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Synthesis, Structure, and Reactivity of Titanium Phosphinimide Thiolate Complexes

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A series of titanium−phosphinimide thiolate complexes were prepared employing either thiolate for chloride metathesis or protonolysis of metal−carbon bonds by thiols. In these ways the following species were obtained: $CpTi(NPR'_3)(SR)_2$ ($R' = i\text{-}Pr$, $R = CH_2Ph$ **3**; Ph **4**, *t*-Bu **5**, $(SR)_2 = S_2(CH_2)_2$ **6**, $S_2(CH_2)_3$ **7**, $S_2(CH_2)_2C_6H_4$ **8**; $R' = t\text{-}Bu$, $R = CH_2Ph$ **9**; Ph **10**, *t*-Bu **11**); $Cp(t\text{-}Bu_3PN)TiMe(SPh)$ **12**; and $(t\text{-}Bu_3PN)_2Ti(SR)_2$ ($R = CH_2Ph$ **14**; Ph **15**, *t*-Bu **16**). Reactions of $(t\text{-}Bu_3PN)_2TiMe_2$ with 1 equiv of $HSCH_2Ph$ gave a cyclometalated species **17**, $(t\text{-}Bu_3PN)_2Ti(\eta^2\text{-}SCHPh)$. The analogous reaction of 1 equiv of phenylthiol generated the species $(t\text{-}Bu_3PN)_2Ti(Me)(SPh)$ **18**. While **17** and **18** could not be isolated free of **14** and **15**, respectively, the analogous reaction of *tert*-butylthiol afforded $(t\text{-}Bu_3PN)_2Ti(Me)(St\text{-}Bu)$ **19** cleanly. Attempts to effect sulfur insertion into Ti−Me bonds were undertaken via the reaction of $(t\text{-}Bu_3PN)_2TiMe_2$ with S_8 but gave instead the species $(t\text{-}Bu_3PN)_2Ti(\eta^2\text{-}S_5)$ **20**. The reactivity of the thiolate derivatives, **3**−**5** with excess $AlMe_3$, was examined. Spectroscopic and crystallographic studies revealed the formation of $(CpTi(\mu\text{-}SR)(\mu\text{-}NPi\text{-}Pr_3)(C)(AlMe_2)_2(\mu\text{-}SR)AlMe$ ($R = CH_2Ph$ **21**, Ph **22**, *t*-Bu **23**). Analogous reactions of **7** and **8** with $AlMe_3$ afforded $[Cp(i\text{-}Pr_3PN)Ti(SRS)]\cdot(AlMe_3)_3$ ($R = (CH_2)_3$ **24**, $((CH_2)_2(C_6H_4))$ **25**). The mechanistic implications of the observed multiple C−H bond activation are considered. Crystallographic studies of **4**, **6**, **7**, **14**, **16**, and **20**−**23** are reported.

Introduction

While much of early metal chemistry is based on metallocene derivatives, more recently attention has focused on related monocyclopentadienyl and noncyclopentadienyl analogues, as such systems have proved to be more reactive, affording novel reactivity. In the case of Ti-thiolate chemistry, we have observed that complexes of the form $CpTi(SR)_xCl_{2-x}$ undergo either β-C−H or C−S bond activation of the thiolate ligands depending on reaction conditions.[1−5] In developing related systems, we are exploring ancillary ligands that act as steric analogues to cyclopentadienyl ligands. In the case of Ti-phosphinimide complexes, we have uncovered a family of complexes of the form $CpTi(NPR_3)X_2$ and $(R_3PN)_2TiX_2$ that are effective ethylene polymerization catalysts.[6,7] In addition, we have shown that the reactions $CpTi(NPR_3)Me_2$ with $AlMe_3$ result in unprecedented triple C−H bond activation of a methyl group, yielding the Ti-Al-carbide aggregates $CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NPR_3)(\mu^4\text{-}C)(AlMe_2)_3$ and $CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NPR_3)(\mu^4\text{-}C)(AlMe_2)_3(AlMe_3)$.[8,9] In these cases, the central carbide carbon was found to be four- or five-coordinate. Related C−H bond activation has been observed in the formation of the Tebbe reagent, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$,[10] and in the clusters $[(Cp^*MMe)(\mu\text{-}F)_2AlMe_2]_2$ and $[(Cp^*M)_3Al_6Me_8(\mu^3\text{-}CH_2)_2(\mu^4\text{-}CH)_4(\mu^3\text{-}CH)]$[11,12] and very recently in the Zr-C aggregates $(Cp^*Zr)_4(\mu\text{-}Cl)_5(Cl)(\mu\text{-}CH)_2$ and $(Cp^*Zr)_5(\mu\text{-}Cl)_6(\mu\text{-}CH)_3$.[13] In this article, we describe the synthesis and structures of a series of Ti-phosphinimide-thiolate complexes. The reactions of such complexes with $AlMe_3$ are examined, the nature of the resulting products of C−H bond activation is described, and the mechanistic implications are considered. A preliminary account of some of this chemistry has been previously communicated.[14]

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line

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techniques and Innovative Technology, M.Braun, or Vacuum Atmospheres inert atmosphere gloveboxes. Solvents were purified employing Grubbs' type column systems manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references in ^{1}H NMR spectra, and chemical shifts (δ) are reported relative to SiMe$_4$. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H$_3$PO$_4$. All NMR spectra were recorded in C$_6$D$_6$ unless otherwise noted. Guelph Chemical Laboratories performed combustion analyses. The compounds CpTi(NP*i*-Pr$_3$)Cl$_2$ **1**,[7] CpTi(NP*i*-Pr$_3$)Me$_2$ **2**,[7] CpTi(NP*t*-Bu$_3$)Me$_2$ **9**,[7] (*t*-Bu$_3$PN)$_2$TiMe$_2$ **13**,[6] and CpTi(μ^2-Me)(μ^2-NP*i*-Pr$_3$)(μ^4-C)(AlMe$_2$)$_3$[15] were prepared via published methods. AlMe$_3$ and the thiols were purchased from Aldrich and Strem Chemical Companies and used without further purification.

