Functionalizing Titanium−Phosphinimide Complexes

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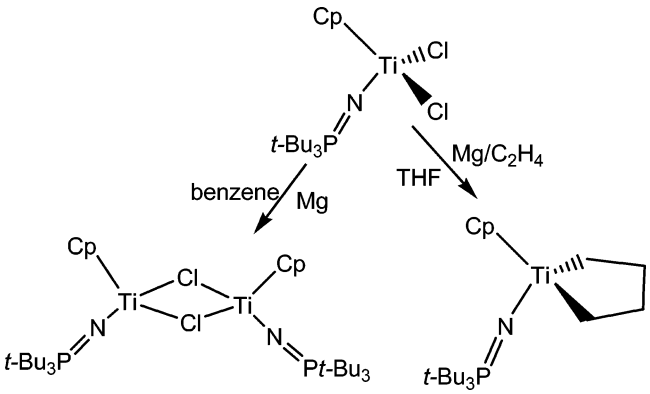
Received June 27, 2006

The reaction of the titanacycle CpTi(NP*t*-Bu_3)(C_4H_8) (**1**) with benzyl halides, 4-bromo-1-butene, and allyl chloride proceeds with loss of ethylene to give CpTiX(NP*t*-Bu_3)(CH_2Ph) (X = Cl, **3**; Br, **4**), CpTiBr(NP*t*-Bu_3)($CH_2CH_2CHCH_2$) (**5**), and CpTiCl(NP*t*-Bu_3)(CH_2CHCH_2) (**6**), respectively. Complexes **4** and **6** were readily alkylated to CpTiMe(NP*t*-Bu_3)(CH_2Ph) (**7**) and CpTiMe(NP*t*-Bu_3)(CH_2CHCH_2) (**8**), respectively. Loss of ethylene also occurs on reaction of **1** with bipyridine to give CpTi(NP*t*-Bu_3)(bipy) (**9**). In contrast, reaction of **1** with $ClSiMePh_2$ in the presence of PMe_3 gave CpTiCl(NP*t*-Bu_3)($CH_2CH_2SiPh_2Me$) (**10**). In a similar fashion, the two-carbon derivatives CpTiCl(NP*t*-Bu_3)($CH_2CH_2SiMe_3$) (**11**), CpTiCl(NP*t*-Bu_3)($CH_2CH_2Si(SiMe_3)_3$) (**12**), CpTi(NP*t*-Bu_3)($CH_2CH_2SiMe_3$)(OSO_2CF_3) (**13**), CpTiCl(NP*t*-Bu_3)(CH_2CH_2Sn*n*-Bu_3) (**14**), CpTiCl(NP*t*-Bu_3)($CH_2CH_2SiCl_3$) (**15**), and [CpTiCl(NP*t*-Bu_3)(CH_2CH_2)]$_2$-$SiCl_2$ (**16**) were produced. In the absence of PMe_3, reaction of **1** with $SiCl_4$ and $ClSnMe_3$ gave the four-carbon derivatives CpTiCl(NP*t*-Bu_3)($CH_2CH_2CH_2CH_2SiCl_3$) (**17**) and CpTiCl(NP*t*-Bu_3)($CH_2CH_2CH_2CH_2$-$SnMe_3$) (**18**), while reaction of **1** with $ClSnPh_3$ gave only the two-carbon chain derivative CpTiCl(NP*t*-Bu_3)($CH_2CH_2SnPh_3$) (**19**). Nonetheless, in the presence and absence of PMe_3 reaction of **1** with ClBcat or $ClPPh_2$ gave the analogous two- and four-carbon derivatives CpTiCl(NP*t*-Bu_3)(CH_2CH_2Bcat) (**20**), CpTiCl(NP*t*-Bu_3)($CH_2CH_2CH_2CH_2$Bcat) (**21**), CpTiCl(NP*t*-Bu_3)($CH_2CH_2PPh_2$)(**22**), and CpTiCl(NP*t*-Bu_3)($CH_2CH_2CH_2CH_2PPh_2$) (**23**), respectively. The corresponding species CpTiCl(NP*t*-Bu_3)($CH_2CH(CH_3)CH(CH_3)CH_2PPh_2$) (**24**) was prepared from CpTi(NP*t*-Bu_3)($CH_2CHMe)_2$ (**2**), while complexation of **23** and **24** afforded CpTiCl(NP*t*-Bu_3)($CH_2CH_2CH_2CH_2PPh_2$)RhCl(cod) (**25**) and CpTiCl(NP*t*-Bu_3)($CH_2CH(CH_3)CH(CH_3)CH_2PPh_2$)RhCl(cod) (**26**). The mechanisms affording the functionalized two- and four-carbon derivatives above are discussed and the implications considered.

Introduction

Reviews in the recent literature have described the synthesis and structure of phosphinimide complexes of transition metal and main group elements[1,2] as well as the development of early metal−phosphinimide catalysts for olefin polymerization.[3] Complexes in which the phosphinimide-nitrogen is accessible have proved to be less active catalysts as they are attacked by Lewis acids which subsequently effect C−H bond activation processes,[4−6] and undergo reduction to give phosphinimide-bridged dimers.[7] The participation of the ligand in the chemistry can be eliminated by employing sterically demanding phosphinimide substituents. Such derivatized ligands offer highly effective polymerization catalysts and are not deactivated by Lewis acids. In these cases, it appears that the steric protection provided by the substituents on P is comparable to that offered by cyclopentadienyl ligands, and yet the displacement of such steric protection from the metal by the intervening nitrogen atom accommodates a reactive metal atom coordination sphere.

Scheme 1



In a recent study probing the reactivity of systems containing sterically demanding, ancillary phosphinimide ligands, we showed that reduction of CpTi(NP*t*-Bu_3)Cl_2 by Mg was solvent dependent. Reduction in benzene afforded the dimer [CpTi(NP*t*-Bu_3)(μ-Cl)]$_2$[8] (Scheme 1), whereas reduction in THF generated a putative Ti(II) species, which could be intercepted by olefins, acetylenes, and CO.[7] The resulting product intercepted by ethylene, CpTi(NP*t*-Bu_3)($CH_2CH_2)_2$ (Scheme 1), exhibits a classical metallocyclic structure in the solid state. However, its reactivity suggested this compound could act as a Ti(II) synthon via loss of ethylene. In this paper, we probe the reactivity of this species with a variety of alkyl and main group halides.

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10.1021/om060565p CCC: $33.50
Publication on Web 08/22/2006

While alkyl halides are shown to afford products best described as arising from oxidative addition to Ti(II), main group halides react differently, affording main group addition to two- or four-carbon chains on Ti. In this fashion, these synthetic strategies offer new approaches to functionalized Ti−phosphinimide complexes. Mechanistic implications of this reactivity are considered in the light of preliminary DFT calculations.

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 MBraun or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs type solvent purification system manufactured by Innovative Technologies. All organic reagents were purified by conventional methods. ^{1}H, ^{31}P{^{1}H}, ^{11}B{^{1}H}, ^{29}Si{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C_6D_6 at 25 °C unless otherwise noted. For ^{1}H and ^{13}C{^{1}H} NMR spectra, trace amounts of protonated solvents were used as reference, and chemical shifts are reported relative to $SiMe_4$. ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and $SiMe_4$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz. Combustion analyses were performed in-house employing a Perkin-Elmer CHN analyzer. CpTi(NP*t*-Bu$_3$)Cl$_2$, CpTi(NP*t*-Bu$_3$)(CH$_2$CH$_2$)$_2$ (**1**), and CpTi(NP*t*-Bu$_3$)(CH$_2$CHMe)$_2$ (**2**) were prepared according to published procedures.[3,9] Alkyl, Si, Sn, P, and B halides employed herein were purchased from Aldrich Chemical Co. and used as received.

