)–N(2) 1.805(7), Ti(1)–N(1) 1.831(7), Ti(1)–C(32) 2.129(8), Ti(1)–C(25) 2.172(8), P(1)–N(1) 1.562(7), P(2)–N(2) 1.576(7); N(2)–Ti(1)–N(1) 117.7(3), N(2)–Ti(1)–C(32) 106.3(4), N(1)–Ti(1)–C(32) 113.2(3), N(2)–Ti(1)–C(25) 103.8(3), N(1)–Ti(1)–C(25) 110.1(4), C(32)–Ti(1)–C(25) 104.6(4), P(1)–N(1)–Ti(1) 168.9(5), P(2)–N(2)–Ti(1) 175.2(5).

$(t\text{-}Bu)_2PN)_2)_2Zr$ **17**. Similarly reaction of $Zr(CH_2Ph)_4$ with one equivalent of a chelating diamido ligand, resulted in cleavage of all alkyl ligands to afford the tetrakis-amido derivatives.[20] The yield of **17** was optimized using a 1 : 2 stoichiometry of metal precursor : ligand precursor.



Preliminary evaluation of compounds **12**, **13** and **15** as ethylene polymerization catalysts was performed in a Büchi autoclave (30 ± 2 °C, 1.82 atm of ethylene). Several activation conditions were attempted. Use of MAO resulted in only traces of polymer while use of a solution of t-i-BAl/$[Ph_3C][B(C_6F_5)_4]$ gave poor polymerization activities (1–200 g PE $mmol^{-1}$ h^{-1} atm^{-1}) relative to zirconocene standards. These data stand in marked contrast to that reported for the species $(t\text{-}Bu_3PN)_2$-$TiMe_2$, despite the structural similarity with the present chelate compounds.[4] This suggests that use of the m-xylyl linkage between the phosphorus atoms significantly reduces the steric protection about the phosphinimide-N atoms. This would, in turn, permit attack of the phosphinimide nitrogen centers by Lewis acid activators, ultimately generating polymerization-inactive species. Similar conclusions have been inferred in studies of deactivation pathways for the related titanium bis-phosphinimide species.[21–23] Efforts are continuing to explore the utility of Ti and Zr complexes of chelating bis-phosphinimide ligands. The results of these studies will be reported in due course.

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References

1 K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19.
2 K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103.
3 D. W. Stephan, J. C. Stewart, F. Guerin, R. E. v. H. Spence, W. Xu and D. G. Harrison, *Organometallics*, 1999, **18**, 1116.
4 D. W. Stephan, F. Guerin, R. E. v. H. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak and D. G. Harrison, *Organometallics*, 1999, **18**, 2046.
5 N. Yue, E. Hollink, F. Guérin and D. W. Stephan, *Organometallics*, 2001, **20**, 4424.
6 D. W. Stephan, J. C. Stewart, F. Guerin, S. Courtenay, J. E. Kickham, E. Hollink, C. Beddie, A. J. Hoskin, T. Graham, P. Wei, R. E. v. H. Spence, W. Xu, L. Koch, X. Gao and D. G. Harrison, *Organometallics*, 2003, **22**, 1937.
7 D. W. Stephan, J. C. Stewart, D. G. Harrison, *Eur. Pat. Appl.*, 890581, 1999, p. 21.
8 R. P. K. Babu, R. McDonald, S. A. Decker, M. Klobukowski and R. G. Cavell, *Organometallics*, 1999, **18**, 4226.
9 R. G. Cavell, R. P. K. Babu, A. Kasani and R. McDonald, *J. Am. Chem. Soc.*, 1999, **121**, 5805.
10 R. P. K. Babu, R. McDonald and R. G. Cavell, *Chem. Commun.*, 2000, 481.
11 M. J. Sarsfield, M. Said, M. Thornton-Pett, L. A. Gerrard and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2001, 822.
12 U. Siemeling, L. Koelling, O. Kuhnert, B. Neumann, A. Stammler, H.-G. Stammler, G. Fink, E. Kaminski, A. Kiefer and R. R. Schrock, *Z. Anorg. Allg. Chem.*, 2003, **629**, 781.
13 U. Siemeling, L. Koelling, A. Stammler and H.-G. Stammler, *J. Chem. Soc., Dalton Trans.*, 2002, 3277.
14 R. Beckhaus, U. Duemichen and K. H. Thiele, *Z. Chem.*, 1986, **26**, 261.
15 D. G. Gusev, M. Madott, F. M. Dolgushin, K. A. Lyssenko and M. Y. Antipin, *Organometallics*, 2000, **19**, 1734.
16 G. M. Sheldrick, SHELXTL, University of Göttingen, Germany, 1997; M. N. Burnett and C. K. Johnson, ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1996.
17 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
18 E. Hollink, PhD Thesis, University of Windsor, Windsor, 2003.
19 S. B. Hawkeswood and D. W. Stephan, *Comprehensive Coordination Chemistry II*, ed. A. Wedd, Elsevier, London, 2003, vol. 3.
20 V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 1162.
21 J. E. Kickham, F. Guerin, J. C. Stewart, E. Urbanska and D. W. Stephan, *Organometallics*, 2001, **20**, 1175.
22 J. E. Kickham, F. Guerin, J. C. Stewart and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2000, **39**, 3263.
23 J. E. Kickham, F. Guerin and D. W. Stephan, *J. Am. Chem. Soc.*, 2002, **124**, 11486.