Synthesis of CpTi(NP*i*-Pr$_3$)(SR)$_2$ (R = CH$_2$Ph 3; Ph 4, *t*-Bu 5); [CpTi(NP*i*-Pr$_3$)(S$_2$(CH$_2$)$_2$)]$_2$ 6; CpTi(NP*i*-Pr$_3$)(S$_2$R) (R = (CH$_2$)$_3$ 7, (CH$_2$)$_2$C$_6$H$_4$ 8); CpTi(NP*t*-Bu$_3$)(SR)$_2$ (R = CH$_2$Ph 9, Ph 10, *t*-Bu 11); (*t*-Bu$_3$PN)$_2$Ti(SR)$_2$ (R = CH$_2$Ph 14, Ph 15, *t*-Bu 16); and (*t*-Bu$_3$PN)$_2$Ti(Me)(S*t*-Bu) 19. These complexes were prepared employing one of two methods using the appropriate thiol or alkyl-thiolate reagent. One representative preparation of each method is presented. (i) To a THF solution (10 mL) of **1** (0.250 g; 0.698 mmol) was added solid LiSCH$_2$Ph (0.200 g; 1.550 mmol) at room temperature. The yellow solution turned dark red within 30 min and was stirred for 12 h. The solvent was removed under vacuum, the solid extracted with benzene (3 × 10 mL), and the solution filtered through Celite. The volume of the solution was reduced to 5 mL. A red microcrystalline solid was formed upon addition of 20 mL of hexanes. Red solid **3** (0.280 g; 0.525 mmol) was isolated by filtration and dried under vacuum in 75% yield. (ii) To a solution of **2** (0.056 g; 0.156 mmol) in benzene was added HS*t*-Bu (0.028 g; 0.312 mmol). The solution was allowed to stir for 12 h and the solvent removed under vacuum to afford **5** as a yellow powder in 83% yield. **3**: method (i): yield 65%. ^{1}H NMR: 7.57 (m, 4H, SCH$_2$*Ph*), 7.20 (m, 4H, SCH$_2$*Ph*), 7.06 (m, 1H, SCH$_2$*Ph*), 6.27 (s, 5H, Cp), 4.75 (d, $^{2}J_{\mathrm{HH}}$ = 13 Hz, 2H, SC*H*$_2$), 4.65 (d, $^{2}J_{\mathrm{HH}}$ = 13 Hz, 2H, SC*H*$_2$), 1.62 (d of sept, $^{2}J_{\mathrm{PH}}$ = 11 Hz, $^{3}J_{\mathrm{HH}}$ = 7 Hz, PC*H*Me$_2$), 0.91 (dd, $^{3}J_{\mathrm{PH}}$ = 15 Hz, $^{3}J_{\mathrm{HH}}$ = 7 Hz 18H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR: 31.6. ^{13}C{^{1}H} NMR: 144.9, 129.0, 126.1, 110.9, 43.4, 26.1 (d, $^{1}J_{\mathrm{PC}}$ = 56 Hz, P*C*HMe$_2$), 16.8. Anal. Calcd for C$_{28}$H$_{40}$NPS$_2$Ti: C, 63.03; H, 7.56; N: 2.62. Found: C, 62.78; H, 7.24; N, 2.33. **4**: method (i): yield 68%; (ii): yield 61%. ^{1}H NMR: 8.04 (d, 4H, S*Ph*), 7.13 (t, 4H, S*Ph*), 6.97 (t, 2H, S*Ph*), 6.16 (s, 5H, *Cp*), 1.50 (d of d, $^{2}J_{\mathrm{PH}}$ = 11.6 Hz, $^{3}J_{\mathrm{HH}}$ = 7 Hz, 3H, PC*H*Me$_2$), 0.81 (dd, $^{3}J_{\mathrm{PH}}$ = 15 Hz, $^{3}J_{\mathrm{HH}}$ = 7 Hz, 18H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR: 34.9. ^{13}C{^{1}H} NMR: 147.7, 133.1, 124.3, 112.0, 25.8 (d, $^{1}J_{\mathrm{PC}}$ = 55 Hz), 16.7. Anal. Calcd for C$_{26}$H$_{36}$NPS$_2$Ti: C, 61.77; H, 7.18; N, 2.77. Found: C, 61.58; H, 7.25; N, 2.83. **5**: method (ii): yield 83%. ^{1}H NMR: 6.36 (s, 5H, *Cp*), 1.82 (s, 18H, SC*Me*$_3$), 1.24 (m, $^{2}J_{\mathrm{PH}}$ = 15 Hz, $^{3}J_{\mathrm{HH}}$ = 7 Hz, 3H, PC*H*Me$_2$), 0.96 (dd, $^{3}J_{\mathrm{PH}}$ = 14 Hz, $^{3}J_{\mathrm{HH}}$ = 8 Hz, 18H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR: 29.3. ^{13}C{^{1}H} NMR: 110.7, 36.3, 26.5 (d, $^{1}J_{\mathrm{PC}}$ = 56 Hz), 17.1. Anal. Calcd for C$_{26}$H$_{36}$NPS$_2$Ti: C, 56.75; H, 9.53; N, 3.01. Found: C, 56.38; H, 9.25; N, 2.86. **6**: method (ii): yield 93%. ^{1}H NMR: 6.34 (s, 5H, *Cp*), 4.61 (t, $^{3}J_{\mathrm{HH}}$ = 15 Hz, 4H, SC*H*$_2$), 4.02 (t, $^{3}J_{\mathrm{HH}}$ = 15 Hz, 4H, SC*H*$_2$), 1.74 (m, 3H, PC*H*Me$_2$), 1.04 (m, 18, PCH*Me*$_2$). ^{31}P{^{1}H} NMR: 30.2. ^{13}C{^{1}H} NMR: 111.8, 33.6, 31.5, 24.3 (d, $^{1}J_{\mathrm{PC}}$ = 54 Hz,), 15.8. Anal. Calcd for C$_{32}$H$_{60}$N$_2$P$_2$S$_4$Ti$_2$: C, 50.65; H, 7.97; N, 3.69. Found: C, 50.21; H, 7.81; N, 3.60. **7**: method (ii): yield 87%. ^{1}H NMR: 6.31 (s, 5H, *Cp*), 3.86 (t, $^{2}J_{\mathrm{HH}}$ = 13.0 Hz, 2H, SC*H*$_2$), 3.51 (t, $^{2}J_{\mathrm{HH}}$ = 13.0 Hz, 2H, SC*H*$_2$), 1.61 (m, 3H, PC*H*Me$_2$), 0.97 (m, 2H, C*H*$_2$), 0.85 (m, 18H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR: 27.0. ^{13}C{^{1}H} NMR: 110.7, 37.6, 34.7, 26.8 (d, J_{PC} = 56 Hz), 16.8. Anal. Calcd for C$_{17}$H$_{32}$NPS$_2$Ti: C, 51.90; H, 8.20; N, 3.56. Found: C, 51.24; H, 8.25; N, 3.46. **8**: method (ii): yield 80%. ^{1}H NMR (C$_6$D$_6$): 7.32 (m, 2H, C$_6$*H*$_4$) 7.09 (m, 2H, C$_6$*H*$_4$), 6.15 (s, 5H, *Cp*), 5.07 (d, $^{2}J_{\mathrm{HH}}$ = 12 Hz, 2H, SC*H*$_2$), 4.70 (d, $^{2}J_{\mathrm{HH}}$ = 12 Hz, 2H, SC*H*$_2$), 1.60 (m, 3H, PC*H*Me$_2$), 0.93 (m, 18H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR: 28.6. ^{13}C{^{1}H} NMR: 110.6, 39.6, 26.7 (d, J_{PC} = 56 Hz), 16.7. Anal. Calcd for C$_{22}$H$_{34}$NPS$_2$Ti: C, 58.01; H, 7.52; N, 3.08. Found: C, 57.62; H, 7.68; N, 2.95. **9**: yield 80%. ^{1}H NMR: 7.55 (d, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 4H, *o*-Ar-*H*), 7.18 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 4H, *m*-Ar*H*), 7.05 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 2H, *p*-Ar*H*), 6.30 (s, 5H, *Cp*), 4.63 (s, 4H, SC*H*$_2$Ph), 1.18 (d, $^{3}J_{\mathrm{PH}}$ = 13 Hz, 27H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 40.8. ^{13}C{^{1}H} NMR: 30.1, 41.7 (d, $^{1}J_{\mathrm{PC}}$ = 43 Hz), 43.2, 111.9, 26.6, 128.8, 129.4, 145.2. Anal. Calcd for C$_{31}$H$_{46}$NPS$_2$Ti: C, 64.68; H, 8.05; N, 2.43. Found: C, 64.58; H, 7.95; N, 2.23. **10**: method (ii): yield 93%. ^{1}H NMR: 7.98 (d, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 4H, *o*-Ph*H*), 7.11 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 4H, *m*-Ph*H*), 6.95 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 2H, *p*-Ph*H*), 6.18 (s, 5H, *Cp*), 1.11 (d, $^{3}J_{\mathrm{PH}}$ = 14 Hz, 27H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 43.7. ^{13}C{^{1}H} NMR: 29.9, 41.8 (d, $^{1}J_{\mathrm{PC}}$ = 43 Hz), 113.3, 125.0, 128.7, 133.6, 147.7. Anal. Calcd for C$_{29}$H$_{42}$NPS$_2$Ti: C, 63.60; H, 7.73; N, 2.56. Found: C, 63.55; H, 7.22; N, 2.21. **11** method (ii): yield 87%. ^{1}H NMR: 6.49 (s, 5H, *Cp*), 1.73 (s, 18H, SC*Me*$_3$), 1.28 (d, $^{3}J_{\mathrm{PH}}$ = 13 Hz, 27H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 39.9. ^{13}C{^{1}H} NMR: 110.5, 46.6, 41.8 (d, $^{1}J_{\mathrm{PC}}$ = 43 Hz), 36.5, 30.1. Anal. Calcd for C$_{26}$H$_{36}$NPS$_2$Ti: C, 59.15; H, 9.93; N, 2.76. Found: C, 58.88; H, 9.65; N, 2.63. **14**: method (ii): yield 95%. ^{1}H NMR: 7.70 (d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 4H, *o*-SCH$_2$Ph); 7.19 (pseudo t, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 4H, *m*-SCH$_2$Ph); 7.11 (t, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 2H, *p*-SCH$_2$Ph); 4.96 (s, 4H, SCH$_2$); 1.35 (d, $^{3}J_{\mathrm{PH}}$ = 12.7 Hz, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 33.4. ^{13}C{^{1}H} NMR: 145.3 (s, *ipso*-Ph); 129.2 (s, *o*-Ph); 128.3 (s, *m*-Ph); 125.9 (s, *p*-Ph); 40.9 (d, $^{1}J_{\mathrm{PC}}$ = 47 Hz, P*C*Me$_3$); 37.1 (s, S*C*H$_2$); 29.9 (s, PC*Me*$_3$). Anal. Calcd for C$_{38}$H$_{64}$N$_2$P$_2$S$_2$Ti: C, 62.79; H, 9.43; N, 3.85. Found: C, 62.51; H, 9.19; N, 3.76. **15**: method (ii): yield 90%. ^{1}H NMR: 8.21 (d, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 4H, *o*-SPh); 7.21 (pseudo t, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 2H, *p*-SPh); 7.11 (t, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, 4H, *m*-SPh); 1.23 (d, $^{3}J_{\mathrm{PH}}$ = 13.0 Hz, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 34.8. ^{13}C{^{1}H} NMR: 144.8 (s, *ipso*-Ph); 143.2 (s, *o*-Ph); 133.8 (s, *m*-Ph); 123.8 (s, *p*-Ph); 40.8 (d, $^{1}J_{\mathrm{PC}}$ = 38.4 Hz, P*C*Me$_3$); 29.7 (s, PC*Me*$_3$). Anal. Calcd for C$_{36}$H$_{64}$N$_2$P$_2$S$_2$Ti: C, 61.87; H, 9.23; N, 4.01. Found: C, 62.10; H, 9.43; N, 3.72. **16**: method (ii): yield 90%. ^{1}H NMR: 1.97 (s, 18H, SC*Me*$_3$); 1.43 (d, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 31.7. ^{13}C{^{1}H} NMR: 45.3 (s, S*C*Me$_3$); 41.5 (d, $^{1}J_{\mathrm{PC}}$ = 46.1 Hz, P*C*Me$_3$); 37.9 (s, SC*Me*$_3$); 30.3 (s, PC*Me*$_3$). Anal. Calcd for C$_{32}$H$_{72}$N$_2$P$_2$S$_2$Ti: C, 58.33; H, 11.01; N, 4.25. Found: C, 58.61; H, 10.74; N, 4.50. **19:** method (ii): yield 89%. ^{1}H NMR: 1.94 (s, 9H, SC*Me*$_3$); 1.39 (d, $^{3}J_{\mathrm{PH}}$ = 12.8 Hz, 54H, PC*Me*$_3$); 1.06 (s, 3H, Ti*Me*). ^{31}P{^{1}H} NMR: 29.2. ^{13}C{^{1}H} NMR: 45.0 (s, S*C*Me$_3$); 41.1 (d, $^{1}J_{\mathrm{PC}}$ = 47 Hz, P*C*Me$_3$); 38.0 (s, SC*Me*$_3$); 37.8 (s, Ti*C*H$_3$); 30.1 (s, PC*Me*$_3$). Anal. Calcd for C$_{29}$H$_{66}$N$_2$P$_2$STi: C, 59.57; H, 11.38; N, 4.79. Found: C, 59.24; H, 11.32; N, 4.85.