Synthesis of CpTiX(NP*t*-Bu$_3$)(CH$_2$Ph) (X = Cl, 3; Br, 4), CpTiBr(NP*t*-Bu$_3$)(CH$_2$CH$_2$CHCH$_2$) (5), and CpTiCl(NP*t*-Bu$_3$)(CH$_2$CHCH$_2$) (6). These compounds were prepared in a similar fashion using the appropriate alkyl halide reagent, and thus only one example is detailed. Compound **1** (261 mg, 0.68 mmol) was dissolved in 6 mL of toluene, and PMe_3 (270 μL, 2.61 mmol) and benzyl bromide (81 μL, 0.68 mmol) were added at room temperature. After 2 h the solvent was removed in vacuo to yield 220 mg (65%) of the product **4**. It was subsequently shown that addition of PMe_3 is not required and its presence had no effect on the yield. **3**: Yield: 44%. ^{1}H NMR: 7.40 (m, 4 H, Ph), 7.02 (m, 1 H, Ph), 6.17 (s, 5 H, Cp), 3.79, 2.79 (d, $^2J_{HH}$ = 10, 1 H, TiCH$_2$), 1.24 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu$_3$). ^{13}C{^{1}H} NMR: 152.4, 127.4, 121.5, 115.0 (Ph), 113.7 (Cp), 71.4 (TiCH$_2$), 41.5 (d, $^1J_{PC}$ = 45, *t*-Bu$_3$), 29.5 (*t*-Bu$_3$). ^{31}P{^{1}H} NMR: 40.2. **4**: Yield: 65%. ^{1}H NMR: 7.29 (m, 4 H, Ph), 6.95 (m, 1 H, Ph), 6.10 (s, 5 H, Cp), 3.55, 2.59 (d, $^2J_{HH}$ = 10, 1 H, TiCH$_2$), 1.17 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu$_3$). ^{13}C{^{1}H} NMR (partial): 152.3, 127.4, 121.5 (Ph), 114.0 (Cp), 74.7 (TiCH$_2$), 41.6 (d, $^1J_{PC}$ = 42, *t*-Bu$_3$), 29.6 (*t*-Bu$_3$). ^{31}P{^{1}H} NMR: 42.0. Anal. Calcd for $C_{24}H_{39}BrNPTi$: C, 57.61, H, 7.86, N, 2.80. Found: C, 57.04, H, 8.10, N, 2.21. Preliminary X-ray data: a = 14.727(6) Å, b = 17.836(7) Å, c = 17.836(8) Å, orthorhombic space group not unambiguously determined. **5**: Yield: 74%. X-ray-quality crystals were obtained via recrystallization from toluene. ^{1}H NMR: 6.28 (s, 5 H, Cp), 5.99 (m, 1 H, C*H*CH$_2$), 5.09, 4.94 (m, 1 H, CHC*H*$_2$), 2.63 (m, 2 H, TiCH$_2$C*H*$_2$), 2.13, 1.61 (dt, $^2J_{HH}$ = 5, $^3J_{HH}$ = 11, 1 H, TiC*H*$_2$), 1.16 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu$_3$). ^{13}C{^{1}H} NMR: 144.0 (*C*HCH$_2$), 111.1 (CH*C*H$_2$), 112.5 (Cp), 68.8 (TiCH$_2$), 41.4 (d, $^1J_{PC}$ = 45, *t*-Bu$_3$), 39.0 (TiCH$_2$*C*H$_2$), 29.6 (*t*-Bu$_3$). ^{31}P{^{1}H} NMR: 39.5. Anal. Calcd for $C_{21}H_{39}BrNPTi$: C, 54.32, H, 8.47, N, 3.02. Found: C, 54.53, H, 8.66, N, 2.99. **6**: Yield: 59%. ^{1}H NMR: 6.50 (quin, $^3J_{HH}$ = 11, 1 H, C_3H_5), 6.27 (s, 5 H, Cp), 3.82 (d, $^3J_{HH}$ = 11, 4 H, C_3H_5), 1.14 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu$_3$). ^{13}C{^{1}H} NMR: 146.5 (C_3H_5), 114.0 (Cp), 87.1 (C_3H_5), 41.5 (d, $^1J_{PC}$ = 45, *t*-Bu$_3$), 29.5 (*t*-Bu$_3$). ^{31}P{^{1}H} NMR: 39.8. Anal. Calcd for $C_{20}H_{37}ClNPTi$: C, 59.19, H, 9.19, N, 3.45. Found: C, 59.37, H, 9.32, N, 3.64.

Synthesis of CpTiMe(NP*t*-Bu$_3$)(CH$_2$Ph) (7) and CpTiMe(NP*t*-Bu$_3$)(CH$_2$CHCH$_2$) (8). These compounds were prepared in a similar fashion, and thus one preparation is detailed. Compound **4** (87 mg, 0.17 mmol) was dissolved in 4 mL of toluene, and methyl Grignard solution (57 μL, 3M in THF) was added at room temperature. After 0.5 h the solvent was removed in vacuo and the brown residue extracted with pentane. Cooling overnight (−35 °C) afforded orange crystals (30 mg, 40%). **7**: ^{1}H NMR: 7.26 (t, $^3J_{HH}$ = 8, 2 H, *m*-Ph), 7.03 (d, $^3J_{HH}$ = 7, 2 H, *o*-Ph), 6.92 (t, $^3J_{HH}$ = 8, 1 H, *p*-Ph), 6.01 (s, 5 H, Cp), 2.96, 2.36 (d, $^2J_{HH}$ = 10, 1H, TiCH$_2$), 1.18 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu$_3$), 0.77 (s, 3 H, TiMe). ^{13}C{^{1}H} NMR (partial): 153.0, 126.2, 120.5 (Ph), 112.1 (Cp), 69.0 (TiCH$_2$), 42.1 (TiMe), 41.3 (d, $^1J_{PC}$ = 47, *t*-Bu$_3$), 29.6 (*t*-Bu$_3$). ^{31}P{^{1}H} NMR: 34.1. Anal. Calcd for $C_{25}H_{42}NPTi$: C, 68.95, H, 9.72, N, 3.22. Found: C, 68.20, H, 9.92, N, 3.17. Preliminary X-ray data: a = 20.194(4) Å, b = 14.670(3) Å, c = 8.578(2) Å, orthorhombic space group: *Pna*2$_1$. **8**: Yield: 22% (brown powder). ^{1}H NMR: 6.37 (quin, $^3J_{HH}$ = 11, 1 H, C_3H_5), 6.18 (s, 5 H, Cp), 3.52 (d, $^3J_{HH}$ = 11, 4 H, C_3H_5), 1.15 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu$_3$), 0.72 (s, 3 H, TiCH$_3$). ^{13}C{^{1}H} NMR: 148.3 (C_3H_5), 111.8 (Cp), 84.2 (C_3H_5), 41.3 (d, $^1J_{PC}$ = 49, *t*-Bu$_3$), 39.9 (TiCH$_3$), 29.6 (*t*-Bu$_3$). ^{31}P{^{1}H} NMR: 31.6. Anal. Calcd for $C_{21}H_{40}NPTi$: C, 65.44, H, 10.46, N, 3.63. Found: C, 65.21, H, 10.33, N, 3.47.

Synthesis of CpTi(NP*t*-Bu$_3$)(bipy) (9). The titanacycle **1** (242 mg, 0.62 mmol) and 2,2′-bipyridyl (98 mg, 0.62 mmol) were dissolved in 6 mL of toluene at room temperature. The dark blue solution was stirred for 2 h. After filtration through Celite the solvent was removed partly in vacuo. Cooling overnight afforded dark blue crystals in 61% yield (185 mg). ^{1}H NMR: 7.49 (br d, 2 H, bipy), 7.29 (d, $^3J_{HH}$ = 9, 2 H, bipy), 6.43 (s, 5 H, Cp), 5.31, 4.03 (br m, 2 H, bipy), 1.02 (d, $^3J_{HH}$ = 12, 27 H, *t*-Bu). ^{1}H NMR (−80 °C, toluene-d_8): 7.43 (d, $^3J_{HH}$ = 6, 2 H, bipy), 7.34 (d, $^3J_{HH}$ = 9, 2 H, bipy), 6.37 (br t, 2 H, bipy), 6.31 (s, 5 H, Cp), 5.35 (t, $^3J_{HH}$ = 6, 2 H, bipy), 1.02 (br d, 18 H, *t*-Bu), 0.83 (br d, 9 H, *t*-Bu).^{13}C{^{1}H} NMR: 149.5, 116.6 (bipy), 109.6 (Cp), 40.4 (d, $^1J_{PC}$ = 46, *t*-Bu). More signals of the bipy ligand were not detected. Dept135 (−30 °C, toluene-d_8): 149.9, 125.8, 121.9, 104.9 signals detected for the bipy ligand. ^{31}P{^{1}H} NMR: 33.8. Anal. Calcd for $C_{27}H_{40}N_3PTi$: C, 66.80, H, 8.30, N, 8.66. Found: C, 65.94, H, 8.29, N, 8.58.

