Synthesis and Reactivity of Neutral, Zwitterionic and Cationic Pentamethylcyclopentadienyl−Tantalum−Phosphinimide Complexes

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This paper focuses on the synthesis and reactivity of Cp*Ta(V)−phosphinimide complexes. Reaction of stoichiometric mixtures of Cp^*TaCl_4 and phosphinimine $R_3PNSiMe_3$ affords the complexes $Cp^*Ta(NPR_3)Cl_3$, R = *t*-Bu **1**, *i*-Pr **2**. These species are readily derivatized to the alkylated complexes $Cp^*Ta(NPR_3)Me_3$, R = *t*-Bu **3**, *i*-Pr **4**; $Cp^*Ta(NPt\text{-}Bu_3)(CH_2Ph)Cl_2$, **5**; and $Cp^*Ta(NPt\text{-}Bu_3)(CH_2Ph)Me_2$, **6**. Reaction with 3 equiv of BnMgCl afforded the robust alkylidene species $Cp^*Ta(NPR_3)(CHPh)(CH_2Ph)$, R = *t*-Bu **7**, *i*-Pr **8**. Reaction of **7** with MeI gives the metallacycle $Cp^*Ta(NPt\text{-}Bu_3)(\eta^2\text{-}CHPhCH_2)(CH_2Ph)$, **9**. Alkylation of **1** and **2** with 2 equiv of EtMgCl results in formation of the complexes $Cp^*Ta(NPR_3)(\eta^2\text{-}C_2H_4)Cl$, R = *t*-Bu **10**, *i*-Pr **11**, while further reaction of **10** with EtMgCl affords $Cp^*Ta(NPt\text{-}Bu_3)(\eta^2\text{-}C_2H_4)(CH_2\text{-}CH_3)$, **12**. Reaction of **1** with 1 equiv of $B(C_6F_5)_3$ results in generation of the salt $[Cp^*Ta(NPt\text{-}Bu_3)Cl_2][ClB(C_6F_5)_3]$, **13**, while the analogous reaction with $Ph_3C[B(C_6F_5)_4]$ affords the related salt $[Cp^*Ta(NPt\text{-}Bu_3)Cl_2][B(C_6F_5)_4]$, **14**. The zwitterionic species $Cp^*Ta(NPR_3)Me_2(MeB(C_6F_5)_3)$ (R = *t*-Bu **15**, *i*-Pr **16**) are derived via reaction of **3** or **4** with $B(C_6F_5)_3$. The analogous reaction of **3** and **4** with $[Ph_3C][B(C_6F_5)_4]$ affords the related salts $[Cp^*Ta(NPR_3)Me_2][B(C_6F_5)_4]$ (R = *t*-Bu **17**, *i*-Pr **18**). Treatment of **10** with $Ph_3CB(C_6F_5)_4$, Ph_3CBF_4, or $B(C_6F_5)_3$ gives the complexes $[Cp^*Ta(NPt\text{-}Bu_3)(Cl)CH_2CH_2CPh_3][B(C_6F_5)_4]$, **20**, $[Cp^*Ta(NPt\text{-}Bu_3)(Cl)(CH_2CH_2CPh_3)][BF_4]$, **21** and the zwitterionic species $[Cp^*Ta(NPt\text{-}Bu_3)(Cl)(CH_2CH_2B(C_6F_5)_3)]$, **22**, respectively. The relevance of this chemistry to the related group IV metal olefin polymerization catalysts is discussed and considered. X-ray structural studies of **1**, **3**, **5**, **7**, **9**, **10**, and **22** are reported.

Introduction

The advent of industrial interest in early metal metallocene-based single-site olefin polymerization catalysis some twenty years ago has spurred more recent studies of related systems that incorporate non-cyclopentadienyl ancillary ligands. A growing variety of such systems have and continue to be examined.[1] In our own efforts, we have recently implemented the steric analogy between phosphinimide ligands and cyclopentadienyl groups to prepare several families of titanium-based ethylene polymerization precatalysts.[2,3] In some cases, unprecedented activity was seen for the resulting catalysts.[2] This was attributed to the unique synergy of steric features of phosphinimide ligands which provide significant steric encumbrance that is somewhat remote from the metal, thus making the immediate coordination sphere of the metal center accessible. Continuing to probe the utility of group IV phosphinimide complexes in catalysis,[4−7] we are investigating the chemistry of related group V complexes. While others have recently demonstrated that selected nonmetallocene derivatives of Ta do show moderate activity in olefin polymerization catalysis,[8] our perspective is that the chemistry of Ta-phosphinimide systems may provide insight relating to our active group IV systems. Thus, in this article we report the synthesis and structure of a family of neutral, zwitterionic and cationic Ta-phosphinimide complexes. The chemistry exhibited is considered in relation to the analogous group IV systems.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and Innovative Technologies, Braun, or Vacuum Atmospheres inert atmosphere gloveboxes. Solvents were

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purified employing a Grubb's type column system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance-300 and 500 operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. ^{31}P NMR, ^{11}B NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H_3PO_4, $NaBH_4/H_2O$, and F_3CCOOH, respectively. Guelph Chemical Laboratories in Guelph Ontario performed combustion analyses. $TaCl_5$ and Cp* were purchased from the Strem Chemical Co. Cp*$TaCl_4$[9] and the phosphinimines $R_3PNSiMe_3$ (R = *t*-Bu, *i*-Pr) were prepared by literature methods.[10,11]

Synthesis of Cp*Ta(NPR$_3$)Cl$_3$ (R = *t*-Bu 1, *i*-Pr 2). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. To a suspension of Cp*$TaCl_4$ (1.00 g, 2.183 mmol) in 70 mL of toluene was added *t*-$Bu_3PNSiMe_3$ (630 mg, 2.176 mmol). The reaction mixture was heated under reflux for 6 h and then allowed to cool to room temperature. The solvent was evaporated, and the resulting deep yellow powder **1** was washed twice with toluene, yielding the product in 77% yield: ^{1}H NMR (C_6D_6) δ 2.26 (s, 15H, $C_5(CH_3)_5$), 1.23 (d, $|J_{P-H}|$ = 13.8 Hz, 27H, $PC(CH_3)_3$), (CD_2Cl_2) δ 2.29 (s, 15H, $C_5(CH_3)_5$), 1.56 (d, $|J_{P-H}|$ = 13.8 Hz, 27H, $PC(CH_3)_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 127.61 (s, $C_5(CH_3)_5$), 46.28 (d, $|J_{P-C}|$ = 43 Hz, $PC(CH_3)_3$), 33.36 (s, $PC(CH_3)_3$), 16.83 (s, $C_5(CH_3)_5$); ^{1}H NMR (CD_2Cl_2) δ 124.30 (s, $C_5(CH_3)_5$), 43.10 (d, $|J_{P-C}|$ = 43 Hz, $PC(CH_3)_3$), 29.87 (s, $PC(CH_3)_3$), 13.03 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 60.89, (CD_2Cl_2) δ 63.69 (s). Anal. Calcd for $C_{22}H_{42}Cl_3NPTa$: C, 41.36; H, 6.63; N, 2.19. Found: C, 41.67; H, 6.24; N, 2.13. **2**: 80% yield, ^{1}H NMR (C_6D_6) δ 2.28 (s, 15H, $C_5(CH_3)_5$), 2.03 (m, 3H, $PCH(CH_3)_2$), 0.93 (dd,$|J_{P-H}|$ = 15.7 Hz, $|J_{H-H}|$ = 7.2 Hz, 18H, $PCH(CH_3)_2$); ^{13}C{^{1}H} NMR (C_6D_6) δ 123.96 (s, $C_5(CH_3)_5$), 24.88 (d, $|J_{P-C}|$ = 56 Hz, $PCH(CH_3)_2$), 16.85 (s, $PCH(CH_3)_2$), 13.31 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 51.81 (s). Anal. Calcd for $C_{19}H_{36}Cl_3NPTa$: C, 38.24; H, 6.08; N, 2.35. Found: C, 38.21; H, 6.09; N, 2.30.