Generation of (*t*-Bu$_3$PN)$_2$Ti-(η^2SCHPh) 17. A resealable NMR tube equipped with a Teflon screw-cap was charged with **13** (0.022 g, 43 μmol) and C$_6$D$_6$ (0.6 mL). Benzylthiol was added to the NMR tube, which was immediately sealed. This method consistently gave a mixture of starting material **13**, **14**, and **17** and thus could not be isolated analytically pure. **17** was generated in 60% yield as judged by NMR spectroscopy. ^{1}H NMR: 7.89 (d, $^{3}J_{\mathrm{HH}}$ = 4.6 Hz, 2H, *o*-SPh); 7.25 (pseudo t, $^{3}J_{\mathrm{HH}}$ = 4.6 Hz, 1H, *p*-SPh); 6.92 (d, $^{3}J_{\mathrm{HH}}$ = 4.6 Hz, 2H, *m*-SPh); 4.85 (s, 1H, TiSC*H*Ph); 1.35 (obscured, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 26.6, 27.9 (2 s, N*P* *syn* and *anti* to Ph). ^{13}C{APT} NMR: 152.9 (s, *ipso*-Ph), 126.9 (s, *o*-Ph); 124.4 (s, *p*-Ph); 121.0 (s, *m*-Ph); 88.0 (s, TiS*C*HPh); 41.05 (d, $^{1}J_{\mathrm{PC}}$ = 47 Hz, P*C*Me)$_3$); 30.6 (s, PCMe$_3$).

Generation of CpTi(NP*t*-Bu$_3$)Me(SPh) 12; (*t*-Bu$_3$PN)$_2$Ti(Me)(SPh) 18. These complexes were prepared employing similar methods; thus one representative preparation is

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presented. Method (ii) described above was employed. However, this method consistently gave a mixture of starting material, **15**, and **18**, and thus **18** could not be isolated analytically pure. Compound **18** was generated in 81% yield as judged by NMR spectroscopy. **12**: method (ii): yield 85%. ^{1}H NMR: 7.61 (d, $^{3}J_{HH} = 7$ Hz, 2H, *o*-Ph*H*), 7.10 (t, $^{3}J_{HH} = 7$ Hz, 2H, *m*-Ph*H*), 6.96 (t, $^{3}J_{HH} = 7$ Hz, 1H, *p*-Ph*H*), 6.06 (s, 5H, *Cp*), 1.21(d, $^{3}J_{PH} = 13$ Hz, 27H, PC*Me*$_3$), 1.07 (s, 3H, Ti*Me*). ^{31}P{^{1}H} NMR: 37.5. ^{13}C{^{1}H} NMR: 147.1, 128.6, 124.8, 113.5, 112.0, 41.8 (d, $^{1}J_{PC} = 43$ Hz), 39.7, 30.0. **18**: ^{1}H NMR: 7.93 (d, $^{3}J_{HH} = 6.8$ Hz, 2H, *o*-SPh); 7.09 (pseudo t, $^{3}J_{HH} = 7.7$ Hz, 2H, *m*-SPh); 6.93 (t, $^{3}J_{HH} = 6.8$ Hz, 1H, *p*-SPh); 1.29 (d, $^{3}J_{PH} = 12.8$ Hz, 54H, PC*Me*$_3$); 1.19 (s, 3H, Ti*Me*), 0.14 (s, C*H*$_4$). ^{31}P{^{1}H} NMR: 29.8. ^{13}C{^{1}H} NMR: 144.6 (s, *ipso*-Ph); 133.9 (s, *o*-Ph); 128.2 (s, *m*-Ph); 123.6 (s, *p*-Ph); 40.9 (d, $^{1}J_{PC} = 46.9$ Hz, P*C*Me$_3$); 37.4 (s, Ti*Me*); 29.8 (s, PC*Me*$_3$).

Synthesis of (*t*-Bu$_3$PN)$_2$Ti(η^2-S$_5$) 20. A sintered glass vial was charged with **13** (0.028 g, 55 μmol), and toluene (6 mL) was added. Addition of S$_8$ (0.022 g, 86 μmol) resulted in the immediate formation of a bright yellow solution that was stirred overnight. The toluene was removed in vacuo, yielding a yellow powder. Yield: 0.030 g, 85%. ^{1}H NMR: 1.29 (d, $^{3}J_{PH} = 12.9$ Hz, 54H, PC*Me*$_3$). ^{31}P{^{1}H} NMR: 33.2. ^{13}C{^{1}H} NMR: 41.2 (d, $^{1}J_{PC} = 46.1$ Hz, P*C*Me$_3$); 29.9 (s, PC*Me*$_3$). Anal. Calcd for $C_{24}H_{54}N_2P_2S_5Ti$: C, 44.98; H, 8.49; N, 4.37. Found: C, 44.88; H, 8.44; N, 4.33.