Synthesis of CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$SiPh$_2$Me) (10), CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$SiMe$_3$) (11), CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$Si(SiMe$_3$)$_3$) (12), CpTi(NP*t*-Bu$_3$)(CH$_2$CH$_2$SiMe$_3$)(OSO$_2$CF$_3$) (13), CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$Sn*n*-Bu$_3$) (14), CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$SiCl$_3$) (15), and [CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$)]$_2$SiCl$_2$ (16). These compounds were prepared in a similar fashion using the appropriate alkyl halide reagent and stoichiometry, and thus only one example is detailed. Complex **1** (625 mg, 1.62 mmol) was dissolved in 8 mL of pentane, and 600 μL (5.80 mmol) of PMe_3 was added. After 5 min $ClSiMePh_2$ (341 μL, 1.63 mmol) was added at room temperature and stirred for 3 h. After filtration through Celite the solvent was removed partly in vacuo. Cooling overnight afforded red-brown crystals in 59% yield (559 mg). **10**: ^{1}H NMR: 7.66 (br t, 4 H, *o*-SiPh$_2$), 7.22 (br t, 6 H, *p*-SiPh$_2$, *m*-SiPh$_2$), 6.25 (s, 5 H, Cp), 2.30, 1.47 (br dt, 1 H, TiCH$_2$), 1.81 (m, 2 H, TiCH$_2$C*H*$_2$Si), 1.13 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu), 0.59 (s, 3 H, SiMe). ^{13}C{^{1}H} NMR: 139.0, 138.8, 135.2, 135.1, 129.0 (SiPh$_2$), 112.4 (Cp), 60.6 (TiCH$_2$), 41.4 (d, $^1J_{PC}$ = 45, *t*-Bu), 29.5 (*t*-Bu), 21.1 (TiCH$_2$*C*H$_2$Si), −4.1 (SiMe). ^{31}P{^{1}H} NMR: 37.8, ^{29}Si{^{1}H} NMR: −8.6. Anal. Calcd for $C_{32}H_{49}ClNPSiTi$: C, 65.13, H, 8.37, N, 2.37. Found: C, 65.72, H, 8.60, N, 2.34. **11**: Yield: 95%. ^{1}H NMR: 6.28 (s, 5 H, Cp), 2.12, 1.61 (m, 1 H, TiCH$_2$), 1.25 (m, 2 H, TiCH$_2$C*H*$_2$Si), 1.18 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu), 0.10 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR: 112.5 (Cp), 62.2 (TiCH$_2$), 41.5 (d, $^1J_{PC}$ = 45, *t*-Bu), 29.6 (*t*-Bu), 24.6 (TiCH$_2$*C*H$_2$Si), −1.6 (SiMe). ^{31}P{^{1}H}

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NMR: 37.6. ^{29}Si{^{1}H} NMR: −31.0. Anal. Calcd for $C_{22}H_{45}ClNPSiTi$: C, 56.71, H, 9.73, N, 3.01. Found: C, 56.39, H, 9.60, N, 3.34. **12**: Yield: 100%. ^{1}H NMR: 6.30 (s, 5 H, Cp), 2.37 (m, 2 H, $TiCH_2$), 1.63 (m, 2 H, $SiCH_2$), 1.23 (d, $^3J_{P-H}$ = 12, 27 H, *t*-Bu), 0.35 (s, 27 H, SiMe); ^{13}C{^{1}H} NMR: 112.3 (Cp), 69.0 ($TiCH_2$), 41.5 (d, $^1J_{P-C}$ = 46, *t*-Bu), 29.7 (*t*-Bu), 15.1 (CH_2Si), 1.78($SiMe_3$), ^{31}P{^{1}H} NMR: 38.5, ^{29}Si{^{1}H} NMR: −13.1, −79.3. Anal. Calcd for $C_{28}H_{63}ClNPSi_4Ti$: C, 52.51, H, 9.92, N, 2.19. Found: C, 52.72, H, 9.78, N, 2.34. **13**: Yield: 100%. ^{1}H NMR: 6.30 (s, 5 H, Cp), 2.18 (m, 2 H, $TiCH_2$), 1.70 (m, 2 H, $SiCH_2$), 1.08 (d, $^3J_{P-H}$ = 12, 27 H, *t*-Bu), 0.11 (s, 9 H, SiMe). ^{13}C{^{1}H} NMR: 112.0 (Cp), 65.6 ($TiCH_2$), 41.0 (d, $^1J_{P-C}$ = 46, *t*-Bu), 29.5 (*t*-Bu), 21.9 (CH_2Si), 1.1 ($SiMe_3$). ^{31}P{^{1}H} NMR: 43.2. ^{29}Si{^{1}H} NMR: −31.5. Anal. Calcd for $C_{23}H_{45}F_3O_3NPSiTi$: C, 47.66, H, 7.83, N, 2.42. Found: C, 47.52, H, 7.67, N, 2.31. **14**: Yield: 78% (dark red oil). ^{1}H NMR: 6.31 (s, 5 H, Cp), 2.43 (m, 1 H, $TiCH_2$), 1.75 (m, 9 H, $SnCH_2$ + $TiCH_2$), 1.44 (m, 12 H, $SnCH_2(CH_2)_2CH_3$), 1.22 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu), 1.00 (br d, 9 H, $Sn(CH_2)_3CH_3$). ^{13}C{^{1}H} NMR: 112.3 (Cp), 67.7 ($TiCH_2$), 41.6 (d, $^1J_{PC}$ = 46, *t*-Bu), 30.0, 28.0, 14.1, 9.5 (*n*-Bu), 29.7 (*t*-Bu), 18.0 ($SnCH_2$). ^{31}P{^{1}H} NMR: 37.6. Anal. Calcd for $C_{31}H_{63}ClNPSnTi$: C, 54.52, H, 9.70, N, 2.05. Found: C, 54.12, H, 9.29, N, 2.04. **15**: Yield: 78%. ^{1}H NMR: 6.12 (s, 5 H, Cp), 2.07, 1.45 (m, 1 H, $TiCH_2$), 1.95 (m, 2 H, $TiCH_2CH_2Si$), 1.12 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR: 112.8 (Cp), 47.9 ($TiCH_2$), 41.5 (d, $^1J_{PC}$ = 46, *t*-Bu), 29.6 (*t*-Bu), 26.3 ($TiCH_2CH_2Si$). ^{31}P{^{1}H} NMR: 40.7. ^{29}Si NMR: −31.5. Anal. Calcd for $C_{19}H_{36}Cl_4NPSiTi$: C, 43.28, H, 6.88, N, 2.66. Found: C, 44.38, H, 7.20, N, 2.70. **16**: Yield: 44%. ^{1}H NMR: 6.27 (s, 10 H, Cp), 2.15, 1.72 (m, 2 H, $TiCH_2$), 1.91 (m, 4 H, $TiCH_2CH_2Si$), 1.20 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR: 112.7 (Cp), 54.0 ($TiCH_2$), 41.5 (d, $^1J_{PC}$ = 45, *t*-Bu), 30.1 ($TiCH_2CH_2Si$), 29.5 (*t*-Bu). ^{31}P{^{1}H} NMR: 40.7. Anal. Calcd for $C_{38}H_{72}Cl_4N_2P_2SiTi$: C, 51.59, H, 8.20, N, 3.17. Found: C, 50.98, H, 8.22, N, 3.19.

Synthesis of CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$CH$_2$CH$_2$SiCl$_3$) (17), CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$CH$_2$CH$_2$SnMe$_3$) (18), and CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$SnPh$_3$) (19). These compounds were prepared in a similar fashion using the appropriate alkyl halide reagent, and thus only one example is detailed. The titanacycle **1** (189 mg, 0.49 mmol) and $ClSnPh_3$ (189 mg, 0.49 mmol) were dissolved in a mixture of 5 mL of pentane and 1 mL of THF. After 3 h at room temperature without stirring red crystals of **19** in 49% yield (185 mg) were obtained. **17**: Yield: 62%. ^{1}H NMR: 6.25 (s, 5 H, Cp), 2.03, 1.49 (dt, $^2J_{HH}$ = 5, $^3J_{HH}$ = 11, 1 H, $TiCH_2$), 1.76 (m, 2 H, $TiCH_2CH_2$), 1.44 (m, 2 H, CH_2CH_2Si), 1.16 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). The signal for CH_2 attached to Si is covered by the resonance of the *t*-Bu group. ^{13}C{^{1}H} NMR: 112.2 (Cp), 65.8 ($TiCH_2$), 41.2 (d, $^1J_{PC}$ = 46, *t*-Bu), 36.7 ($TiCH_2CH_2$), 29.6 (*t*-Bu), 27.5 (CH_2CH_2Si), 23.8 (CH_2CH_2Si). ^{31}P{^{1}H} NMR: 39.4. **18**: Yield: 73% (dark red oil). ^{1}H NMR: 6.30 (s, 5 H, Cp), 2.22 (dt, $^2J_{HH}$ = 5, $^3J_{HH}$ = 11, 1 H, $TiCH_2$), 1.91 (m, 2 H, $TiCH_2CH_2$), 1.77 (dt, $^2J_{HH}$ = 5, $^3J_{HH}$ = 11, 1 H, $TiCH_2$), 1.60 (m, 2 H, CH_2CH_2Sn), 1.19 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu), 0.94 (m, 2 H, CH_2CH_2Sn), 0.13 (t, $^3J_{SnH}$ = 26, 9 H, $SnMe_3$). ^{13}C{^{1}H} NMR: 112.3 (Cp), 69.4 ($TiCH_2$), 41.5 (d, $^1J_{PC}$ = 45, *t*-Bu), 39.9 ($TiCH_2CH_2$), 32.7 (CH_2CH_2Sn), 29.7 (*t*-Bu), 11.2 (CH_2CH_2Sn), 10.2 ($SnMe_3$). ^{31}P{^{1}H} NMR: 38.2. **19**: Yield: 49%. ^{1}H NMR: 7.71 (m, 6 H, *o*-$SnPh_3$), 7.21 (m, 9 H, *m*-$SnPh_3$ + *p*-$SnPh_3$), 6.26 (s, 5 H, Cp), 2.63 (m, 1 H, $TiCH_2$), 2.34 (m, 2 H, $SnCH_2$), 1.71 (m, 1 H, $TiCH_2$), 1.10 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR: 141.0, 137.8, 129.0 ($SnPh_3$), 112.4 (Cp), 64.1 ($TiCH_2$), 41.4 (d, $^1J_{PC}$ = 45, *t*-Bu), 29.5 (*t*-Bu), 18.8 ($SnCH_2$). ^{31}P{^{1}H} NMR: 38.3. Anal. Calcd for $C_{37}H_{51}ClNPSnTi$: C, 59.83, H, 6.92, N, 1.89. Found: C, 59.40, H, 7.13, N, 1.88.