Synthesis of Cp*Ta(NPR$_3$)Me$_3$ (R = *t*-Bu 3, *i*-Pr 4). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. To a suspension of **1** (200 mg, 0.318 mmol) in 10 mL of THF was added a suspension of MeLi (21 mg, 0.955 mmol) in 2 mL of THF. After 2 h of stirring the solvent was evaporated, and the resulting yellow solid was taken up in 3 mL of toluene, filtered, and evacuated to dryness. The yellow-white powder **3** was isolated in 72% yield: ^{1}H NMR (C_6D_6) δ 1.93 (s, 15H, $C_5(CH_3)_5$), 1.15 (d, $|J_{P-H}|$ = 13.0 Hz, 27H, $PC(CH_3)_3$), 0.56 (s, 6H, Ta−CH_3), 0.46 (s, 3H, Ta−CH_3); ^{13}C-{^{1}H} NMR (C_6D_6) δ 116.32 (s, $C_5(CH_3)_5$), 48.47 (s, Ta-CH_3), 45.43 (s, Ta-CH_3), 45.14 (d $|J_{P-C}|$ = 46.5 Hz, $PC(CH_3)_3$), 33.31 (s, $PC(CH_3)_3$), 15.18 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 50.30. Anal. Calcd for $C_{25}H_{51}NPTa$: C, 51.99; H, 8.90; N, 2.42. Found: C, 51.91; H, 8.54; N, 2.38. **4**: 83% yield; ^{1}H NMR (C_6D_6) δ 1.96 (s, 15H, $C_5(CH_3)_5$), 1.72 (m, 3H, $PCH(CH_3)_2$), 0.88 (dd, $|J_{P-H}|$ = 14.7 Hz, $|J_{H-H}|$ = 7.2 Hz, 18H, $PCH(CH_3)_2$), 0.54 (s, 6H, Ta−CH_3), 0.49 (s, 3H, Ta−CH_3); ^{13}C{^{1}H} NMR (C_6D_6) δ 113.23 (s, $C_5(CH_3)_5$), 45.82 (s, Ta-CH_3), 41.06 (s, Ta-CH_3), 25.40 (d, $|J_{P-C}|$ = 57.3 Hz, $PCH(CH_3)_2$), 17.01 (s, $PCH(CH_3)_2$), 11.71(s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 39.94. Anal. Calcd for $C_{22}H_{45}NPTa$: C, 49.34; H, 8.47; N, 2.62. Found: C, 48.52; H, 8.43; N, 2.27.

Synthesis of Cp*Ta(NP*t*-Bu$_3$)(CH$_2$Ph)Cl$_2$, 5. To a suspension of **1** (100 mg, 0.156 mmol) in 5 mL of toluene was added BnMgCl (0.08 mL, 2 M solution in ether). The yellow-orange solution was stirred for 2 h, filtered, and evaporated to dryness, giving the product in 72% yield: ^{1}H NMR (C_6D_6) δ 7.91 (d, $|J_{H-H}|$ = 7.3 Hz, 2H, $CH_2C_6H_5$), 7.35 (t, $|J_{H-H}|$ = 7.5 Hz, 2H, $CH_2C_6H_5$) 6.87 (t, $|J_{H-H}|$ = 7.2 Hz, 1H, $CH_2C_6H_5$), 2.40 (s, 2H, $CH_2C_6H_5$), 2.10 (s, 15H, $C_5(CH_3)_5$), 1.07 (d, $|J_{P-H}|$ = 13.5 Hz, 27H, $PC(CH_3)_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 151.36, 130.55, 126.93, 122.44 (s, $CH_2C_6H_5$), 121.31 (s, $C_5(CH_3)_5$), 77.11(s, $CH_2C_6H_5$), 42.36 (d, $|J_{P-C}|$ = 44.2 Hz, $PC(CH_3)_3$), 29.68 (s, $PC(CH_3)_3$), 12.83 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 55.87 (s). Anal. Calcd for $C_{29}H_{49}Cl_2NPTa$: C, 50.15; H, 7.11; N, 2.02. Found: C, 50.36; H, 6.93; N, 1.96.

Synthesis of Cp*Ta(NP*t*-Bu$_3$)(CH$_2$Ph)Me$_2$, 6. To a solution of **5** (150 mg, 0.216 mmol) in 3 mL of THF was added MeLi (10 mg, 0.455 mmol) in 2 mL of THF. The orange solution was stirred for 2 h, evaporated to dryness, dissolved in benzene, and filtered. Evaporation of the solvent resulted in isolation of the product as a red powder in 58% yield: ^{1}H NMR (C_6D_6) δ 7.67 (d, $|J_{H-H}|$ = 7.6 Hz, 2H, $CH_2C_6H_5$), 7.31 (t, $|J_{H-H}|$ = 7.4 Hz, 2H, $CH_2C_6H_5$), 6.93 (t, $|J_{H-H}|$ = 7.3 Hz, 2H, $CH_2C_6H_5$), 2.11 (s, 2H, $CH_2C_6H_5$) 1.88 (s, 15H, $C_5(CH_3)_5$), 0.98 (d, $|J_{P-H}|$ = 13.0 Hz, 27H, $PC(CH_3)_3$), 0.78 (s, 6H, Ta−CH_3); ^{13}C{^{1}H} NMR (C_6D_6) δ 155.32, 126.93, 121.03, 113.71 (s, $CH_2C_6H_5$), 110.00 (s, $C_5(CH_3)_5$), 62.37 (s, $CH_2C_6H_5$), 45.12 (s, Ta-CH_3), 41.60 (d, $|J_{P-H}|$ = 45.6 Hz, $PC(CH_3)_3$), 29.79 (s, $PC(CH_3)_3$), 11.79 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 50.41 (s). Anal. Calcd for $C_{31}H_{55}NPTa$: C, 56.96; H, 8.48; N, 2.14. Found: C, 56.55; H, 8.34; N, 2.01.