Synthesis of [CpTi(μ^2-SR)(μ^2-NP*i*-Pr$_3$)(μ^4-C)(AlMe$_2$)$_2$(μ-SR)AlMe] (R = CH$_2$Ph 21, Ph 22, *t*-Bu 23). These compounds were prepared in a similar manner, and thus one representative preparation is detailed. To a solution of **4** (0.200 g; 0.396 mmol) in benzene was added 2.0 M AlMe$_3$ (0.75 mL; 1.500 mmol). The solution was stirred for 10 h and the solvent removed under vacuum. Recrystallization of the product from benzene afforded **23** as red crystals. **21**: Yield: 74%. ^{1}H NMR: 7.27 (d, 4H, SCH$_2$*Ph*), 7.13 (t, 4H, SCH$_2$*Ph*), 7.03 (t, 2H, SCH$_2$*Ph*), 6.26 (s, 5H, Cp), 3.85 (d, $^{2}J_{HH} = 13$ Hz, 2H, SC*H*$_2$-Ph), 3.75 (d, $^{2}J_{HH} = 13$ Hz, 2H, SC*H*$_2$Ph), 1.64 (d of sept, $^{2}J_{PH} = 13$ Hz, $^{3}J_{HH} = 7$ Hz, 3H, PC*H*Me$_2$), 0.74 (dd, $^{3}J_{PH} = 15$ Hz, $^{3}J_{HH} = 7$ Hz, 9H, PCH*Me*$_2$), 0.57 (dd, $^{3}J_{PH} = 15$ Hz, $^{3}J_{HH} = 7$ Hz, 9H, PCH*Me*$_2$), 0.27 (s, 3H, AlMe), 0.11 (s, 3H, AlMe), −0.01 (s, 3H, AlMe), −0.07 (s, 3H, AlMe), −0.29 (s, 3H, AlMe). ^{31}P{^{1}H} NMR: 52.9. ^{13}C{^{1}H} NMR: 141.2, 129.0, 129.0, 127.0, 126.8, 110.1, 38.3, 32.6, 26.5 (d, $^{1}J_{PC} = 56.4$, P*C*HMe$_2$), 16.4 (d, $^{2}J_{PC} = 34$ Hz, PCH*Me*$_2$), 14.3, −4.8, −6.9, −7.2, −7.8. Anal. Calcd for $C_{34}H_{55}Al_3NPS_2Ti$: C, 58.19; H, 7.90; N, 2.00. Found: C, 58.02; H, 761; N, 1.89. **22:** Yield: 83%. ^{1}HNMR: 7.58 (d, 2H, S*Ph*), 7.55 (d, 2H, S*Ph*), 7.05 (m, 4H, S*Ph*), 6.95(m, 2H, S*Ph*), 6.18 (s, 5H, *Cp*), 1.80 (d of sept, $^{2}J_{PH} = 13$ Hz, $^{3}J_{HH} = 7$ Hz, 3H, PC*H*Me$_2$), 0.88 (dd, $^{3}J_{PH} = 14$ Hz, $^{3}J_{HH} = 7$ Hz, 9H, PCH*Me*$_2$), 0.85 (dd, $^{3}J_{PH} = 14$ Hz, $^{3}J_{HH} = 7$ Hz, 9H, PCH*Me*$_2$), 0.30 (s, 3H, AlMe), 0.17 (s, 3H, AlMe), 0.06 (s, 3H, AlMe), 0.04 (s, 3H, AlMe), −0.32 (s, 3H, AlMe). ^{31}P{^{1}H} NMR: 54.1. ^{13}C{^{1}H} NMR: 140.0, 133.8, 132.8, 131.7, 126.5, 126.1, 111.3, 26.7 (d, $^{1}J_{PC} = 56.4$, P*C*HMe$_2$), 16.7, −4.4, −5.8, −7.1. Anal. Calcd for $C_{32}H_{51}Al_3NPS_2Ti$: C, 57.05; H, 7.63; N, 2.08. Found: C, 57.16; H, 7.71; N, 2.10. **23**: Yield: 56%. ^{1}H NMR: 6.42 (s, 5H, *Cp*), 1.78 (sept, $^{2}J_{PH} = 6$ Hz, 3H, PC*H*Me$_2$), 0.82 (m, 18H, PCH*Me*$_2$), 0.29 (m, 9H, AlMe) 0.04 (m, 9H, AlMe), −0.16 (s, 3H, AlMe), −0.28 (m, 6H, AlMe), −0.32 (m, 6H, AlMe). ^{31}P{^{1}H} NMR: 51.2. ^{13}C{^{1}H} NMR: 109.5, 35.5 (d, $^{1}J_{PC} = 10$ Hz), 30.4, 27.4, 26.6, 17.1 (d, $^{2}J_{PC} = 14$ Hz), 1.6. Anal. Calcd for $C_{31}H_{62}Al_3NPS_2Ti$: C, 53.07; H, 9.38; N, 2.21. Found: C, 53.49; H, 9.26; N, 2.06.

Alternate Synthesis of 23. To a solution of CpTi(μ^2-Me)(μ^2-NP*i*-Pr$_3$)(μ^4-C)(AlMe$_2$)$_3$ (0.048 g; 0.099 mmol) in benzene was added *t*-BuSH (0.018 g; 0.20 mmol). The reaction was allowed to stir for 10 h and the solvent removed under vacuum. Recrystallization of the product from benzene afforded **22** as burgundy crystals in 60% yield.

Synthesis of [CpTi(NP*i*-Pr$_3$)(S$_2$R)]·(AlMe$_3$)$_3$ (R = (CH$_2$)$_3$ 24, (CH$_2$)$_2$C$_6$H$_4$ 25). These compounds were prepared in a similar manner, and thus one representative preparation is detailed. To a solution of **7** (029 g; 0.073 mmol) in benzene was added 2.0 M AlMe$_3$ (0.11 mL; 0.221 mmol). The solution was allowed to stir for 12 h and the solvent removed under vacuum to afford **24** as a dark orange powder. **24**: Yield: 78%. ^{1}H NMR: 6.43 (s, 5H, *Cp*), 3.50 (m, 2H, SC*H*$_2$), 3.26 (m, 2H, SC*H*$_2$) 2.97 (m, 2H, C*H*$_2$), 1.53 (m, 3H, PC*H*Me$_2$), 0.76 (m, 18H, PCH*Me*$_2$), −0.11 (s, 27H, AlMe). ^{31}P{^{1}H} NMR: 40.8. ^{13}C{^{1}H} NMR: 118.7, 40.7, 35.3, 30.5 (d, $J_{PC} = 52.5$ Hz), 21.1, 20.7. Anal. Calcd for $C_{26}H_{59}Al_3NPS_2Ti$: C, 51.22; H, 9.75; N, 2.30. Found: C, 51.01; H, 9.46; N, 2.02. **25**: Yield: 55%. ^{1}H NMR: 7.42 (m, 2H, C$_6$H$_4$), 7.01 (m, 2H, C$_6$*H*$_4$), 6.27 (s, 5H, *Cp*), 4.55 (m, 4H, SC*H*$_2$), 1.55 (m, 3H, PC*H*Me$_2$), 0.83 (m, 18H, PCH*Me*$_2$), −0.14 (s, 27H, AlMe). ^{31}P{^{1}H} NMR: 41.3. ^{13}C{^{1}H} NMR: 137.5, 130.0, 128.6, 113.9, 25.9 (d, $J_{PC} = 55$ Hz), 16.6, 12.8. Anal. Calcd for $C_{31}H_{61}Al_3NPS_2Ti$: C, 55.43; H, 9.15; N, 2.09. Found: C, 54.96; H, 9.06; N, 2.05.

X-ray Data Collection and Reduction. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O$_2$-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected for 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. 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. 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. For **16** and **22**, which crystallize in noncentrosymmetric space groups, the absolute configurations were obtained by comparison with the inverted model. In these cases the respective Flack parameters of 0.0720 and −0.0173 were consistent with the correct absolute configuration.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[16] The heavy atom positions were determined using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on *F*, minimizing the function $w(F_o - F_c)^2$, where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

Synthesis and Structure. Formation of a series of titanium−phosphinimide thiolate complexes was achieved employing two standard synthetic strategies involving thiolate for chloride metathesis and protonolysis of metal−carbon bonds by thiols (Scheme 1). For example, reaction of CpTi(NP*i*-Pr$_3$)Cl$_2$ **1** with the lithium salts LiSR (R = CH$_2$Ph; Ph) resulted in the formation

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[16] Cromer, D. T.; Mann, J. B. *Acta Crystallogr. A* **1968**, *A24*, 321−324.

of the species $CpTi(NP\textit{i}\text{-}Pr_3)(SR)_2$ (R = CH_2Ph **3**; Ph **4**). These products could also be obtained by reactions of $CpTi(NP\textit{i}\text{-}Pr_3)Me_2$ **2** with the corresponding thiol with liberation of methane. In this way, species **3**, **4**, and $CpTi(NP\textit{i}\text{-}Pr_3)(S\textit{t}\text{-}Bu)_2$ **5** were prepared. In a similar manner, protonolysis of **2** by dithiols yielded products that exhibited spectroscopic parameters consistent with the empirical formula $CpTi(NP\textit{i}\text{-}Pr_3)(S_2R)$ (R = $(CH_2)_2$ **6**, $(CH_2)_3$ **7**, $(CH_2)_2C_6H_4$ **8**). Similarly, employing the precursor $CpTi(NP\textit{t}\text{-}Bu_3)Me_2$ **9**, the species $CpTi(NP\textit{t}\text{-}Bu_3)(SR)_2$ (R = CH_2Ph **9**; Ph **10**; *t*-Bu **11**) were isolated. Employing the species $(\textit{t}\text{-}Bu_3PN)_2TiMe_2$ **13**, the species $(\textit{t}\text{-}Bu_3PN)_2Ti(SR)_2$ (R = CH_2Ph **14**; Ph **15**; *t*-Bu **16**) were prepared.