Synthesis of CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$Bcat) (20). Compound **1** (248 mg, 0.64 mmol) was dissolved in 3 mL of pentane, and PMe_3 (about 200 μL) was added. After 5 min a solution of *B*-chlorocatecholborane (100 mg, 0.64 mmol) in 3 mL of pentane was added. The reaction mixture was filtered through Celite and cooled overnight, affording a brown powder in 52% yield (171 mg). ^{1}H NMR: 7.05 (m, 2 H, $O_2C_6H_4$), 6.78 (m, 2 H, $O_2C_6H_4$), 6.27 (s, 5 H, Cp), 2.35, 1.82 (m, 1 H, $TiCH_2$), 1.93 (m, 2 H, $TiCH_2CH_2B$), 1.16 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{11}B{^{1}H} NMR: 34.6. ^{13}C{^{1}H} NMR: 149.3, 122.4, 112.4 ($O_2C_6H_4$), 112.6 (Cp), 58.0 ($TiCH_2$), 41.4 (d, $^1J_{PC}$ = 45, *t*-Bu), 30.0 ($TiCH_2CH_2B$), 29.6 (*t*-Bu). ^{31}P{^{1}H} NMR: 38.9. Anal. Calcd for $C_{25}H_{40}BClNO_2PTi$: C, 58.68, H, 7.88, N, 2.74. Found: C, 58.26, H, 8.03, N, 2.78.

Synthesis of CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$CH$_2$CH$_2$Bcat) (21). Compound **1** (203 mg, 0.52 mmol) was dissolved in 3 mL of pentane, and a solution of *B*-chlorocatecholborane (81 mg, 0.52 mmol) in 3 mL of pentane was added dropwise. The reaction mixture was filtered through Celite and cooled overnight, affording the product as a yellow solid (about 25 mg) and oil (about 173 mg) in 62% yield (spectroscopically identical). ^{1}H NMR: 7.02, 6.80 (m, 2 H, $O_2C_6H_4$), 6.25 (s, 5 H, Cp), 2.11, 1.71 (m, 1 H, $TiCH_2$), 1.95 (m, 2 H, $TiCH_2CH_2$), 1.68 (m, 2 H, CH_2CH_2B), 1.27 (br t, 2 H, CH_2B), 1.17 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{11}B{^{1}H} NMR: 35.4. ^{13}C{^{1}H} NMR: 149.0, 122.6, 112.5 ($O_2C_6H_4$), 112.3 (Cp), 68.4 ($TiCH_2$), 42.0 (d, $^1J_{PC}$ = 45, *t*-Bu), 39.7 ($TiCH_2CH_2$), 29.6 (*t*-Bu), 10.4 (CH_2CH_2B). The resonance for the CH_2CH_2B group is covered by the signal of the *t*-Bu group. ^{31}P{^{1}H} NMR: 38.3. Anal. Calcd for $C_{27}H_{44}BClNO_2PTi$: C, 60.08, H, 8.22, N, 2.59. Found: C, 59.84, H, 8.15, N, 2.78.

Synthesis of CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$PPh$_2$) (22). The titanacycle **1** (259 mg, 0.67 mmol) was dissolved in 5 mL of toluene, 260 μL (2.51 mmol) of PMe_3 was added, and the solution was cooled to −35 °C. After 20 min $ClPPh_2$ (121 μL, 0.67 mmol) was added, and the solution was allowed to warm to room temperature slowly. After 2 h evaporation of solvent afforded a brown oil. The oil was suspended in 6 mL of pentane and stirred for 5 min. A yellow powder formed, which was isolated by decanting the pentane by pipet. The powder was dried in vacuo (258 mg, 70%). ^{1}H NMR: 7.67, 7.60 (br t, 4 H, *o*-PPh_2), 7.19 (br t, 2 H, *p*-PPh_2), 7.12 (m, 4 H, *m*-PPh_2), 6.18 (s, 5 H, Cp), 2.78 (m, 2 H, PCH_2), 2.38, 1.47 (m, 1 H, $TiCH_2$), 1.08 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR: 133.9, 133.7, 133.4, 133.2, 128.4 (PPh_2), 112.3 (Cp), 59.5 ($TiCH_2$), 41.3 (d, $^1J_{PC}$ = 46, *t*-Bu), 33.6 (br m, PCH_2), 29.4 (*t*-Bu). ^{31}P{^{1}H} NMR: 39.1 (NP*t*-Bu_3), −8.7 (PPh_2). Anal. Calcd for $C_{31}H_{46}ClNP_2Ti$: C, 64.42, H, 8.02, N, 2.42. Found: C, 64.77, H, 7.98, N, 2.48.

Synthesis of CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH$_2$CH$_2$CH$_2$PPh$_2$) (23) and CpTiCl(NP*t*-Bu$_3$)(CH$_2$CH(CH$_3$)CH(CH$_3$)CH$_2$PPh$_2$) (24). These compounds were prepared in a similar fashion using **1** and **2** as starting materials, and thus only one example is detailed. The titanacycle **1** (299 mg, 0.77 mmol) was dissolved in 5 mL of toluene and cooled to −35 °C. After 20 min $ClPPh_2$ (140 μL, 0.77 mmol) was added, and the solution was allowed to warm to room temperature slowly. After 2 h evaporation of the solvent afforded a brown oil. The oil was suspended in 6 mL of pentane and stirred for 5 min. A yellow powder formed, which was isolated by decanting the overlaying solution by pipet. The powder **20** was dried in vacuo (299 mg, 67%). **23**: ^{1}H NMR: 7.50, 7.48 (br t, 4 H, *o*-PPh_2), 7.10 (br t, 4 H, *m*-PPh_2), 7.07 (m, 2 H, *p*-PPh_2), 6.26 (s, 5 H, Cp), 2.13, 1.74 (dt, $^2J_{HH}$ = 5, $^3J_{HH}$ = 11, 1 H, $TiCH_2$), 2.10 (br t, 2 H, PCH_2), 2.01, 1.95 (m, 1 H, $TiCH_2CH_2$), 1.57 (m, 2 H, PCH_2CH_2), 1.15 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR: 134.8, 133.2, 128.6, 128.5, 128.4, 128.3 (PPh_2), 112.3 (Cp), 68.4 ($TiCH_2$), 41.5 (d, $^1J_{PC}$ = 46, *t*-Bu), 36.7 (d, $^3J_{PC}$ = 11, $TiCH_2CH_2$), 31.9 (d, $^2J_{PC}$ = 16, PCH_2CH_2), 29.4 (*t*-Bu), 28.9 (br m, PCH_2). ^{31}P{^{1}H} NMR: 38.1 (NP*t*-Bu_3), −15.2 (PPh_2). Anal. Calcd for $C_{33}H_{50}ClNP_2Ti$: C, 65.40, H, 8.32, N, 2.31. Found: C, 65.10, H, 8.38, N, 2.35. **24**: Yield: 131 mg, 47%, (a brown oil). ^{1}H NMR: 7.63, 7.56 (br t, 4 H, *o*-PPh_2), 7.13 (m, 6 H, *m*-PPh_2), 6.97 (m, 2 H, *p*-PPh_2), 6.20 (s, 5 H, Cp), 2.25 (m, 2 H, PCH_2), 2.02 (m, 2 H, $TiCH_2$ + $TiCH_2CH$), 1.56 (m, 1 H, $CHCH_2P$), 1.34 (d, $^2J_{HH}$ = 13,

3 H, $TiCH_2CHCH_3$), 1.16 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu), 1.00 (d, $^2J_{HH}$ = 13, 3 H, CH_3CHCH_2P). $^{13}C\{^1H\}$ NMR: 134.8, 133.8, 133.1, 128.7 (PPh_2), 112.3 (Cp), 75.9 ($TiCH_2$), 43.7 (br d, $^3J_{PC}$ = 7, $TiCH_2CH$), 41.6 (d, $^1J_{PC}$ = 45, *t*-Bu), 36.3 (br d, $^2J_{PC}$ = 11, PCH_2CH), 29.6 (*t*-Bu), 18.8 ($TiCH_2CHCH_3$), 15.7 (d, $^3J_{PC}$ = 8, CH_3CHCH_2P). The signal for the CH_2 group attached to P was not detected. $^{31}P\{^1H\}$ NMR: 37.7 ($NPt\text{-}Bu_3$), −18.6 (br s, PPh_2). Anal. Calcd for $C_{35}H_{54}ClNP_2Ti$: C, 66.30, H, 8.58, N, 2.21. Found: C, 66.10, H, 8.38, N, 2.15.