Synthesis of Cp*Ta(NPR$_3$)(CHPh)(CH$_2$Ph), R = *t*-Bu 7, *i*-Pr 8. These compounds were prepared in a similar fashion, and thus only one preparation is detailed. To a suspension of **1** (300 mg, 0.469 mmol) in 5 mL of benzene was added BnMgCl (1.41 mL, 1 M solution in ether). The resulting red solution was stirred for 2 h, filtered, and evaporated to dryness. Addition of 1 mL of hexane resulted in the formation of red crystals in 51% yield: ^{1}H NMR (C_6D_6) δ 9.13 (s, 1H, CHC_6H_5), 7.62 (d, $|J_{H-H}|$ = 7.5 Hz, 2H, C_6H_5) 7.37 (t, $|J_{H-H}|$ = 7.7 Hz, 2H, C_6H_5) 7.14−6.78 (m, C_6H_5) 3.22 (d, $|J_{H-H}|$ = 11.4 Hz, 1H, $CH_2C_6H_5$), 2.23 (d, $|J_{H-H}|$ = 11.4 Hz, 1H, $CH_2C_6H_5$), 1.95 (s, 15H, $C_5(CH_3)_5$), 1.14 (d, $|J_{P-H}|$ = 12.9 Hz, 27H, $PC(CH_3)_3$); ^{13}C-{^{1}H} NMR (C_6D_6) δ 213.11 (s, CHC_6H_5), 153.31, 152.46, 130.89, 130.39,129.03, 128.51, 122.24, 121.87 (s, C_6H_5) 112.98 (s, $C_5(CH_3)_5$), 50.49 (s, $CH_2C_6H_5$) 41.03 (d, $|J_{P-C}|$ = 46.5 Hz, $PC(CH_3)_3$), 29.97 (s, $PC(CH_3)_3$), 12.07 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 49.03 (s). Anal. Calcd for $C_{36}H_{55}NPTa$: C, 60.58; H, 7.77; N, 1.96. Found: C, 59.98; H, 7.64; N, 1.85. **8**: 63% yield; ^{1}H NMR (C_6D_6) δ 8.40 (s, 1H, CHC_6H_5), 7.49 (d, $|J_{H-H}|$ = 7.3 Hz, 2H, C_6H_5), 7.33 (t, $|J_{H-H}|$ = 7.5 Hz, 2H, C_6H_5), 7.12−6.67 (m, C_6H_5), 2.50 (d, $|J_{H-H}|$ = 11.7 Hz, 1H, $CH_2C_6H_5$), 2.36 (d, $|J_{H-H}|$ = 11.7 Hz, 1H, $CH_2C_6H_5$), 1.99 (s, 15H, $C_5(CH_3)_5$), 1.67 (m, 3H, $PCH(CH_3)_2$), 0.85 (dd, $|J_{P-H}|$ = 14.7 Hz, $|J_{H-H}|$ = 7.1 Hz, 9H, $PCH(CH_3)_2$) 0.80 (dd, $|J_{P-H}|$ = 14.6 Hz, $|J_{H-H}|$ = 7.2 Hz, 9H, $PCH(CH_3)_2$); ^{13}C{^{1}H} NMR (tol-d_8) δ 222.88 (s, CHC_6H_5), 154.07, 152.68, 130.14, 127.33, 127.06, 125.31, 125.12, 121.30 (s, C_6H_5), 112.67 (s, $C_5(CH_3)_5$), 52.41 (s, $CH_2C_6H_5$), 26.09 (d, $|J_{P-C}|$ = 57.2 Hz, $PCH(CH_3)_2$), 16.88 (s, $PCH(CH_3)_2$), 11.79 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 40.44 (s).

Formation of Cp*Ta(NP*t*-Bu$_3$)(η^2-CHPhCH$_2$)(CH$_2$Ph), 9. To a solution of **7** (100 mg, 0.140 mmol) in 0.5 mL of C_6D_6 was added MeI (20 mg, 0.141 mmol) in a resealable NMR tube. The tube was heated for 2 h at 87 °C, resulting in a product mixture by ^{1}H NMR. After 1 week, deep brownish red crystals of **9** were isolated from the product mixture in 19% yield: ^{1}H NMR (C_6D_6) δ 7.63 (d, $|J_{H-H}|$ = 7.8 Hz, 2H, C_6H_5), 7.25 (t, $|J_{H-H}|$ = 7.6 Hz, 2H, C_6H_5), 7.13−6.98 (m, C_6H_5), 2.82 (d, $|J_{H-H}|$ = 14.4 Hz, 1H, $CH_2C_6H_5$), 2.45 (d, $|J_{H-H}|$ = 14.3 Hz, 1H, $CH_2C_6H_5$), 1.86 (m, 1H, $CHPh$), 1.68 (s, 15H, $C_5(CH_3)_5$), 1.52 (m, 1H $CHPh$) 1.03 (d, $|J_{P-H}|$ = 13.1 Hz) 0.64 (m, 1H, $CHPh$); ^{13}C{^{1}H} NMR (C_6D_6) δ 145−124 (s, C_6H_5), 114.26 (s, $C_5(CH_3)_5$), 70.18 (s, $CH_2C_6H_5$) 62.74 (s, CHR), 53.52 (s, $CHPh$) 44.75 (d, $|J_{P-C}|$ = 45.2 Hz, $PC(CH_3)_3$), 33.46 (s, $PC(CH_3)_3$), 17.85 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 52.01 (s). The low yield and sensitivity of this species precluded elemental analysis.

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Synthesis of Cp*Ta(NPR$_3$)(η^2-C$_2$H$_4$)Cl, R = *t*-Bu 10, *i*-Pr 11. These compounds were prepared in a similar fashion, and thus only one preparation is detailed. To a suspension of **1** (200 mg, 0.313 mmol) in 5 mL of toluene was added EtMgCl (0.314 mL, 2 M solution in ether) and stirred overnight. The suspension was filtered, and the solvent evaporated, isolating the reddish product in 63% yield: ^{1}H NMR (C_6D_6) δ 2.35 (m, $|J^2_{H-H}|$ = 9.0 Hz, $|J^3_{H-H}|$ = 12.5 Hz, $|J^3_{H-H}|$ = 9.2 Hz, Ta(η^2-C$_2$H$_4$)), 1.94 (s, 15H, C$_5$(CH$_3$)$_5$), 1.82 (m, $|J^3_{H-H}|$ = 10.7 Hz, $|J^2_{H-H}|$ = 5.9 Hz, $|J^3_{H-H}|$ = 9.2 Hz, Ta(η^2-C$_2$H$_4$)), 1.68 (m, $|J^3_{H-H}|$ = 10.0 Hz, $|J^2_{H-H}|$ = 5.9 Hz, $|J^3_{H-H}|$ = 12.5 Hz, Ta(η^2-C$_2$H$_4$)), 1.11 (d, $|J_{P-H}|$ = 13.1 Hz, 27H, PC(CH$_3$)$_3$), 0.79 (m, $|J^3_{H-H}|$ = 10.0 Hz, $|J^3_{H-H}|$ = 10.7 Hz, $|J^2_{H-H}|$ = 9.0 Hz, Ta(η^2-C$_2$H$_4$)); ^{13}C{^{1}H} NMR (C_6D_6) δ 111.93 (s, C_5(CH$_3$)$_5$), 57.31 (s, Ta(η^2-C_2H$_4$)), 46.45 (s, Ta(η^2-C_2H$_4$)), 41.00 (d, $|J_{P-H}|$ = 46.3 Hz, PC(CH$_3$)$_3$), 29.67 (s, PC(CH$_3$)$_3$), 11.71 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 54.16 (s); ^{1}H NMR (CD_2Cl_2)(partial) δ 1.88 (s, 15H, C$_5$(CH$_3$)$_5$), 1.36 (d, $|J_{P-H}|$ = 13.1 Hz, 27H, PC(CH$_3$)$_3$), 0.12 (m, Ta(η^2-C$_2$H$_4$)); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 111.98 (s, C_5(CH$_3$)$_5$), 55.25(s, Ta(η^2-C_2H$_4$)), 45.45 (s, Ta(η^2-C_2H$_4$)), 41.31 (d, $|J_{P-H}|$ = 46.3 Hz, PC(CH$_3$)$_3$), 29.57 (s, PC(CH$_3$)$_3$), 11.37 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 54.85 (s). Anal. Calcd for $C_{24}H_{46}ClNPTa$: C, 48.36; H, 7.78; N, 2.35. Found: C, 48.57; H, 7.34; N, 2.35. **11**: 58% yield. H NMR (C_6D_6) δ 2.29 (m, Ta(η^2-C$_2$H$_4$)), 1.97 (s, 15H, C$_5$(CH$_3$)$_5$), 1.83 (m, Ta(η^2-C$_2$H$_4$)), 1.71 (m, Ta(η^2-C$_2$H$_4$)), 1.60 (m, 3H, PCH(CH$_3$)$_2$), 0.84 (dd, $|J_{P-H}|$ = 14.8 Hz, $|J_{H-H}|$ = 7.3 Hz, 9H, PCH(CH$_3$)$_2$), 0.83 (obscured, Ta(η^2-C$_2$H$_4$)), 0.82 (dd, $|J_{P-H}|$ = 14.8 Hz, $|J_{H-H}|$ = 7.3 Hz, 9H, PCH(CH$_3$)$_2$; ^{13}C{^{1}H} NMR (C_6D_6) δ 115.75 (s, C_5(CH$_3$)$_5$), 60.37 (s, Ta(η^2-C_2H$_4$)), 49.90 (s, Ta(η^2-C_2H$_4$)), 28.92 (d, $|J_{P-H}|$ = 57.2 Hz, PCH(CH$_3$)$_2$), 20.31 (s, PCH(CH$_3$)$_2$), 15.35 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (C_6D_6) δ 43.44 (s). Anal. Calcd for $C_{21}H_{40}ClNPTa$: C, 45.53; H, 7.28; N, 2.53. Found: C, 45.40; H, 6.91; N, 2.34.