While the spectroscopic and elemental analysis data were consistent with the formulation of these products, the structures of these molecules were confirmed by X-ray crystallography in several cases. The structure of compound **4** (Figure 1) revealed the Ti−N distance of 1.770(3) Å, slightly longer than the 1.753(3) Å found for the dichloride precursor **1**. The P−N−Ti angle of 166.0(3)° approaches linearity, as is typical of most Ti-phosphinimide complexes. The average Ti−S bond distance was found to be 2.395(15) Å, while the S(1)−Ti−S(2) average bonding angle was determined to be 105.30(6)°. These values compare with the average Ti−S bond distances of 2.315 Å and the S(1)−Ti−S(2) angle of 107.6(2)° found for the Ti-aryloxide complex $Cp(OAr')Ti(SEt)_2$.[1]

An X-ray crystallographic study of **6** revealed a centrosymmetric dimeric formulation in which two pseudo-tetrahedral titanium centers are linked by two dithiolate fragments (Figure 2). The resulting macrocycle adopts a crown-like conformation with axial phosphinimide ligands on either end. The average Ti−N and Ti−S bond distances in **6** are 1.790(4) and 2.370(16) Å, respectively, while the P−N−Ti and S(1)−Ti−S(2) angles are 162.4(3)° and 109.06(6)°, respectively. This geometry stands in contrast to related metallocenes of the form $[Cp_2M(SCH_2CH_2S)]_n$ (M = Ti, Zr, V), in which an additional metal−sulfur interaction gives rise to twisted-bridging conformations which dynamically interconvert in solution.[17,18] Variable-temperature studies of **6** showed no temperature dependence of the NMR resonances. This observation suggests that despite the fact that chemical evidence suggests that the $CpTi(NPR_3)$ fragment is more electrophilic than Cp_2Ti, a twisted-conformation of **6** is precluded, as such a geometry would bring the sterically demanding phosphinimide ligands in close proximity to the opposite cyclopentadienyl ligand.

In contrast to **6**, an X-ray crystallographic study of **7** revealed it to be a monometallic, pseudo-tetrahedral Ti complex (Figure 3) The average Ti−N and Ti−S distances in **7** are 1.854(5) and 2.40(2) Å, respectively. This Ti−N distance is slightly longer than that seen in **6**, although the reasons for this remain unclear. The Ti−S distances are also slightly longer than those seen in the Ti-aryloxide thiolate species $Cp(OAr')Ti(S_2(CH_2)_3)$ ($Ti-S_{av}$) value of 2.357(4) Å.[19] This suggests the phosphin-

Table 1. Crystallographic Parameters

	4	**6**	**7**	**14**	**16**	**20**	**21**	**22**	**23**
formula	$C_{26}H_{36}NPS_2Ti$	$C_{32}H_{60}N_2P_2S_4Ti_2$	$C_{17}H_{32}NPS_2Ti$	$C_{38}H_{68}N_2P_2S_2Ti$	$C_{32}H_{72}N_2P_2S_2Ti$	$C_{24}H_{54}N_2P_2S_5Ti$	$C_{34}H_{55}Al_3NPS_2Ti$	$C_{32}H_{51}Al_3NPS_2Ti$	$C_{31}H_{62}Al_3NPS_2Ti$
fw	505.55	758.80	393.43	726.90	658.88	640.83	701.7	673.67	672.75
a (Å)	11.3824(6)	10.5817(3)	40.4144(3)	12.2498(6)	9.372(5)	13.9488(13)	10.065(2)	13.01820(10)	38.3786(4)
b (Å)	14.1636(7)	11.6667(3)	45.2706(3)	14.4267(7)	18.089(10)	14.4967(13)	15.340(3)	13.5639(2)	43.8431(4)
c (Å)	17.0420(8)	16.5553(5)	10.18870(10)	24.1201(12)	12.488(7)	17.0111(16)	26.120(7)	21.1859(2)	10.52970(10)
β (deg)	101.0660(10)	97.9100(10)		93.7900(10)	101.983(10)	94.970(2)	93.24(2)		
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$Fdd2$	$P2_1/n$	$P2_1$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$Fdd2$
volume (Å^3)	2696.4(2)	2024.36(10)	18641.1(3)	4253.3(4)	2071(2)	3426.9(5)	4026.7(15)	3740.96(7)	17717.7(3)
D_{calc} (g cm^{-1})	1.245	1.245	1.121	1.135	1.057	1.242	1.158	1.196	1.009
Z	4	4	32	2	2	4	4	4	16
abs coeff, μ (cm^{-1})	0.545	0.703	0.613	0.401	0.405	0.665	0.444	0.475	0.401
θ range (deg)	1.88−25.00	2.14−25.00	1.35−25.00	1.65−25.00	2.01−23.27	1.97−23.26	1.54−25.00	1.78−25.00	1.86−24.00
no. of reflns collected	12 635	3527	8045	7297	5645	4920	7034	6552	6659
data $F_o^2 > 3\sigma(F_o^2)$	4720	3005	7110	5487	3886	3890	4980	6105	4568
no. of params	280	190	397	370	352	307	379	361	343
R (%)[a]	0.0780	0.0427	0.0595	0.0985	0.0722	0.0280	0.0406	0.0295	0.0824
R_w (%)[a]	0.1742	0.0993	0.1844	0.3062	0.1895	0.0737	0.1158	0.0802	0.1355
goodness of fit	0.799	0.524	0.822	1.332	0.965	0.986	0.917	0.899	1.219

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{0.5}$.

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(19) Firth, A. V.; Stephan, D. W. *Inorg. Chem.* **1998**, *37*, 4726−4731.

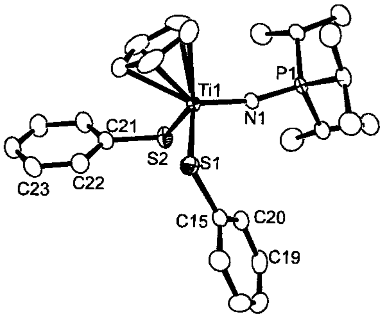
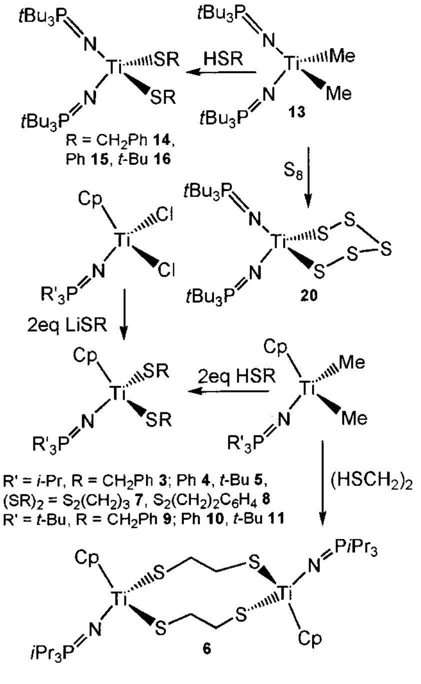


Figure 1. ORTEP drawing of **4**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−N(1) 1.770(3), Ti(1)−S(2) 2.3903(14), Ti(1)−S(1) 2.4008(14), P(1)−N(1) 1.614(3), S(1)−C(15) 1.767(5), S(2)−C(21) 1.775(4), N(1)−Ti(1)−S(2) 95.88(12), N(1)−Ti(1)−S(1) 106.76(12), S(2)−Ti(1)−S(1) 105.28(5), P(1)−N(1)−Ti(1) 166.0(3), C(15)−S(1)−Ti(1) 112.36(16), C(21)−S(2)−Ti(1) 110.93(15).

Scheme 1



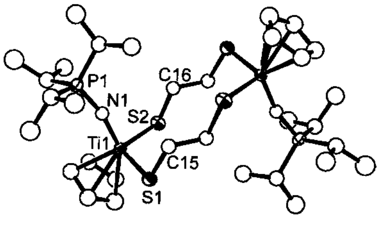


Figure 2. ORTEP drawing of **6**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−N(1) 1.791(2), Ti(1)−S(1) 2.3701(8), Ti(1)−S(2) 2.3743(8), S(1)−C(15) 1.827(3), S(2)−C(16) 1.829(3), P(1)−N(1) 1.594(2), N(1)−Ti(1)−S(1) 104.00(8), N(1)−Ti(1)−S(2) 101.94(7), S(1)−Ti(1)−S(2) 109.02(3), C(15)−S(1)−Ti(1) 104.86(9), C(16)−S(2)−Ti(1) 104.68(9), P(1)−N(1)−Ti(1) 162.47(15).

imide ligand is a better donor than aryloxide. The S(1)−Ti−S(2) angle in **7** is 98.62(10)°, which is smaller than that reported for **6**, presumably a result of chelation.