Synthesis of $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2CH_2CH_2PPh_2)RhCl(cod)$ (25) and $CpTiCl(NPt\text{-}Bu_3)(CH_2CH(CH_3)CH(CH_3)CH_2PPh_2)RhCl(cod)$ (26). These compounds were prepared in a similar fashion using **23** and **24** as starting materials, and thus only one example is detailed. Compound **23** (95 mg, 0.16 mmol) and $[(cod)RhCl]_2$ (41 mg, 0.16 mmol) were mixed and dissolved in 2.5 mL of toluene. After 15 min the solvent was removed in vacuo and the oily residue was suspended in 4 mL of pentane. The overlaying solution was transferred by pipet, and a yellow powder was isolated (118 mg, 87%) after drying in vacuo. **25**: ^1H NMR: 7.74, 7.70 (br t, 4 H, *o*-PPh_2), 7.03 (m, 6 H, *m*-PPh_2, *p*-PPh_2), 6.44 (s, 5 H, Cp), 5.83, 3.12 (m, 2 H, cod), 2.67 (m, 2 H, PCH_2), 2.18 (m, 3 H, cod + PCH_2CH_2), 2.07 (m, 7 H, cod + $TiCH_2CH_2$ + $TiCH_2$), 1.94 (m, 1 H, $TiCH_2$), 1.72 (m, 2 H, cod), 1.61 (m, 1 H, PCH_2CH_2), 1.19 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu). $^{13}C\{^1H\}$ NMR: 134.3, 134.2, 134.1, 133.8, 129.8, 129.7, 128.3 (PPh_2), 112.4 (Cp), 104.4 (m, cod), 69.8 (d, $^1J_{RhC}$ = 14, cod), 69.7 (d, $^1J_{RhC}$ = 14, cod), 67.8 ($TiCH_2$), 41.5 (d, $^1J_{PC}$ = 45, *t*-Bu), 37.0 (d, $^3J_{PC}$ = 14, $TiCH_2CH_2$), 33.3 (d, $^2J_{PC}$ = 29, PCH_2CH_2), 32.0, 29.2, 29.0 (cod), 29.7 (*t*-Bu), 28.0 (d, $^3J_{PC}$ = 25, PCH_2). $^{31}P\{^1H\}$ NMR: 38.4 ($NPt\text{-}Bu_3$), 27.8 (d, $^1J_{RhP}$ = 149, PPh_2). Anal. Calcd for $C_{41}H_{62}Cl_2NP_2RhTi$: C, 57.76, H, 7.33, N, 1.64. Found: C, 57.75, H, 7.35, N, 1.40. **26**: Yield: 171 mg, 44% (brown powder). ^1H NMR: 7.99, 7.81 (br t, $^3J_{HH}$ = 9, 2 H, *o*-PPh_2), 7.06 (m, 6 H, *m*-PPh_2, *p*-PPh_2), 6.29 (s, 5 H, Cp), 5.85 (m, 2 H, cod), 3.27, 3.19 (br s, 1 H, cod), 2.83 (m, 2 H, PCH_2), 2.55 (m, 1 H, $TiCH_2CH$), 2.42 (m, 1 H, $TiCH_2$), 2.35 (m, 1 H, PCH_2CH), 2.21, 1.65 (m, 4 H, cod), 1.56 (m, 1 H, $TiCH_2$), 1.47 (d, $^3J_{HH}$ = 7, 3 H, $TiCH_2CHCH_3$), 1.19 (d, $^3J_{PH}$ = 13, 27 H, *t*-Bu), 1.04 (d, $^3J_{HH}$ = 7, 3 H, PCH_2CHCH_3). $^{13}C\{^1H\}$ NMR: 135.0 (d, J_{PC} = 11), 134.6 (d, J_{PC} = 10), 134.2 (d, J_{PC} = 10), 129.8 (d, J_{PC} = 17), 129.3, 128.2 (PPh_2), 112.4 (Cp), 103.6 (m, cod), 76.5 ($TiCH_2$), 70.0 (d, $^1J_{RhC}$ = 14, cod), 69.7 (d, $^1J_{RhC}$ = 14, cod), 45.4 (d, $^2J_{PC}$ = 9, PCH_2CH), 41.6 (d, $^1J_{PC}$ = 46, *t*-Bu), 36.3 ($TiCH_2CH$), 35.0 (d, $^3J_{PC}$ = 23, PCH_2), 33.3 (d, $^2J_{RhC}$ = 24, cod), 29.7 (*t*-Bu), 29.1 (d, $^2J_{RhC}$ = 14, cod), 18.8 ($TiCH_2CHCH_3$), 16.7 (br s, PCH_2CHCH_3). $^{31}P\{^1H\}$ NMR: 38.5 ($NPt\text{-}Bu_3$), 25.0 (d, $^1J_{RhP}$ = 148, PPh_2). Anal. Calcd for $C_{43}H_{66}Cl_2NP_2RhTi$: C, 58.65, H, 7.55, N, 1.59. Found: C, 58.65, H, 7.84, N, 1.59.

X-ray Data Collection and Reduction. 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. A hemisphere of data was collected in 1329 frames with 10 s 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. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[10] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are deposited.

Computations. All DFT calculations were performed using the Gaussian 03 suite of programs.[11] The basis set consisted of the LANL2DZ basis set on Ti in combination with the 6-31G(d) basis set[12−15] on the all other atom types.

Results and Discussion

We have previously reported the synthesis of the titanacycles $CpTi(NPt\text{-}Bu_3)(C_4H_8)$ (**1**) and $CpTi(NPt\text{-}Bu_3)(CH_2CHMe)_2$ (**2**) from the reduction of the precursor dichloride in the presence of ethylene and propylene, respectively. Structural data showed these compounds are best formulated as Ti(IV) metallacycles.[7] Nonetheless, herein we demonstrate that these compounds are indeed quite reactive. For example, reaction of compound **1** with PMe_3 in toluene followed by addition of benzyl chloride or benzyl bromide proceeds at room temperature to give the products **3** and **4** in 44% and 65% yield, respectively. It was subsequently shown that addition of PMe_3 was not required to form these products. In both cases the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were consistent with the formulation of **3** and **4** as $CpTiX(NPt\text{-}Bu_3)(CH_2Ph)$ (X = Cl, **3**; Br, **4**) (Scheme 2). In the case of **4**, preliminary X-ray data were consistent with this formulation, although the poor quality of the data precluded a publishable solution. A similar reaction of 4-bromo-1-butene with **1** proceeds to give 74% isolated yield of the product **5** formulated on the basis of NMR data as $CpTiBr(NPt\text{-}Bu_3)(CH_2CH_2CHCH_2)$ (**5**) (Scheme 2). The nature of the pendant olefinic fragment is consistent with the observations of ^1H NMR

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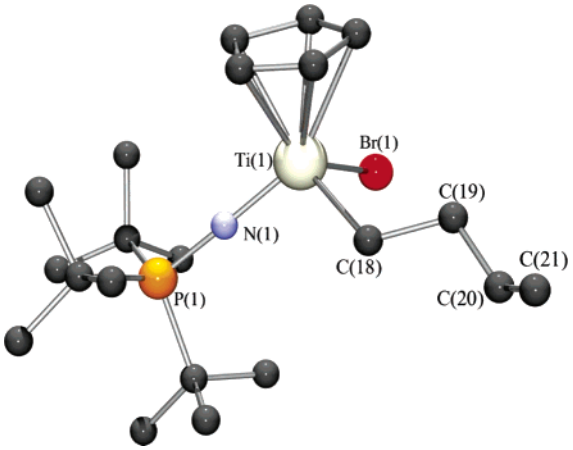
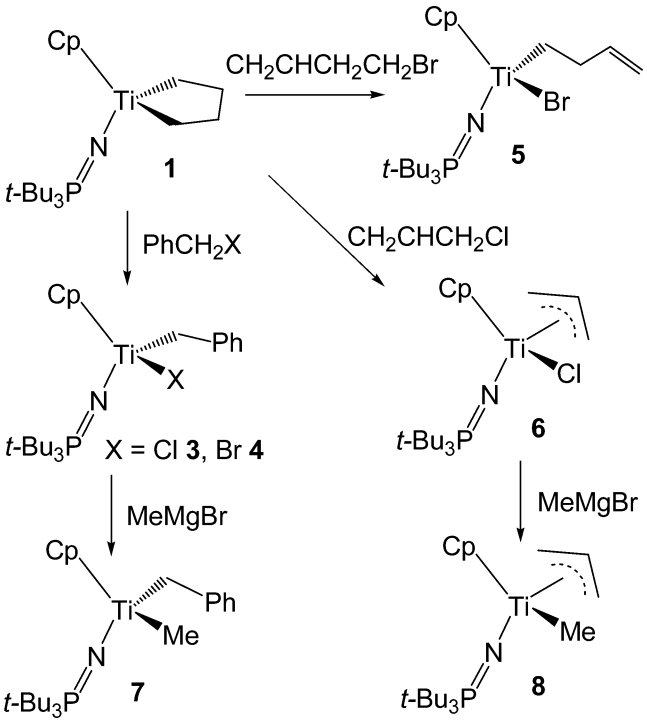


Figure 1. ORTEP drawing of the cation of **5**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Ti(1)−N(1) 1.777(4), Ti(1)−C(18) 2.176(6), Ti(1)−Br(1) 2.4512(11), P(1)−N(1) 1.594(4), C(20)−C(21) 1.237(12), N(1)−Ti(1)−C(18) 99.5(2), N(1)−Ti(1)−Br(1) 104.60(13), C(18)−Ti(1)−Br(1) 97.63(17), P(1)−N(1)−Ti(1) 175.4(3).