Synthesis of Cp*Ta(NP*t*-Bu$_3$)(η^2-C$_2$H$_4$)(CH$_2$CH$_3$), 12. To a suspension of **10** (200 mg, 0.313 mmol) in 5 mL of toluene was added EtMgCl (0.470 mL, 2 M solution in ether). The suspension was stirred overnight, filtered, and evaporated to dryness, giving the product as an orange, crystalline solid in 60% yield: ^{1}H NMR (tol-d_8) δ 2.02 (t, $|J_{H-H}|$ = 7.6 Hz, Ta−CH$_2$CH_3), 1.90 (s, 15H, C$_5$(CH_3)$_5$), 1.71 (m, Ta(η^2-C$_2$H$_4$)), 1.49 (m, $|J_{H-H}|$ = 7.6 Hz, Ta-CH_2CH$_3$), 1.08 (m, Ta(η^2-C$_2$H$_4$)), 1.08 (d, $|J_{P-H}|$ = 12.9 Hz, 27H, PC(CH_3)$_3$), 0.73 (m, Ta(η^2-C$_2$H$_4$)), 0.16 (m, Ta(η^2-C$_2$H$_4$)); ^{13}C{^{1}H} NMR (tol-d_8) δ 108.28 (s, C_5(CH$_3$)$_5$), 48.40 (s, Ta(η^2-C_2H$_4$)), 40.56 (d, $|J_{P-C}|$ = 47.1 Hz, PC(CH$_3$)$_3$), 33.17 (s, Ta(η^2-C_2H$_4$)), 29.39 (s, PC(CH$_3$)$_3$), 27.40 (s, Ta-CH$_2$CH$_3$), 18.08 (s, Ta-CH$_2$$CH_3$), 11.38 (s, C$_5$($CH_3$)$_5$); ^{31}P-{^{1}H} NMR ($C_6D_6$) δ 48.14 (s). Anal. Calcd for $C_{26}H_{51}NPTa$: C, 52.96; H, 8.72; N, 2.38. Found: C, 52.58; H, 8.22; N, 2.23. Preliminary X-ray data: $P21/c$ a = 8.7750(2) Å, b = 14.6401(3) Å, c = 21.6376(5) Å, β = 90.564(1)°, Z = 4.

Generation/Synthesis of [Cp*Ta(NP*t*-Bu$_3$)Cl$_2$]A (A = [ClB(C$_6$F$_5$)$_3$]$^-$ 13, [B(C$_6$F$_5$)$_4$]$^-$ 14), Cp*Ta(NPR$_3$)Me$_2$(MeB(C$_6$F$_5$)$_3$) (R = *t*-Bu 15, *i*-Pr 16), [Cp*Ta(NPR$_3$)Me$_2$][B(C$_6$F$_5$)$_4$] (R = *t*-Bu 17, *i*-Pr 18), [Cp*Ta(NP*t*-Bu$_3$)BnCl][ClB(C$_6$F$_5$)$_3$], 19. These compounds were generated in similar NMR experiments using the appropriate neutral precursor and either B(C$_6$F$_5$)$_3$ or [Ph$_3$C][B(C$_6$F$_5$)$_4$]; thus only one preparation is detailed. To a solution of **3** (33 mg, 0.057 mmol) in CH_2Cl_2 was added [Ph$_3$C][B(C$_6$F$_5$)$_4$] (53 mg, 0.057 mmol). The solution was stirred for 1 h, the solvent removed, and the residue washed several times with hexanes. The solid was recrystallized to give **17** in 68% yield. In cases where the products were only generated in solution, the reactions were monitored by NMR spectroscopy. The extreme sensitivity of these species precluded satisfactory elemental analysis; ^{1}H NMR spectra of these species have been deposited as supplementary data. **13**: ^{1}H NMR (CD_2Cl_2) δ 2.44 (s, 15H, C$_5$(CH_3)$_5$), 1.57 (d, $|J_{P-H}|$ = 14.7 Hz, 27H, PC(CH_3)$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 150−130 (br, B(C_6F_5)$_3$), 128.13 (s, C_5(CH$_3$)$_5$), 43.17 (d, $|J_{P-C}|$ = 37.8 Hz, PC(CH$_3$)$_3$), 29.66 (s, PC(CH$_3$)$_3$), 12.64 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 74.69 (s); ^{11}B NMR (CD_2Cl_2) δ −0.16 (br); ^{19}F NMR (CD_2Cl_2) δ −54.57 (s, 6F), −82.37 (s, 3F), −88.84 (s, 6F). **14**: ^{1}H NMR (CD_2Cl_2) δ 7.25 (m, br, (C$_6$H$_5$)$_3$CCl), 2.44 (s, 15H, C$_5$(CH_3)$_5$), 1.58 (d, $|J_{P-H}|$ = 14.7 Hz, 27H, PC(CH_3)$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 145.58, 138.29, 131.47, 129.99 (s, (C$_6$H$_5$)$_3$CCl), 128.13 (s, C_5(CH$_3$)$_5$), 43.18 (d, $|J_{P-C}|$ = 37.8 Hz, PC(CH$_3$)$_3$), 29.66 (s, PC(CH$_3$)$_3$), 12.62 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 74.68 (s); ^{11}B NMR (CD_2Cl_2) δ −18.84 (s); ^{19}F NMR (CD_2Cl_2) δ −55.78 (s, 8F), −86.45 (t, $|J_{F-F}|$ = 20.3 Hz, 4F), −90.27 (s, 8F). **15**: ^{1}H NMR (CD_2Cl_2) δ 2.10 (s, 15H, C$_5$(CH_3)$_5$), 1.51 (d, $|J_{P-H}|$ = 14.0 Hz, 27H, PC(CH_3)$_3$), 0.44 (s, 9H, Ta-CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 150−130 (br, B(C_6F_5)$_3$), 121.85 (s, C_5(CH$_3$)$_5$), 58.73 (s, Ta-CH$_3$), 42.43 (d, $|J_{P-C}|$ = 41.4 Hz, PC(CH$_3$)$_3$), 29.84 (s, PC(CH$_3$)$_3$), 11.86 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 66.62 (s); ^{11}B NMR (CD_2Cl_2) δ −17.08 (s); ^{19}F NMR (CD_2Cl_2) δ −55.44 (d, $|J_{F-F}|$ = 20.0 Hz, 6F), −87.70 (t, $|J_{F-F}|$ = 20.0 Hz, 3F), −90.23 (t, $|J_{F-F}|$ = 19.1 Hz, 6F). **16**: ^{1}H NMR (CD_2Cl_2) δ 2.45 (m, 3H, PCH(CH$_3$)$_2$) 2.15 (s, 15H, C$_5$(CH_3)$_5$), 1.38 (dd, $|J_{P-H}|$ = 15.9 Hz, $|J_{H-H}|$ = 7.2 Hz, 18H, PCH(CH_3)$_2$), 0.49 (s, 9H, Ta-CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 150−130 (br, B(C_6F_5)$_3$), 121.68 (s, C_5(CH$_3$)$_5$), 57.94 (s, Ta-CH$_3$), 26.48 (d, $|J_{P-C}|$ = 54.4 Hz, PCH(CH$_3$)$_2$), 16.84 (s, PCH(CH$_3$)$_2$), 11.69 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 58.30 (s); ^{11}B NMR (CD_2Cl_2) δ −17.12 (s); ^{19}F NMR (CD_2Cl_2) δ −55.91 (d, $|J_{F-F}|$ = 20.6 Hz, 6F), −88.12 (t, $|J_{F-F}|$ = 20.3 Hz, 3F), −90.68 (t, $|J_{F-F}|$ = 18.9 Hz, 6F). **17**: ^{1}H NMR (CD_2Cl_2) δ 2.13 (s, 15H, C$_5$(CH_3)$_5$), 1.55 (d $|J_{P-H}|$ = 14.0 Hz, 27H, PC(CH_3)$_3$), 0.48 (s, 6H, Ta-CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 121.28 (s, C_5(CH$_3$)$_5$), 58.12 (s, Ta-CH$_3$), 41.86 (d, $|J_{P-C}|$ = 41.5 Hz, PC(CH$_3$)$_3$), 29.25 (s, PC(CH$_3$)$_3$), 11.25 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 66.68 (s); ^{11}B NMR (CD_2Cl_2) δ −19.06 (s); ^{19}F NMR (CD_2Cl_2) δ −55.80 (s, 8F), −86.46 (t, 18.0 Hz, 4F), −90.29 (s, 8F). **18**: ^{1}H NMR (CD_2Cl_2) δ 7.30−7.11 (m, 15H, (C$_6$H$_5$)$_3$CCH$_3$) 2.44 (m, 3H, PCH(CH$_3$)$_2$) 2.19 (s, 3H, (C$_6$H$_5$)$_3$CCH_3) 2.14 (s, 15H, C$_5$(CH_3)$_5$), 1.37 (dd $|J_{P-H}|$ = 15.9 Hz, $|J_{H-H}|$ = 7.2 Hz, 18H, PCH(CH_3)$_2$), 0.49 (s, 6H, Ta-CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2) (partial) δ 149.53, 129.07, 128.20, 126.31 (s(C$_6$H$_5$)$_3$CCH$_3$), 121.52 (s, C_5(CH$_3$)$_5$), 57.81 (s, Ta-CH$_3$), 30.64 (s, (C$_6$H$_5$)$_3$$CCH_3$) 26.32 (d, $|J_{P-C}|$ = 54.9 Hz, PCH(CH$_3$)$_2$), 16.73 (s, PCH(CH$_3$)$_2$), 11.61 (s, C$_5$(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 58.28 (s); ^{11}B NMR (CD_2Cl_2) δ − 18.79 (s); ^{19}F NMR (CD_2Cl_2) δ − 55.75 (s, 8F), − 86.42 (t, 20.3 Hz, 4F), − 90.26 (t, 19.4 Hz, 8F). **19**: ^{1}H NMR (CD_2Cl_2) δ 7.25 (t, $|J_{H-H}|$ = 7.5 Hz, 2H, Ta-CH$_2$(C$_6$H$_5$)), 7.01 (t, $|J_{H-H}|$ = 7.5 Hz, 1H, Ta-CH$_2$(C$_6$H$_5$)), 6.90 (d, $|J_{H-H}|$ = 7.5 Hz, 2H, Ta-CH$_2$(C$_6$H$_5$)), 3.40 (d, $|J_{H-H}|$ = 14.4 Hz, 1H, Ta-CH_2(C$_6$H$_5$)) 2.59 (d, $|J_{H-H}|$ = 14.4 Hz, 1H, Ta-CH_2(C$_6$H$_5$)) 2.20 (s, 15H, C$_5$(CH_3)$_5$), 1.50 (d, $|J_{P-H}|$ = 14.7 Hz, 27H, PC(CH_3)$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 150−135 (br, B(C_6F_5)$_4$), 141.97, 130.69, 128.62, 126.25 (s, Ta-CH$_2$-(C_6H$_5$)), 125.45(s, C_5(CH$_3$)$_5$), 78.61 (s, Ta-CH$_2$(C$_6$H$_5$)) 42.60 (d, $|J_{P-C}|$ = 39.3 Hz, PC(CH$_3$)$_3$), 29.70 (s, PC(CH$_3$)$_3$), 12.22 (s, C$_5$-(CH$_3$)$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 72.13 (s); ^{11}B NMR (CD_2Cl_2) δ −2.64 (br); ^{19}F NMR (CD_2Cl_2) δ −54.00 (s, 6F), −82.38 (s, br, 3F), −88.58 (s, 6F).