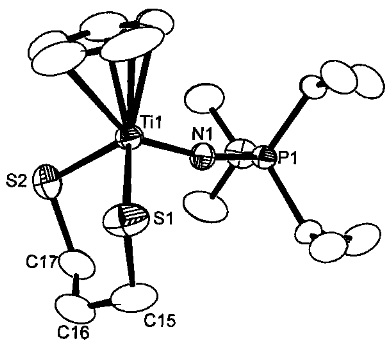


Figure 3. ORTEP drawing of one of the two molecules of **7** in the asymmetric unit; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−N(1) 1.843(5), Ti(1)−S(2) 2.392(2), Ti(1)−S(1) 2.415(2), S(1)−C(15) 1.893(8), S(2)−C(17) 1.889(9), P(1)−N(1) 1.631(5), N(1)−Ti(1)−S(2) 104.02(15), N(1)−Ti(1)−S(1) 104.58(17), S(2)−Ti(1)−S(1) 98.62(10), C(15)−S(1)−Ti(1) 98.8(3), C(17)−S(2)−Ti(1) 99.7(3), P(1)−N(1)−Ti(1) 168.1(3). Distances and angles in second molecule in the asymmetric unit: Ti(2)−N(2) 1.830(6), Ti(2)−S(4) 2.4067(19), Ti(2)−S(3) 2.410(2), S(3)−C(32) 1.878(7), S(4)−C(34) 1.877(7), P(2)−N(2) 1.647(6), N(2)−Ti(2)-S(4) 103.67(18), N(2)−Ti(2)−S(3) 104.54(16), S(4)−Ti(2)−S(3) 97.32(8), C(32)−S(3)−Ti(2) 100.1(2), C(34)−S(4)−Ti(2) 98.7(2), P(2)−N(2)−Ti(2) 167.8(3).

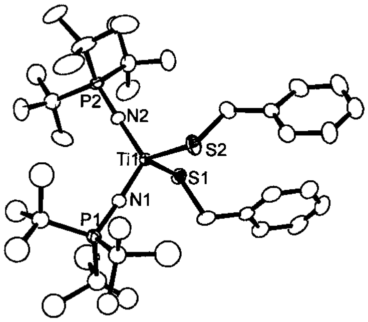


Figure 4. ORTEP drawing of **14**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−N(1) 1.801(4), Ti(1)−N(2) 1.804(4), Ti(1)−S(1) 2.3596(18), Ti(1)−S(2) 2.3628(17), S(1)−C(25) 1.835(7), S(2)−C(32) 1.826(7), P(1)−N(1) 1.581(4), P(2)−N(2) 1.577(4), N(1)−Ti(1)−N(2) 118.7(2), N(1)−Ti(1)−S(1) 111.76(15), N(2)−Ti(1)−S(1) 102.44(16), N(1)−Ti(1)−S(2) 101.48(15), N(2)−Ti(1)−S(2) 114.68(16), S(1)−Ti(1)−S(2) 107.62(7), C(25)−S(1)−Ti(1) 103.8(3), C(32)−S(2)−Ti(1) 104.9(2), P(1)−N(1)−Ti(1) 175.8(3), P(2)−N(2)−Ti(1) 175.5(3).

The solid-state structures of **14** (Figure 4) and **16** (Figure 5) reveal pseudo-tetrahedral geometries about Ti, comprised of two phosphinimide and two thiolate ligands. The Ti−N distances vary from 1.801(4) to 1.813(4) Å, slightly shorter than those seen in **4**, **6**, and **7**. Similarly the Ti−S distances range from 2.332(3) to 2.389(3) Å, consistent with the electron-deficient metal centers in **14** and **16**. The remaining metric parameters are unexceptional. In the case of **14**, the phenyl rings of the benzyl groups adopt a parallel arrangement, suggestive of π-stacking.

Reactions of **9** with 1 equiv of phenylthiol proceeds to generate an inseparable mixture of CpTi(NPt-Bu$_3$)Me(SPh) **12** and **10**. In an similar reaction of **13** with 1 equiv of benzylthiol, a mixture of the products **14** and a new species presumed to be (t-Bu$_3$PN)$_2$Ti(Me)(SCH$_2$Ph) was observed spectroscopically. This latter species exhibits a $^{31}P\{^1H\}$ NMR resonance at 29.4 ppm. This

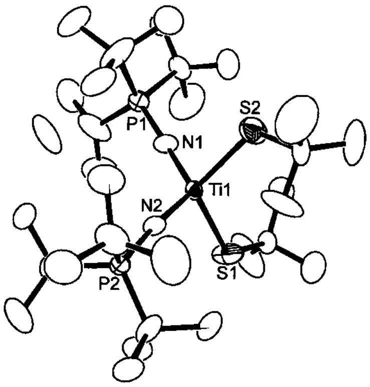


Figure 5. ORTEP drawing of **16**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−N(1) 1.804(6), Ti(1)−N(2) 1.813(5), Ti(1)−S(1) 2.332(3), Ti(1)−S(2) 2.389(3), S(1)−C(28) 1.803(7), S(2)−C(32) 1.781(9), P(1)−N(1) 1.592(7), P(2)−N(2) 1.590(6), N(1)−Ti(1)−N(2) 118.2(3), N(1)−Ti(1)−S(1) 117.4(2), N(2)−Ti(1)−S(1) 98.62(19), N(1)−Ti(1)−S(2) 90.3(2),N(2)−Ti(1)−S(2) 118.9(2), S(1)−Ti(1)−S(2) 115.06(16), C(28)−S(1)−Ti(1) 121.2(3), C(32)−S(2)−Ti(1) 118.7(4), P(1)−N(1)−Ti(1) 171.7(4), P(2)−N(2)−Ti(1) 172.1(4).

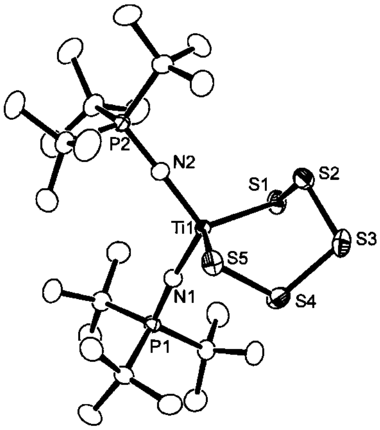


Figure 6. ORTEP drawing of **20**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−N(1) 1.8092(17), Ti(1)−N(2) 1.8124(17), Ti(1)−S(5) 2.4204(7), Ti(1)−S(1) 2.4243(7), Ti(1)−S(2) 2.8711(8), Ti(1)−S(4) 2.8935(8), S(1)−S(2) 2.0375(10), S(2)−S(3) 2.0608(10), S(3)−S(4) 2.0763(10), S(4)−S(5) 2.0290(10), P(1)−N(1) 1.5842(18), P(2)−N(2) 1.5767(17), N(1)−Ti(1)−N(2) 113.35(8), N(1)−Ti(1)−S(5) 107.05(6), N(2)−Ti(1)−S(5) 102.69(6), N(1)−Ti(1)−S(1) 104.30(6), N(2)−Ti(1)−S(1) 107.97(6), S(5)−Ti(1)−S(1) 121.80(3), N(1)−Ti(1)−S(2) 142.48(6), N(2)−Ti(1)−S(2) 98.38(6), S(5)−Ti(1)−S(2) 83.67(2), S(1)−Ti(1)−S(2) 44.26(2), N(1)−Ti(1)−S(4) 95.90(6), N(2)−Ti(1)−S(4) 142.41(6), S(5)−Ti(1)−S(4) 43.78(2), S(1)−Ti(1)−S(4) 85.65(2), S(2)−Ti(1)−S(4) 66.72(2), S(2)−S(1) Ti(1) 79.59(3), S(1)−S(2)−S(3) 108.21(4), S(1)−S(2)−Ti(1) 56.15(2), S(3)−S(2)−Ti(1) 97.11(3), S(2)−S(3)−S(4) 100.04(4), S(5)−S(4)−S(3) 107.96(4), S(5)−S(4)−Ti(1) 55.62(2), S(3)−S(4)−Ti(1) 96.07(3), S(4)−S(5)−Ti(1) 80.61(3), P(1)−N(1)−Ti(1) 174.07(12), P(2)−N(2)−Ti(1) 175.58(12).