Scheme 2



resonances at 5.99, 5.09, and 4.94 ppm. This was affirmed via a crystallographic study (Figure 1). The coordination sphere about Ti is pseudo-tetrahedral with Ti−N, Ti−Br, and Ti−C_{alkyl} distances of 1.777(4), 2.4512(11), and 2.176(6) Å. The phosphinimide ligand is approximately linear at N as expected, and the remaining metric parameters are unexceptional. A similar reaction of **1** with allyl chloride led to the formation of the related product CpTiCl(NP*t*-Bu_3)(CH_2CHCH_2) (**6**) in 59% yield (Scheme 2). Observation of quintet and doublet ^{1}H NMR resonances at 6.50 and 3.82 ppm suggests an η^3-allyl formulation of **6**. Complexes **4** and **6** were readily converted to CpTiMe(NP*t*-Bu_3)(CH_2Ph) (**7**) and CpTiMe(NP*t*-Bu_3)(CH_2CHCH_2) (**8**), respectively (Scheme 2). Preliminary X-ray data for **7** were consistent with this formulation, although again poor crystal quality precluded a publishable solution.

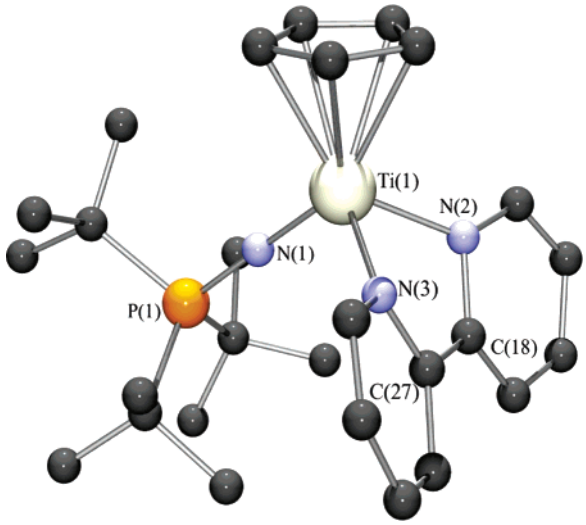


Figure 2. ORTEP drawing of the cation of **9**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Ti(1)−N(1) 1.834(3), Ti(1)−N(2) 2.044(3), Ti(1)−N(3) 2.055(3), P(1)−N(1) 1.577(3), N(2)−C(18) 1.362(5), N(2)−C(22) 1.396(5), N(3)−C(27) 1.360(5), N(3)−C(23) 1.399(5), C(18)−C(19) 1.347(6), C(19)−C(20) 1.407(7), C(20)−C(21) 1.352(6), C(21)−C(22) 1.421(5), C(22)−C(23) 1.411(5), C(23)−C(24) 1.426(5), C(24)−C(25) 1.356(6), C(25)−C(26) 1.407(7), C(26)−C(27) 1.355(6), N(1)−Ti(1)−N(2) 104.12(12), N(1)−Ti(1)−N(3) 104.92(12), N(2)−Ti(1)−N(3) 80.16(12), P(1)−N(1)−Ti(1) 175.1(2), C(18)−N(2)−C(22) 117.5(3), C(18)−N(2)−Ti(1) 134.7(3), C(22)−N(2)−Ti(1) 105.4(2), C(27)−N(3)−C(23) 117.2(3), C(27)−N(3)−Ti(1) 135.5(3), C(23)−N(3)−Ti(1) 105.6(2).

The above chemistry suggests that **1** reacts as a source of Ti(II), losing ethylene and undergoing oxidative addition with alkyl halides to give the products **3**−**6**. This view is supported by the reaction of **1** with bipyridine, which gives the dark blue crystal product **9** in 61% yield. The ^{1}H NMR data in toluene-d_8 at −80 °C showed resonances at 7.43, 7.34, 6.37, and 5.35 ppm attributable to the bipyridine ligand and at 6.31 and 1.02 ppm attributable to the Cp and phosphinimide ligands. X-ray structural data confirmed the formulation of **9** as CpTi(NP*t*-Bu_3)(bipy) (Figure 2). The Ti−N distance for the phosphinimide was 1.834(3) Å. As in **5** and many other phosphinimide derivatives, the geometry at the phosphinimide N was approximately linear. The bipyridine is approximately planar, forming an angle of 72.4° with respect to the plane of the cyclopentadienyl ligand. The C−C bond lengths about the bipyridyl ligand suggest electron transfer from Ti to the ligand, similar to that observed for a number of related Ti−bipyridine complexes.[18−24] This view is supported by the distortion from planar geometry at the N atoms as represented by the C(18)−N(2)−Ti(1) and C(27)−N(3)−Ti(1) angles of 134.7(3)° and

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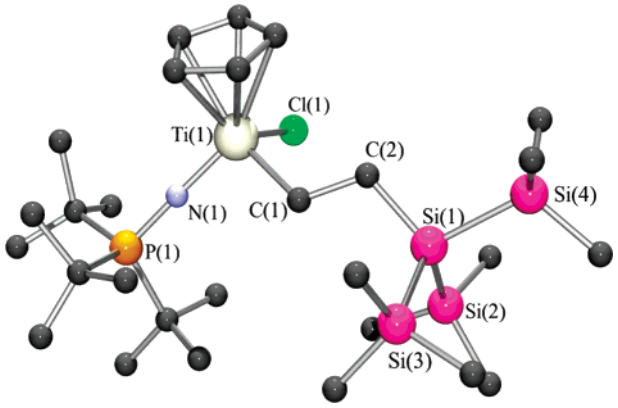


Figure 3. ORTEP drawing of the cation of **12**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Ti(1)−N(1) 1.785(2), Ti(1)−C(1) 2.129(3), Ti(1)−Cl(1) 2.3041(11), Si(1)−C(2) 1.905(3), Si(1)−Si(2) 2.3337(13), Si(1)−Si(3) 2.3417(13), Si(1)−Si(4) 2.3449(12), P(1)−N(1) 1.583(2), N(1)−Ti(1)−C(1) 98.64(11), N(1)−Ti(1)−Cl(1) 106.07(8), C(1)Ti(1)−Cl(1) 97.43(10), P(1)−N(1)−Ti(1) 178.82(15).

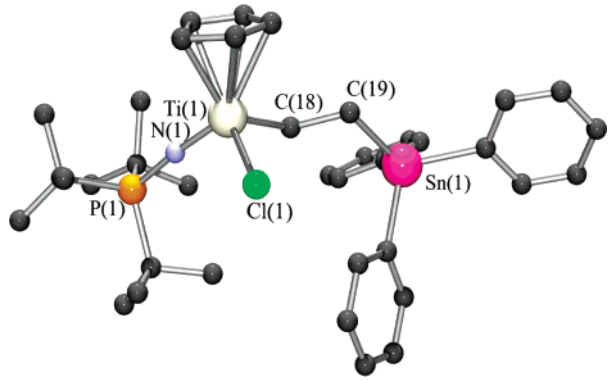
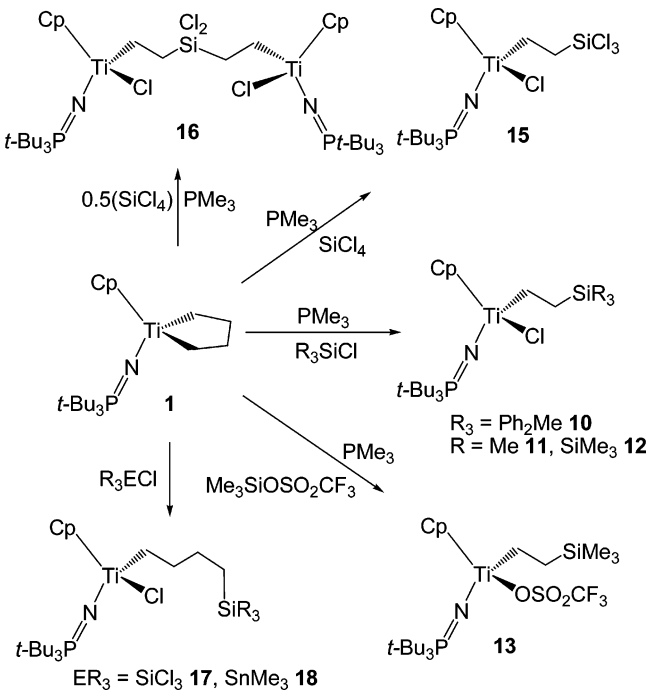


Figure 4. ORTEP drawing of the cation of **19**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. One orientation of the disordered *t*-Bu groups are shown. Distances (Å) and angles (deg): Ti(1)−N(1) 1.777(3), Ti(1)−C(18) 2.131(4), Ti(1)−Cl(1) 2.3227(13), Sn(1)−C(19) 2.155(4), P(1)−N(1) 1.595(4), N(1)−Ti(1)−C(18) 97.94(14), N(1)−Ti(1)−Cl(1) 105.07(11), C(18)−Ti(1)−Cl(1) 100.68(12), P(1)−N(1)−Ti(1) 175.0(2).