Synthesis of [Cp*Ta(NP*t*-Bu$_3$)(Cl)(CH$_2$CH$_2$CPh$_3$)]A (A = [B(C$_6$F$_5$)$_4$] 20, BF$_4$ 21). These compounds were generated in similar NMR experiments using the appropriate neutral precursor and either Ph$_3$C[B(C$_6$F$_5$)$_4$] or Ph$_3$C[BF$_4$]; thus only one preparation is detailed. To a solution of **10** (30 mg, 0.050 mmol) in CD_2Cl_2 was added Ph$_3$C[B(C$_6$F$_5$)$_4$] (46 mg, 0.050 mmol). Evaporation of the solvent yielded the product in quantitative yield. The extreme sensitivity of this species precluded satisfactory elemental analysis; ^{1}H NMR spectra of these species have been deposited as supplementary data. **20**: ^{1}H NMR (CD_2Cl_2) δ 7.30−7.18 (m, 15H, CH$_2$C(C$_6$H$_5$)$_3$) 3.11 (m, TaCH$_2$CH_2CPh), 2.90 (m, TaCH$_2$CH_2CPh) 2.22 (m, TaCH_2CH$_2$-CPh), 2.12 (s, 15H, C$_5$(CH_3)$_5$), 1.46 (d $|J_{P-H}|$ = 14.4 Hz, 27H, PC(CH_3)$_3$) 1. 02 (m, TaCH_2CH$_2$CPh); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 146.72, 129.57, 128.38, 126.59 (s, CH$_2$C(C$_6$H$_5$)$_3$)) 124.88 (s, C_5(CH$_3$)$_5$), 70.65 (s, TaCH$_2$CH$_2$CPh), 62.48 (s, TaCH$_2$CH$_2$$C$Ph), 42.72 (d, $|J_{P-C}|$ = 14.1 Hz, PC(CH$_3$)$_3$), 42.29 (s, TaCH$_2$$CH_2$-CPh), 29.74 (s PC($CH_3$)$_3$), 12.13 (s, C$_5$($CH_3$)$_5$); ^{31}P{^{1}H} NMR ($CD_2Cl_2$) 71.06 (s); ^{11}B NMR (CD_2Cl_2) δ −22.88 (s); ^{19}F NMR