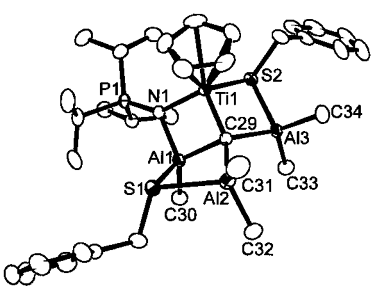


Figure 7. ORTEP drawing of **21**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−C(29) 1.900(3), Ti(1)−N(1) 2.005(2), Ti(1)−S(2) 2.4588(10), Al(1)−N(1) 1.883(2), Al(1)−C(30) 1.953(3), Al(1)−C(29) 2.002(3), Al(1)−S(1) 2.3599(12), Al(2)−C(31) 1.955(4), Al(2)−C(32) 1.969(4), Al(2)−C(29) 1.991(3), Al(2)−S(1) 2.4564(13), Al(3)−C(33) 1.962(3), Al(3)−C(34) 1.963(3), Al(3)−C(29) 2.001(3), Al(3)−S(2) 2.4103(12), P(1)−N(1) 1.604(2), C(29)−Ti(1)−N(1) 92.82(10), C(29)−Ti(1)−S(2) 93.17(8), N(1)−Ti(1)−S(2) 104.53(6), N(1)−Al(1)−C(30) 119.66(13), N(1)−Al(1)−C(29) 93.41(10), C(30)−Al(1)−C(29) 126.68(13), N(1)−Al(1)−S(1) 113.31(7), C(30)−Al(1)−S(1) 109.79(11), C(29)−Al(1)−S(1) 90.20(8), C(31)−Al(2)−C(32) 113.8(2), C(31)−Al(2)−C(29) 120.1(2), C(32)−Al(2)−C(29) 115.43(14), C(31)−Al(2)−S(1) 106.75(14), C(32)−Al(2)−S(1) 108.54(13), C(29)−Al(2)−S(1) 87.73(8), C(33)−Al(3)−C(34) 116.0(2), C(33)−Al(3)−C(29) 114.80(13), C(34)−Al(3)−C(29) 115.88(13), C(33)−Al(3)−S(2) 103.96(12), C(34)−Al(3)−S(2) 110.46(12), C(29)−Al(3)−S(2) 92.14(8), C(15)−S(1)−Al(1) 110.51(14), C(15)−S(1)−Al(2) 110.80(13), Al(1)−S(1)−Al(2) 75.15(4), C(22)−S(2)−Al(3) 112.82(13), C(22)−S(2)−Ti(1) 117.02(11), Al(3)−S(2)−Ti(1) 73.55(3), P(1)−N(1)−Al(1) 131.25(13), P(1)−N(1)−Ti(1) 141.24(13), Al(1)−N(1)−Ti(1) 87.07(9), Ti(1)−C(29)−Al(2) 141.36(14), Ti(1)−C(29)−Al(3) 96.68(12), Al(2)−C(29)−Al(3) 114.10(13), Ti(1)−C(29)−Al(1) 86.69(10), Al(2)−C(29)−Al(1) 94.75(11), Al(3)−C(29)−Al(1) 123.08(13).

product is unstable and evolves CH_4 over a couple of hours to give a cyclometalated species (*t*-Bu$_3$PN)$_2$Ti(η^2-SCHPh) **17**. This compound exhibits two ^{31}P{^{1}H} NMR resonances at 26.6 and 27.9 ppm, as a result of the phosphinimide groups *syn* and *anti* to the phenyl group. A ^{1}H NMR resonance at 4.85 ppm is assigned the metalated methine proton, while a ^{13}C{APT} NMR spectrum reveals the methine carbon resonance at 88.0 ppm. A two-dimensional HMQC C−H correlation spectrum confirms the connectivity of these resonances. Despite the fact that **17** could be characterized in solution, all efforts to isolate it from **14** and residual **13** were unsuccessful, and thus analytical data for **17** were not obtained. It is noteworthy that we have previously shown that the thermal reaction of Cp(OAr′)TiMe(SEt) affords the similar metalated product [Cp(OAr′)Ti(SCHMe)]$_2$, which has been structurally characterized.[1]

The analogous reaction of 1 equiv of phenylthiol with **13** led to a mixture of **15** and the species (*t*-Bu$_3$PN)$_2$Ti(Me)(SPh) **18**. However, in contrast, reaction of **13** with *tert*-butylthiol afforded (*t*-Bu$_3$PN)$_2$Ti(Me)(S*t*-Bu) **19** in 89% isolated yield. Presumably, the steric demands of the thiol in the latter case preclude formation of the dithiolate derivative **16**.

Meunier et al. have shown that early metal chalcogenates can be derived from the reaction of metallocene-dialkyls with elemental S, Se, or Te.[20] In attempts to effect similar sulfur insertion into Ti−Me bonds, the reaction of (*t*-Bu$_3$PN)$_2$TiMe$_2$ **13** with S_8 in toluene was performed. Workup of the resulting bright yellow solution afforded not the dithiolate, but rather the species (*t*-Bu$_3$PN)$_2$Ti(η^2-S$_5$) **20** in 85% yield. The solid-state structure of **20** (Figure 6) reveals a pseudo-tetrahedral geometry about Ti. The phosphinimide ligands adopt a

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[20] Meunier, P.; Gautheron, B.; Mazouz, A. *J. Organomet. Chem.* **1987**, *320*, C39−C43.

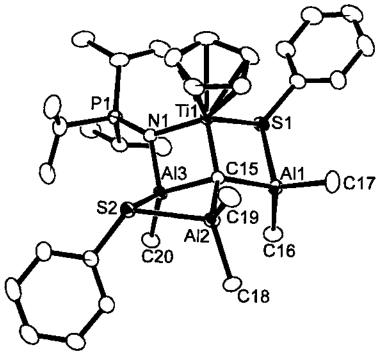

Figure 8. ORTEP drawing of **22**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−C(15) 1.902(2), Ti(1)−N(1) 2.0047(19), Ti(1)−S(1) 2.4712(7), S(1)−C(21) 1.776(3), S(1)−Al(1) 2.4573(11), S(2)−C(27) 1.778(3), S(2)−Al(3) 2.3713(9), S(2)−Al(2) 2.4636(10), P(1)−N(1) 1.601(2), N(1)−Al(3) 1.877(2), C(15)−Ti(1)−N(1) 92.67(9), C(15)−Ti(1)−S(1) 92.59(7), N(1)−Ti(1)−S(1) 105.64(6), C(21)−S(1)−Al(1) 123.28(11), C(21)−S(1)−Ti(1) 115.82(9), Al(1)−S(1)−Ti(1) 73.95(3), C(27)−S(2)−Al(3) 114.68(9), C(27)−S(2)−Al(2) 120.08(10), Al(3)−S(2)−Al(2) 76.18(3), P(1)−N(1)−Al(3) 130.61(12), P(1)−N(1)−Ti(1) 141.66(12), Al(3)−N(1)−Ti(1) 87.14(8), C(16)−Al(1)−C(17) 117.53(18), C(16)−Al(1)−C(15) 114.39(13), C(17)−Al(1)−C(15) 114.54(14), C(16)−Al(1)−S(1) 102.47(12), C(17)−Al(1)−S(1) 113.04(12), C(15)−Al(1)−S(1) 90.90(7), C(19)−Al(2)−C(18) 113.34(15), C(19)−Al(2)−C(15) 118.39(12), C(18)−Al(2)−C(15) 115.81(12), C(19)−Al(2)−S(2) 107.13(12), C(18)−Al(2)−S(2) 112.48(10), C(15)−Al(2)−S(2) 85.97(7), N(1)−Al(3)−C(20) 120.25(12), N(1)−Al(3)−C(15) 93.58(9), C(20)−Al(3)−C(15) 127.19(12), N(1)−Al(3)−S(2) 111.90(7), C(20)−Al(3)−S(2) 110.99(10), C(15)−Al(3)−S(2) 88.23(7), Ti(1)−C(15)−Al(2) 141.60(13), Ti(1)−C(15)−Al(1) 99.23(10), Al(2)−C(15)−Al(1) 111.02(11), Ti(1)−C(15)−Al(3) 86.62(9), Al(2)−C(15)−Al(3) 96.91(10), Al(1)−C(15)−Al(3) 121.07(12).

geometry similar to that observed in **14** and **16**. The Ti−S distances were found to be 2.4204(7) and 2.4243(7) Å. These distances are slightly shorter than those seen in $Cp_2Ti(\eta^2\text{-}S_5)$ (2.45 Å),[21] consistent with the greater Lewis acidity of the Ti center in **20**. Presumably this also accounts for the approach of the β-S atoms to the Ti center at distances of 2.8711(8) and 2.8935(8) Å. S−S distances range from 2.0290(10) to 2.0763(10) Å.