135.5(3)°. This view is also consistent with the comparatively short Ti−N distances of 2.044(3) and 2.055(3) Å.

The characterization of compound **1** as a Ti(II) synthon prompted us to probe reactions with main group halides (Scheme 3). For example reaction of **1** with PMe_3 in the presence of $ClSiMePh_2$ results in the isolation of red-brown crystalline

Scheme 3



product **10** in 59% isolated yield. The ^1H NMR data showed doublet of triplet resonances at 2.30 and 1.47 ppm attributed to the diastereotopic methylene protons. In addition, a multiplet at 1.81 ppm and $^{13}C\{^1H\}$ resonances at 60.6 and 21.1 ppm were attributed to an ethyl linkage between Ti and Si, resulting in the formulation of **10** as CpTiCl(NP*t*-Bu_3)($CH_2CH_2SiPh_2Me$). The analogous product CpTiCl(NP*t*-Bu_3)($CH_2CH_2SiMe_3$) (**11**) was derived from the reaction of **1** with PMe_3 and $ClSiMe_3$. Similar reactions of **1** with PMe_3 and $ClSi(SiMe_3)_3$, $Me_3SiOSO_2CF_3$, and ClSn*n*-Bu_3 gave CpTiCl(NP*t*-Bu_3)($CH_2CH_2Si(SiMe_3)_3$) (**12**), CpTi(NP*t*-Bu_3)($CH_2CH_2SiMe_3$)(OSO_2CF_3) (**13**), and CpTiCl(NP*t*-Bu_3)(CH_2CH_2Sn*n*-Bu_3) (**14**), respectively, all in high yields (Scheme 3). Compound **12** was characterized by X-ray crystallography (Figure 3). These data confirmed the presence of the ethylene linkage between the Ti and Si centers. As expected, the geometry about Ti in **12** is pseudo-tetrahedral with Ti−C, Ti−Cl, and Ti−N distances of 2.129(3), 2.3041(11), and 1.785(2) Å, respectively. A similar reaction of **1**, PMe_3, and $SiCl_4$ proceeds to give CpTiCl(NP*t*-Bu_3)($CH_2CH_2SiCl_3$) (**15**) in 78% yield (Scheme 3). Interestingly, altering the Ti:Si stoichiometry to 2:1 afforded the dimetallic complex [CpTiCl(NP*t*-Bu_3)(CH_2CH_2)]$_2SiCl_2$ (**16**) in 44% isolated yield. It is noteworthy that similar reactions with diethylchlorophosphate were

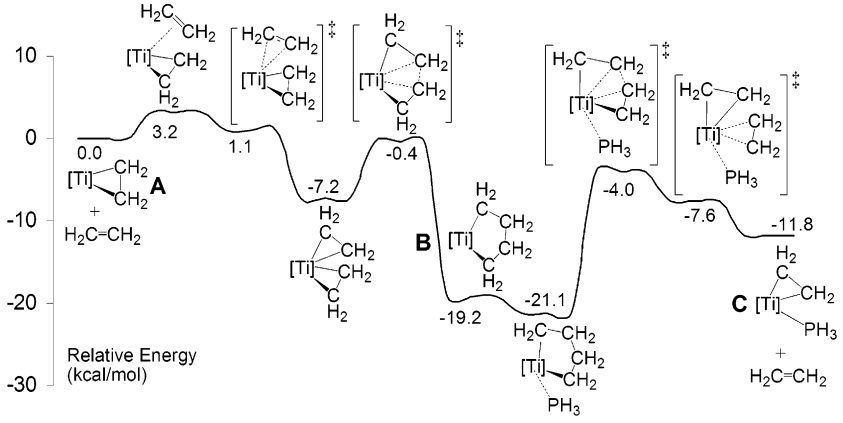


Figure 5. Reaction profile for reaction of CpTi(NPH_3)($CH_2CH_2CH_2CH_2$) with PH_3; [Ti] = CpTi(NPH_3).

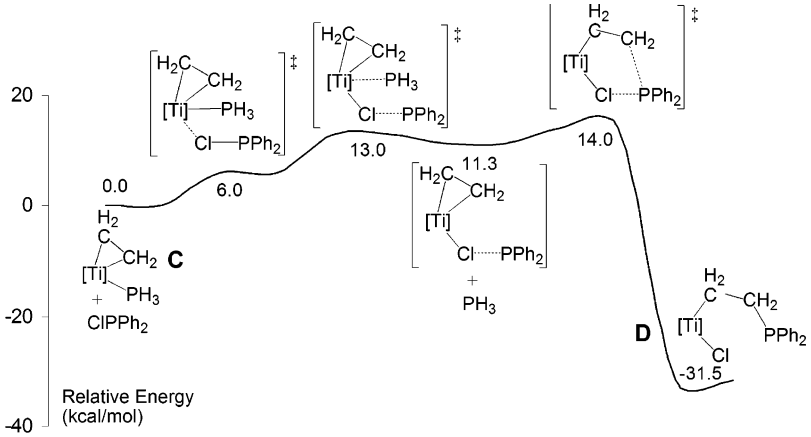
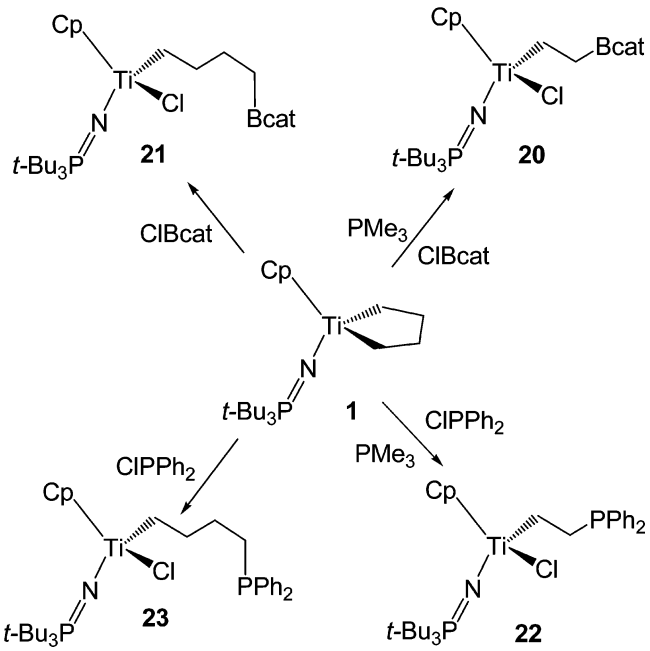
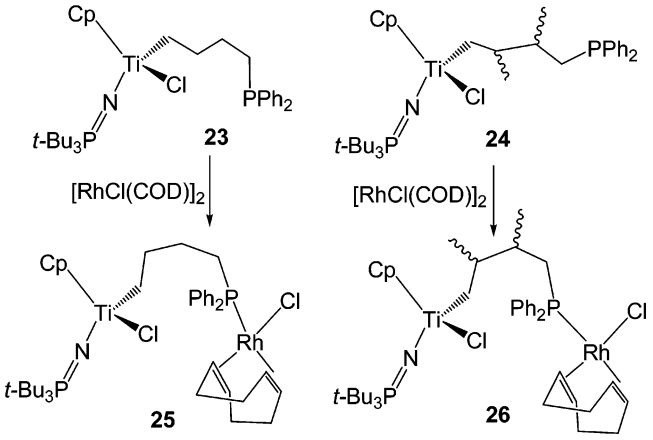


Figure 6. Reaction profile for reaction of $CpTi(NPH_3)(CH_2CH_2)(PH_3)$ with $ClPPh_2$; [Ti] = $CpTi(NPH_3)$.