Table 1. Crystallographic Parameters

	1	**3**	**5**	**7**	**9**	**10**	**22**
formula	$C_{22}H_{42}Cl_3NPTa$	$C_{25}H_{51}NPTa$	$C_{29}H_{49}Cl_2NPTa$	$C_{36}H_{55}NPTa$	$C_{37}H_{56}NPTa$	$C_{24}H_{46}ClNPTa$	$C_{42}H_{46}BClF_{15}NTa$
fw	638.84	577.59	694.51	713.73	726.75	595.99	1107.98
a (Å)	8.6056(9)	8.5530(12)	10.9948(5)	12.1887(17)	11.668(16)	16.9128(2)	9.667(3)
b (Å)	14.8186(16)	17.7655(15)	19.1989(8)	17.329(5)	12.359(18)	14.853	19.373(7)
c (Å)	20.613(4)	17.775(3)	15.0970(6)	16.950(2)	13.053(13)	21.16780(10)	11.920(2)
α (deg)	90.00	90.00	90.00	90.00	87.37(10)	90.00	90.00
β (deg)	90.00	96.635(13)	91.8000(10)	103.290(10)	71.97(9)	90.00	92.20(3)
γ (deg)	90.00	90.00	90.00	90.00	74.65(12)	90.00	90.00
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	Triclinic	Orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	*Pbca*	$P2_1$
vol (Å^3)	2628.6(6)	2682.7(6)	3185.2(2)	3484.2(12)	1725(4)	5317.51(7)	2230.6(12)
D_{calcd} (g cm^{-1})	1.614	1.430	1.448	1.361	1.399	1.489	1.650
Z	4	4	4	4	2	8	2
abs coeff, μ (mm^{-1})	4.556	4.167	3.686	3.223	3.257	4.305	2.654
no. of data collected	3564	13 620	16 302	17 008	9115	25 136	4440
no. of data $F_o^2 > 3\sigma(F_o^2)$	1561	4689	5576	6093	5946	4676	4100
no. of variables	138	253	307	352	361	253	359
R (%)	0.0499	0.0288	0.0381	0.0351	0.0281	0.0351	0.0735
R_w (%)	0.1519	0.0950	0.0955	0.0857	0.0883	0.0883	0.1392
goodness of fit	1.432	0.834	1.011	0.625	0.746	1.028	1.224

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

(CD_2Cl_2) δ −40.41 (s, 8F), −71.11 (t, 17.7 Hz, 4F), −74.89 (d, 16.0 Hz, 8F). **21**: ^{1}H NMR (CD_2Cl_2) δ 7.30−7.18 (m, 15H, $CH_2C(C_6H_5)_3$), 3.09 (m, $TaCH_2CH_2CPh$), 2.90 (m, $TaCH_2CH_2$-CPh), 2.21 (m, $TaCH_2CH_2CPh$), 2.14 (s, 15H, $C_5(CH_3)_5$), 1.47 (d $|J_{P-H}| = 14.4$ Hz, 27H, $PC(CH_3)_3$), 1. 01 (m, $TaCH_2CH_2CPh$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 146.73, 129.39, 128.39, 126.62 (s, $CH_2C(C_6H_5)_3$)), 124.91 (s, $C_5(CH_3)_5$), 70.51 (s, $TaCH_2CH_2CPh$), 62.48 (s, $TaCH_2CH_2CPh$), 42.59 (d, $|J_{P-C}| = 14.1$ Hz, $PC(CH_3)_3$), 42.63 (s, $TaCH_2CH_2CPh$), 29.81 (s $PC(CH_3)_3$), 12.27 (s, C_5-$(CH_3)_5$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 71.23 (s); ^{11}B NMR (CD_2Cl_2) δ −7.35 (s); ^{19}F NMR (CD_2Cl_2) δ −60.54 (s, 4F).

Synthesis of [Cp*Ta(NP*t*-Bu$_3$)(Cl)($CH_2CH_2B(C_6F_5)_3$)], 22. To a solution of **10** (50 mg, 0.084 mmol) in CD_2Cl_2 was added $B(C_6F_5)_3$ (43 mg, 0.084 mmol). Evaporation of solvent gave the crystalline product in quantitative yield: ^{1}H NMR (CD_2Cl_2) δ 2.54 (br m, $TaCH_2CH_2B$), 2.28 (m, $TaCH_2CH_2CB$), 2.11 (s, 15H, $C_5(CH_3)_5$), 1.78 (br m, $TaCH_2CH_2B$), 1.50 (d $|J_{P-H}| = 14.4$ Hz, 27H, $PC(CH_3)_3$), 1.27 (m, $TaCH_2CH_2B$); ^{13}C NMR (CD_2Cl_2) (partial) δ 150−130 (br, $B(C_6F_5)_3$) 122.77 (s, $C_5(CH_3)_5$), 82.62 (s, $TaCH_2CH_2$), 42.35 (d, $|J_{P-C}| = 42.0$ Hz, $PC(CH_3)_3$), 29.71 (s, $PC(CH_3)_3$), 11.99 (s, $C_5(CH_3)_5$); ^{31}P NMR (CD_2Cl_2) δ 68.03 (s); ^{11}B NMR (CD_2Cl_2) δ −17.66 (s). ^{19}F NMR (CD_2Cl_2) δ −38.65 (s, 8F), −71.40 (t, 17.4 Hz, 4F), −74.59 (s, 8F). Anal. Calcd for $C_{42}H_{46}BClF_{15}NPTa\cdot 2CH_2Cl_2$: C, 41.36; H, 3.94; N, 1.09. Found: C, 40.22; H, 3.67; N, 1.10.

X-ray Data Collection and Reduction. X-ray quality crystals were obtained as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed either on a Rigaku AFC6 four-circle or a Siemens SMART System CCD diffractometer. In the later case the data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45-50.0°$). 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 package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a Pentium computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[12] The heavy atom positions were determined using direct methods employing either the SHELXTL or direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. For chiral space groups, the correct enantiomorph was confirmed by data inversion and refinement. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

Refluxing stoichiometric mixtures of Cp^*TaCl_4 and the phosphinimines $R_3PNSiMe_3$ in toluene for 6 h affords the complexes $Cp^*Ta(NPR_3)Cl_3$ (R = *t*-Bu **1**, *i*-Pr **2**) in 77−80% isolated yields (Scheme 1). ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data were consistent with these formulations. In addition the nature of **1** was confirmed by X-ray crystallographic methods (Figure 1). The Ta−Cl distances range from 2.437(5) to 2.449(5) Å, while

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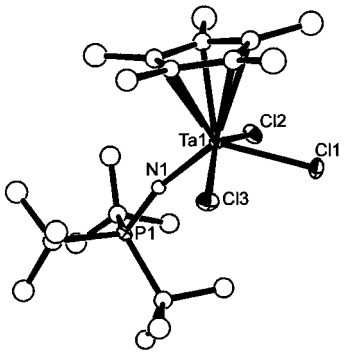
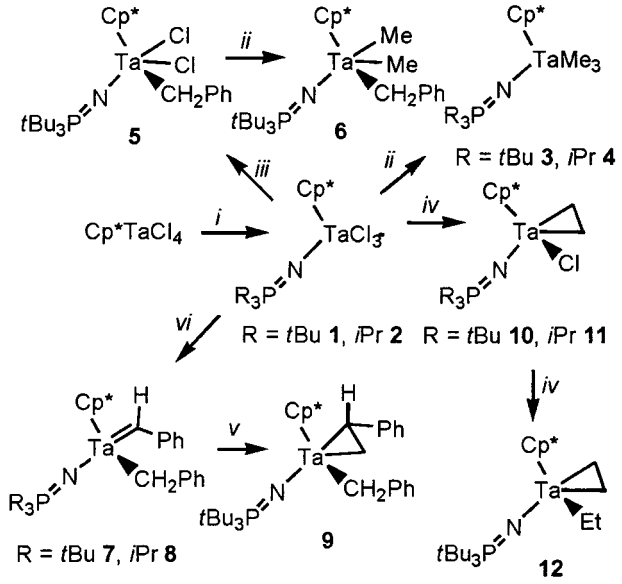


Figure 1. ORTEP drawings of **1**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta(1)−N(1) 1.870(13), Ta(1)−Cl(1) 2.437(5), Ta(1)−Cl(2) 2.440(5), Ta(1)−Cl(3) 2.449(5), P(1)−N(1) 1.585(14), N(1)−Ta(1)−Cl-(1) 127.8(4), N(1)−Ta(1)−Cl(2) 89.4(4), N(1)−Ta(1)−Cl(3) 87.0(4), Cl(1)−Ta(1)−Cl(2) 78.7(2), Cl(1)−Ta(1)−Cl(3) 78.8(2) Cl(2)−Ta(1)−Cl(3) 148.22(19), P(1)−N(1)−Ta(1) 165.7(8).