Reactivity. Having prepared this series of Ti-thiolate derivatives, reactions of **3**−**5** with excess $AlMe_3$ were investigated.[14] Upon standing of the reaction mixtures over a 24 h period at 25 °C, new $^{31}P\{^1H\}$ NMR resonances replaced those of the starting materials, inferring the quantitative formation of new species **21**−**23**, respectively. These species were isolated in 83%, 74%, and 56% yield, respectively. ^1H NMR spectra of these compounds revealed resonances attributable to two inequivalent thiolate ligands and cyclopentadienyl and phosphinimide ligands. In addition, each exhibited five resonances between 0.30 and −0.32 ppm attributable to Al-methyl groups. The corresponding $^{13}C\{^1H\}$ NMR resonances for the ligand fragments were observed, while the signals for the methyl carbons were extremely weak, consistent with Al-bound methyl groups. On the basis of these NMR data, formulations incorporating a Ti and three Al atoms could be proposed, although the precise nature of the molecular structure remained unclear. However, the species **23** was also obtained in the reaction of the previously reported species $CpTi(\mu\text{-}Me)(\mu\text{-}NP\textit{i}\text{-}Pr_3)(\mu\text{-}C)(AlMe_3)_3$[15] with HS*t*-Bu, suggesting a Ti-Al-carbide aggregate structure. Crystallographic studies of **21**−**23** confirmed that these species are analogous and are formulated as $(CpTi(\mu\text{-}SR)(\mu\text{-}NP\textit{i}\text{-}Pr_3)(C)(AlMe_2)_2(\mu\text{-}SR)AlMe$ ($R = CH_2Ph$ **21**, Ph **22**, *t*-Bu **23**) (Figures 7−9). In these molecules, the pseudo-"three-legged piano stool" coordination sphere of Ti is comprised of a cyclopentadienyl ring, a thiolate-sulfur, a phosphinimide-nitrogen, and a carbide carbon. Three Al atoms complete the bonding sphere of the carbide. An $AlMe_2$ moiety bridges the Ti-bound thiolate and the carbide; a second $AlMe_2$ fragment is coordinated to a second thiolate group, which also bridges to a third Al center. This latter AlMe moiety is bonded to the Ti-bound phosphinimide-N. The majority of the metric parameters are unexceptional. The most interesting feature is the geometry about the carbide carbon atoms. The Ti−carbide distances in **21**−**23** are 1.900(3), 1.902(2), and 1.945(6) Å, respectively. The slightly longer Ti−C distance in **23** is consistent with both greater basicity and steric demands of the *tert*-butylthiolate ligands. These distances are significantly shorter than the terminal $Ti-CH_3$ distance in $Cp(\textit{t}\text{-}Bu_3PN)TiMe(\mu\text{-}$

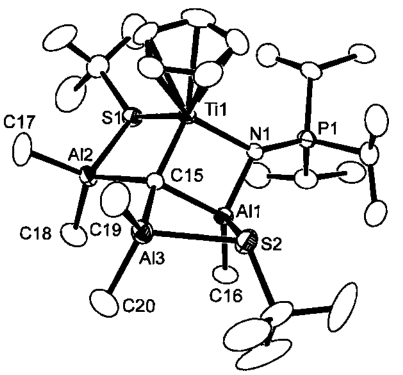

Figure 9. ORTEP drawing of **23**; 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Distances in Å, angles in deg: Ti(1)−C(15) 1.945(6), Ti(1)−N(1) 2.055(5), Ti(1)−S(1) 2.503(2), Al(1)−N(1) 1.929(6), Al(1)−C(16) 2.001(8), Al(1)−C(15) 2.050(7), Al(1)−S(2) 2.422(3), Al(2)−C(17) 2.015(8), Al(2)−C18 2.027(8), Al(2)−C(15) 2.064(7), Al(2)−S(1) 2.440(3), Al(3)−C(20) 2.022(10), Al(3)−C(19) 2.028(9), Al(3)−C(15) 2.032(7), Al(3)−S(2) 2.465(3), S(1)−C(21) 1.909(9), S(2)−C25 1.925(10), P(1)−N(1) 1.644(5), C(15)−Ti(1)−N(1) 92.8(2), C(15)−Ti(1)−S(1) 90.6(2), N(1)−Ti(1)−S(1) 103.79(16), N(1)−Al(1)−C(16) 119.7(3), N(1)−Al(1)−C(15) 93.5(2), C(16)−Al(1)−C(15) 125.8(3), N(1)−Al(1)−S(2) 112.1(2), C(16)−Al(1)−S(2) 113.7(3), C(15)−Al(1)−S(2) 86.7(2), C(17)−Al(2)−C18 113.0(4), C(17)−Al(2)−C(15) 114.4(3), C(18)−Al(2)−C(15) 117.0(4), C(17)−Al(2)−S(1) 116.4(3), C(18)−Al(2)−S(1) 104.0(3), C(15)−Al(2)−S(1) 89.7(2), C(20)−Al(3)−C(19) 114.6(5), C(20)−Al(3)−C(15) 113.2(4), C(19)−Al(3)−C(15) 119.5(4), C(20)−Al(3)−S(2) 111.8(3), C(19)−Al(3)−S(2) 107.8(3), C(15)−Al(3)−S(2) 86.0(2), C(21)−S(1)−Al(2) 121.6(3), C(21)−S(1)−Ti(1) 131.9(3), Al(2)−S(1)−Ti(1) 75.37(8), C(25)−S(2)−Al(1) 124.8(5), C(25)−S(2)−Al(3) 115.8(4), Al(1)−S(2)−Al(3) 77.16(10), P(1)−N(1)−Al(1) 131.8(3), P(1)−N(1)−Ti(1) 140.7(3), Al(1)−N(1)−Ti(1) 87.0(2), Ti(1)−C(15)−Al(3) 143.0(4), Ti(1)−C(15)−Al(1) 86.7(3), Al(3)−C(15)−Al(1) 96.6(3), Ti(1)−C(15)−Al(2) 97.8(3), Al(3)−C(15)−Al(2) 110.3(3), Al(1)−C(15)−Al(2) 123.8(3).

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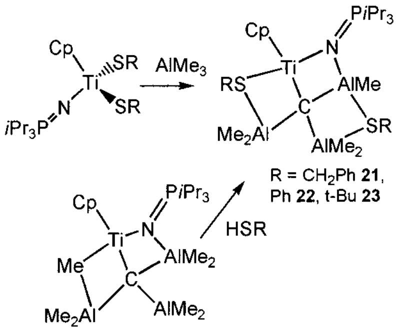
[21] Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742−757.

Scheme 2



$CH_3B(C_6F_5)_3$) (2.123(5) Å),[7] presumably a result of the increase in the Lewis acidity at the Ti center due to diminished donation from S and N donors. The geometry about the carbide centers can best be described as severely distorted from a tetrahedral geometry. The Ti−C−Al and Al−C−Al angles range as high as 143.0(4)° and 123.8(3)°, respectively. These distortions are consistent with the carbide being central to three fused four-membered rings where the corresponding Ti−C−Al and Al−C−Al angles range from 86.6(7)° to 97.0(6)°.

Analogous reactions of chelate dithiolate complexes **7** and **8** with $AlMe_3$ over a period of 10 h with excess $AlMe_3$ resulted in the formation of the new complexes **24** and **25** in 78% and 55% yields, respectively. NMR data showed the formation of new species, as the ^1H resonances were downfield shifted and new broad peaks, attributed to $AlMe_3$ fragments, appeared at −0.11 and 0.14 ppm. Integration suggested the association of 3 equiv of $AlMe_3$ with the precursor complexes and thus the formulas $[Cp(i\text{-}Pr_3PN)Ti(SRS)]\cdot(AlMe_3)_3$ ($R = (CH_2)_3$ **24**, $((CH_2)_2(C_6H_4))$ **25**). The resonance attributed to $AlMe_3$ groups remained broad even on cooling to −80 °C, suggesting a highly fluxional molecule. Although the precise structures of **24** and **25** are not known, it is reasonable to suggest that interaction of the $AlMe_3$ with the S and N atom donors in the Ti complexes accounts for the association of 3 equiv of $AlMe_3$. It is noteworthy that even on standing in the presence of excess $AlMe_3$ for extended periods **24** and **25** do not undergo methyl-thiolate exchange nor C−H activation. This stands in contrast to the monodentate-thiolate precursors, suggesting that the chelate effect in the dithiolate ligand complexes arrests further reaction.

The formation of **24** and **25** suggests the initial interaction between $AlMe_3$ and a Ti-thiolate complex is via the donor atoms. Clearly, such adducts could lead to facile methyl for thiolate exchange, which is ultimately inferred by the nature of the product. Ligand for methyl exchange has been observed previously as in reactions of $CpTi(OAr')_2Cl$ with $AlMe_3$.[22] In addition, methyl exchange between $AlMe_3$ and the carbides $CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NPR_3)(\mu^4\text{-}C)(AlMe_2)_3$ and $CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NPR_3)(\mu^4\text{-}C)(AlMe_2)_4$ has been established as a rapid and facile process by labeling experiments.[15] Subsequent C−H bond-activating steps liberating methane are thought to result from the proximity of the ligand-bound Al-Me fragments and the intermediate Ti-bound methyl group. The mechanistic details of such C−H bond activation reactions are unknown and are the subject of ongoing studies.

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

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

OM011042E

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[22] Firth, A. V.; Stephan, D. W. *Inorg. Chem.* **1998**, *37*, 4732−4734.