Scheme 4



Scheme 5



observed for the zirconocene−ethylene complex $Cp_2Zr(CH_2CH_2)(PMe_3)$ to give $Cp_2ZrCl(CH_2CH_2P(O)(OEt)_2)$.[25] As well, reactions of $Cp_2Zr(CH_2CH_2)(PMe_3)$ with group IV halides gave R_3EEt (E = Si, Ge, Sn; R = Ph or Bu; X = Cl, OEt, or OER_3) upon hydrolysis.[26]

It is interesting and noteworthy that reaction of **1** with $SiCl_4$ in the absence of PMe_3 gave the new product **17**, which was isolated in 49% yield. The ^1H NMR spectrum reveals methylene resonances at 2.03, 1.49, 1.76, 1.44, and 1.16 ppm. These and $^{13}C\{^1H\}$ NMR data were consistent with the formulation of **17** as $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2CH_2CH_2SiCl_3)$ (Scheme 3). In a similar fashion, direct reaction of **1** with $ClSnMe_3$ afforded the complex $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2CH_2CH_2SnMe_3)$ (**18**) in 73% yield as a dark red oil (Scheme 3). While these syntheses suggest that two- and four-carbon chain derivatives are accessible in a controlled fashion by the presence or absence of PMe_3, it should be noted that steric demands appear to play a role as well. This is illustrated by the reaction of **1** with $ClSnPh_3$, which gave the two-carbon chain derivative $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2SnPh_3)$ (**19**). X-ray data for **19** confirmed the formulation with a pseudo-tetrahedral geometry about Ti and Ti−C, Ti−Cl, and Ti−N distances of 2.131(4), 2.3227(13), and 1.777(3) Å (Figure 4).

With the apparent results due to steric demands noted, the syntheses of two- and four-carbon chain derivatives from **1** was explored. Reaction of **1** in the presence of PMe_3 with ClBcat (cat = $O_2C_6H_4$) led to the formation of $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2Bcat)$ (**20**) in 52% yield as a light brown powder (Scheme 4), while reaction of **1** with only ClBcat gave **21**. This latter species was isolated in an overall yield of 62% and formulated as $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2CH_2CH_2Bcat)$ (**21**) (Scheme 4). The ^1H NMR spectrum of **20** showed methylene resonances as 2.35, 1.82, and 1.93, while **21** shows methylene resonances at 2.11, 1.71, 1.95, 1.68, and 1.27 ppm. The $^{11}B\{^1H\}$ NMR spectra for **20** and **21** show resonances at 34.6 and 35.4 ppm, respectively, consistent with the differing formulations. In a similar manner the compounds $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2PPh_2)$ (**22**) and $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2CH_2CH_2PPh_2)$ (**23**) were prepared in 70% and 67% yield, respectively, from the reactions of **1** with $ClPPh_2$ in the presence and absence of PMe_3, respectively (Scheme 4). These complexes show two resonances in the $^{31}P\{^1H\}$ NMR spectra at −80 °C attributable to the phosphinimide and the pendant phosphine fragment. In the case of **22** the chemical shifts are 39.1 and −8.7 ppm, while for **23** they are 38.1 and −15.2 ppm. In a similar fashion, the analogous propylene metallacycle **2** reacts with $ClPPh_2$ to give a brown oil in 47% yield formulated as $CpTiCl(NPt\text{-}Bu_3)(CH_2CH(CH_3)CH(CH_3)CH_2PPh_2)$ (**24**).

Compounds **23** and **24** were further derivatized by complexation of the pendant phosphine fragment by Rh. Reaction of these compounds with $[(cod)RhCl]_2$ afforded $CpTiCl(NPt\text{-}Bu_3)(CH_2CH_2CH_2CH_2PPh_2)RhCl(cod)$ (**25**) and $CpTiCl(NPt\text{-}$

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Table 1. Crystallographic Parameters[a]

	5	9	12	19
formula	$C_{21}H_{39}BrNPTi$	$C_{27}H_{40}N_3PTi$	$C_{28}H_{63}ClNPSi_4Ti$	$C_{37}H_{51}ClNPSnTi$
fw	464.31	485.49	640.47	742.80
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	*Pbca*	$P2_1/c$	$P2_1/n$	$Pna2_1$
a (Å)	14.1420(14)	9.1234(16)	13.990(2)	24.278(3)
b (Å)	13.1491(13)	15.276(3)	16.640(3)	9.6131(11)
c (Å)	26.373(3)	19.170(3)	17.081(3)	16.0617(19)
β (deg)		98.340(2)	100.728(3)	
V (Å^3)	4904.2(8)	2643.4(8)	3906.7(11)	3748.5(8)
Z	8	4	4	4
d(calc) (g cm^{-1})	1.258	1.220	1.089	1.316
abs coeff, μ (cm^{-1})	2.048	0.403	0.468	1.017
no. of data collected	44 568	25 055	18 630	34 687
no. of data $F_o^2 > 3\sigma(F_o^2)$	4309	4634	5493	6605
no. of variables	226	370	325	379
R	0.0569	0.0636	0.0462	0.0319
R_w	0.1495	0.1859	0.1263	0.0795
GOF	1.058	0.881	1.040	1.048

[a] The data were collected at 20 °C with Mo Kα radiation (λ = 0.71073 Å).

$Bu_3)(CH_2CH(CH_3)CH(CH_3)CH_2PPh_2)RhCl(cod)$ (**26**) in 87% and 44% yield, respectively (Scheme 5). Complexation of the phosphine fragment by Rh was evidenced in **25** and **26** by the downfield ^{31}P chemical shifts to 27.8 and 25.0 ppm with Rh−P coupling constants of 149 and 148 Hz, respectively.

The reactivity of compound **1** with main group halides stands in contrast to its behavior with alkyl halides. Moreover, the above synthetic chemistry clearly implies that PMe_3 reacts with **1** to alter the course of subsequent reaction with main group halides. Attempts to explore this reaction in situ by NMR spectroscopy offered no definitive data. Analogous metallocene chemistry showed the facile loss of ethylene from $Cp_2Ti(CH_2CH_2)_2$ to give $Cp_2Ti(CH_2CH_2)$,[27] while the species $Cp_2Zr(CH_2CH_2)(PMe_3)$ was readily prepared and characterized.[28] However, attempts to either observe or isolate the analogous species $CpTi(NPt\text{-}Bu_3)(CH_2CH_2)(PMe_3)$ were inconclusive and unsuccessive.

DFT computations provided some further insight. In particular, they revealed that the model five-membered metallacycle $CpTi(NPH_3)(CH_2CH_2CH_2CH_2)$ (Figure 5 (A)) in solution was thermodynamically favored by 19.2 kcal/mol over the monoethylene three-membered metallacycle $CpTi(NPH_3)(CH_2CH_2)$ (Figure 5 (A)). Computations were also performed to consider the interaction of PH_3 with the model metallacycle. Coordination of phosphine to Ti provided a low-energy route to loss of ethylene and the formation of $CpTi(NPH_3)(CH_2CH_2)(PH_3)$ (Figure 5 (C)). These results support the view that loss of ethylene from the metallacycle **1** via a concerted associative process is a lower energy pathway than simple ethylene dissociation. This is consistent with the stability of **1**, which stands in contrast to the related metallocene compound $Cp_2Ti(CH_2CH_2)_2$,[27] where dissociation of ethylene is facile.

The reaction of the transient phosphine complex with main group halides was modeled using $CpTi(NPH_3)(CH_2CH_2)(PH_3)$ (Figure 6 (C)) and $ClPPh_2$. In this case, ligand exchange was shown to be a relatively low-energy process that led to subsequent P−Cl bond cleavage and formation of the Ti−Cl and C−P bonds, affording the thermodynamically favored product $CpTiCl(NPH_3)(CH_2CH_2PPh_2)$ (Figure 6 (D)). These results suggest that the ability of the main group elements to form the transition state in which the main group element interacts with Cl and the proximal C of ethylene may account for the formation of the functionalized alkyl chain. Presumably a similar mechanism occurs for the formation of the related four-carbon derivatives in the absence of PMe_3, although this aspect was not probed with computations. It is noteworthy that carbon-based halides reacted differently to afford what can be considered the products of oxidation addition to a Ti(II) synthon with loss of 2 equiv of ethylene. This may arise from the ability of the Si, Sn, P, and B to accommodate interaction with the carbon atoms of the metallacycle in the four-centered transition state, thus prompting C−E bond formation.

In conclusion, the phosphinimide-based metallacycles react as a Ti(II) synthon in reactions with alkyl halides. On the other hand, reactions with Si, Sn, P, and B halides proceed to give metal complexes with functionalized alkyl chains. In most cases, both two- and four-carbon chain products can be accessed by performing the reaction in the presence or absence of PMe_3, respectively. The utility the resulting functionalized complexes is now the subject of investigations.

Acknowledgment. Financial support from NSERC of Canada and NOVA Chemicals Corp. is gratefully acknowledged.

Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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