Scheme 1



i = $R_3PNSiMe_3$ (R = *t*Bu, *i*Pr), *ii* = MeLi, *iii* = $PhCH_2MgCl$
iv = EtMgCl, *v* = MeI, *vi* = 3 $PhCH_2MgCl$

the Ta−N distance is 1.870(13) Å. This compares with Ta−N distances of 1.801(3) Å seen in $[TaCl_4(NPt\text{-}Bu_3)]_2$[13] and is slightly shorter than those seen in $[TaCl_2(NP(NMe_2)_3)_3]$.[14] The geometry about Ta mimics that seen in $Cp^*_2TaCl_3$ in that the three chlorine atoms are approximately coplanar with the larger Cl−Ta−Cl angle of 148.22(19)° and the smaller Cl−Ta−Cl angles of 78.7(2)°. The geometry within the phosphinimide ligand is similar to that seen in other early metal phosphinimide complexes with P−N and Ta−N distances of 1.585(14) and 1.870(13) Å, respectively, and a P−N−Ta angle of 165.7(8)°. This geometry of the phosphinimide ligand is not unlike those seen in Ti-phosphinimide complexes,[2−5,7] although the metal−N distance is longer, as expected.

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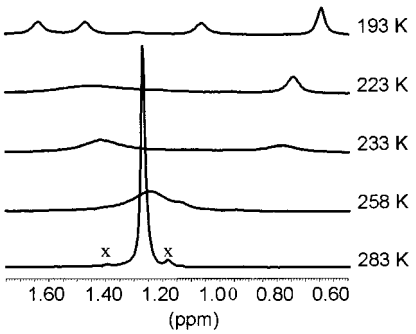

Figure 2. The *tert*-butyl group resonances region of the ^1H NMR spectrum of **1** as a function of temperature.

Variable-temperature ^1H NMR studies of **1** reveal a temperature dependence of the resonances associated with the *t*-Bu groups. Upon cooling, the resonances attributable to the methyl groups broaden and split into two peaks in a ratio of 2:1. The coalescence occurs at approximately −40 °C. These observations are consistent with restricted rotation about the Ta−N bond. The temperature dependence infers a cogwheel effect of the phosphinimide substituents and the pentamethylcyclopentadienyl group. The 2:1 intensities of the resonances are consistent with mirror molecular symmetry. Upon further cooling of **1**, the more intense of these resonances broadens and splits into three signals at −85 °C (Figure 2). These data suggest that the lower energy process involves inhibited rotation of the *tert*-butyl groups, presumably a secondary result of the cogwheel effect. Analysis of these complex processes for kinetic and thermodynamic data was not performed, as these processes are neither independent nor simple two-site exchange. In contrast, while cooling of a solution of **2** results in a broadening of the methyl resonance, the signal does not split into separate resonances upon cooling to −90 °C.

Alkylation of **1** and **2** have been studied (Scheme 1). Reaction with MeLi afforded the yellow-white complexes $Cp^*Ta(NPR_3)Me_3$ (R = *t*-Bu **3**, *i*-Pr **4**) in 72 and 84% isolated yield, respectively. X-ray structural data confirms the similarity of the molecular geometries of **3** and **1** (Figure 3). Stoichiometric alkylation of **1** with BnMgCl gives the yellow-orange species $Cp^*Ta(NPt\text{-}Bu_3)(CH_2Ph)Cl_2$, **5**. The NMR data are consistent with the formation of only one isomer of this species, and X-ray data affirm that the benzyl group replaces the central chloride of **1**, thus yielding the isomer of **5** with mirror-symmetry (Figure 4). The Ta−N distance in **5** (1.882(4) Å) is similar to that seen in **1** and **3**. The Ta−C and Ta−Cl distances of 2.309(5) and 2.4576(13) Å in **5** are slightly longer than those seen in **3**. These observations are consistent with the presence of a benzyl substituent, which is electron poor compared to a methyl group but more electron donating than a chloride.

Further alkylation of **5** is readily achieved by reaction with MeLi. This affords the species $Cp^*Ta(NPt\text{-}Bu_3)(CH_2Ph)Me_2$, **6**. In contrast, reaction of **1** and **2** with greater than 1 equiv of BnMgCl affords the alkylidene species $Cp^*Ta(NPR_3)(CHPh)(CH_2Ph)$ (R = *t*-Bu **7**, *i*-Pr **8**). These species exhibit the characteristic ^1H NMR shift for the alkylidene proton at 9.13 and 8.40 ppm and the ^{13}C resonances for the alkylidene carbons at 213.1 and 222.9 ppm, respectively. The formulations of these compounds

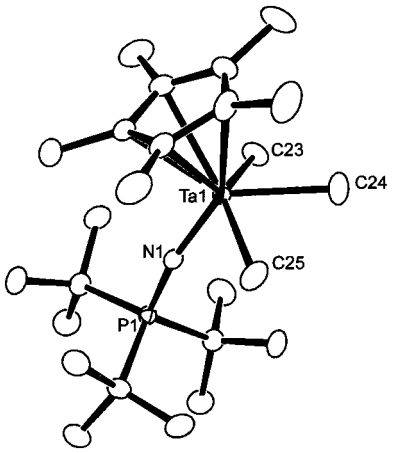

Figure 3. ORTEP drawings of **3**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta(1)−N(1) 1.902(3), Ta(1)−C(23) 2.257(4), Ta(1)−C(25) 2.259(5), Ta(1)−C(24) 2.280(5), P(1)−N(1) 1.579(3), N(1)−Ta(1)−C(23) 89.04(15), N(1)−Ta(1)−C(25) 89.13(16), C(23)−Ta(1)−C(25) 139.5(2), N(1)−Ta(1)−C(24) 124.31(18), C(23)−Ta(1)−C(24) 73.5(2), C(25)−Ta(1)−C(24) 74.3(3), P(1)−N(1)−Ta(1) 169.8(2).

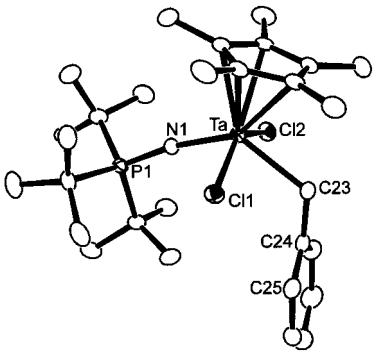

Figure 4. ORTEP drawings of **5**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta−N(1) 1.882(4), Ta−C(23) 2.309(5), Ta−Cl(2) 2.4572(13), Ta−Cl(1) 2.4580(12), P(1)−N(1) 1.614(4), N(1)−Ta−C(23) 128.85(18), N(1)−Ta−Cl(2) 87.99(12), C(23)−Ta−Cl(2) 77.69(14), N(1)−Ta−Cl(1) 88.76(12), C(23)−Ta−Cl(1) 78.22(14), P(1)−N(1)−Ta 169.6(3).

are also supported by the X-ray structural determination of **7** (Figure 5). The akylidene ligand gives rise to a relatively short Ta−C distance of 1.957(7) Å, compared to the Ta−C bond lengths of 2.09(2), 2.030(6), 2.026(10), 1.860(11), and 1.883(14) Å seen in [PhP(CH_2SiMe_2-$NSiMe_2CH_2$)$_2$PPhTaMe(CH_2)],[15] [Cp_2TaCl(CH*t*-Bu)],[16] [Cp_2TaMe(CH_2)],[17,18] [$TaCl_2$(CH*t*-Bu)($Me_2NCH_2CH_2$N-(Me)$CH_2C_6H_4$)],[19] and Cp*Ta(CH_2Ph)$_2$(CHPh),[20] respec-

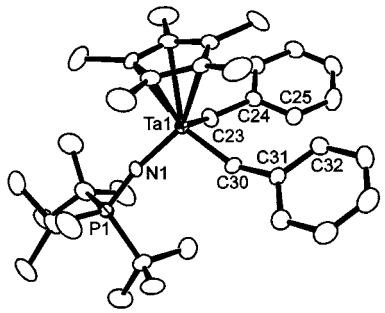

Figure 5. ORTEP drawings of **7**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta(1)−N(1) 1.877(5), Ta(1)−C(30) 1.957(7), Ta(1)−C(23) 2.235(7), P(1)−N(1) 1.593(5), N(1)−Ta(1)−C(30) 105.0(3), N(1)−Ta(1)−C(23) 94.6(2), C(30)−Ta(1)−C(23) 101.2(3), P(1)−N(1)−Ta(1) 169.7(4).

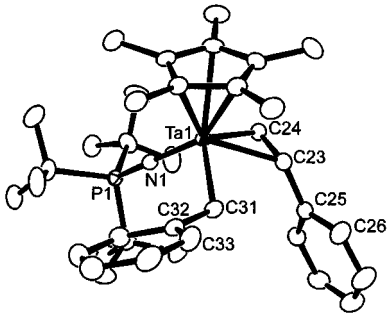

Figure 6. ORTEP drawings of **9**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta(1)−N(1) 1.898(5), Ta(1)−C(24) 2.186(5), Ta(1)−C(31) 2.272(5), Ta(1)−C(23) 2.299(5), P(1)−N(1) 1.597(4), C(23)−C(24) 1.458(−6), N(1)−Ta(1)−C(24) 99.4(2), N(1)−Ta(1)−C(31) 99.1(2), C(24)−Ta(1)−C(31) 114.38(18), N(1)−Ta(1)−C(23) 119.75(18), C(24)−Ta(1)−C(23) 37.83(17), C(31)−Ta(1)−C(23) 79.11(19), P(1)−N(1)−Ta(1) 168.7(2).

tively. The Ta-benzyl carbon distance is 2.235(7) Å, which is slightly shorter than that seen in **3** or **5**, consistent with both steric accessibility and electronic deficiency of the Ta center.

The alkylidene species **7** and **8** were remarkably robust. In refluxing d_8-toluene, there is no evidence of benzyl exchange. Moreover, these species fail to react with a variety of other reagents including $AlMe_3$, MeLi, PhCN, acetylenes, and olefins. In addition, in contrast to the reactivity of the metallocene alkylidene species $Cp_2TaMe(CH_2)$, **7** or **8** show no reactivity with $B(C_6F_5)_3$.[21] These observations seem to imply that the electron deficiency of the Ta center diminishes the nucleophilic nature of the alkylidene.

However, **7** did undergo reaction with methyl iodide in benzene upon heating for 2 h. NMR data revealed a complex mixture of products; however, one of these products was isolated as red-brown crystals upon standing of the solution for 1 week. The product **9** was isolated in 19% yield and characterized by X-ray crystallography. These data confirmed that **9** was the species Cp*Ta(NP*t*-Bu_3)(η^2-CHPhCH_2)(CH_2Ph) (Figure 6). The structural data show that newly formed styrene-Ta metallacycle and the remaining benzyl carbon are approxi-

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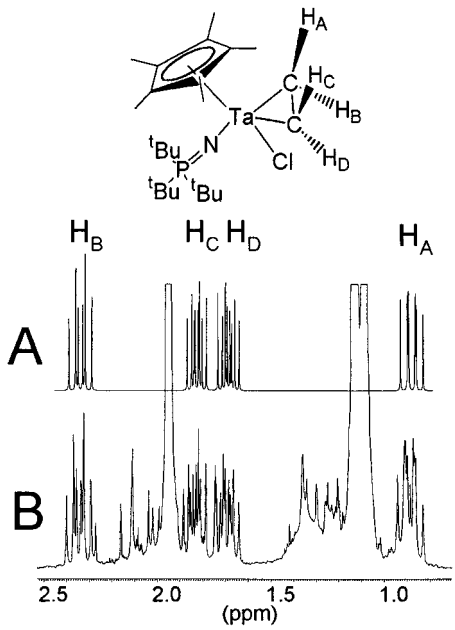

Figure 7. Methylene proton resonances region of the ^{1}H NMR spectrum of **10**.

mately coplanar. The central carbon is the substituted carbon of the styrene fragment with the phenyl ring oriented down away from the Cp* ligand. The Ta−C distances within the metallacycle are 2.186(5) and 2.299(5) Å, while the Ta−C distance for the benzyl group is 2.272(5) Å.

The formation of **9** presumably results from the nucleophilic attack of methyliodide by the alkylidene with the presumed loss of HI. Loss of toluene with the formation of Cp*Ta(NP*t*-Bu$_3$)(η^2-CHPhCH$_2$)(I) was anticipated based on the analogy to the work of Schrock et al.[18] While the formation of some toluene is indeed evidenced by the appearance of toluene resonances in the ^{1}H NMR spectra of the reaction mixture, the Ta-iodide complex was separable. Geometric isomers of **9** and the Ta-iodide species may account for additional products evidenced by the ^{31}P NMR spectra of the reaction mixture.

Alkylation of **1** and **2** with 2 equiv of EtMgCl results in β-hydrogen elimination and formation of the complexes Cp*Ta(NPR$_3$)(η^2-C$_2$H$_4$)Cl (R = *t*-Bu **10** and *i*-Pr **11**) in 63 and 58% yield, respectively. The ^{1}H NMR spectra for these compounds revealed four complex signals for the ethylene protons, as each of the protons are chemically inequivalent, exhibiting resonances centered at 2.4, 1.9, 1.8, and 0.9 ppm. In the case of **10**, a series of NMR experiments, including ^{1}H−^{13}C HETCOR, NOESY, and COSY, were employed to assign the resonances to the respective protons. In addition, the ethylene resonances were simulated using the reported coupling constants (Figure 7). It is important to note that these resonances are temperature invariant, affirming a rigid metallocyclic structure and consistent with a Ta(V) formulation. The structure of **10** was confirmed crystallographically as well (Figure 8). The Ta−C distances within the metallacycle are 2.220(7) and 2.313(5) Å, which is slightly longer than the corresponding distances in **9**. This is consistent with the presence of the relatively electron-rich ancillary chloride ligand. The metric parameters of this metallocyclopropane

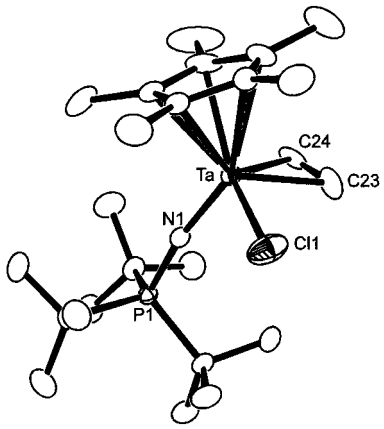

Figure 8. ORTEP drawings of **10**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta(1)−N(1) 1.873(4); Ta(1)−C(23) 2.220(7); Ta(1)−C(24) 2.313(5); Ta(1)−Cl(1)2.455(2); P(1)−N(1) 1.603(4); C(23)−C(24) 1.464(13); N(1)−Ta(1)−C(23) 109.5(3); N(1)−Ta(1)−C(24) 94.3(2); C(23)−Ta(1)−C(24) 37.6(3); C(23)−Ta(1)−Cl(1) 86.1(4); C(24)−Ta(1)−Cl(1) 122.4(2); P(1)−N(1)−Ta(1) 170.9(3); C(24)−C(23)−Ta(1) 74.6(4); C(23)−C(24)−Ta(1) 67.7(4).

fragment are comparable to those seen in Ta(*Ot*-Bu)$_2$(CH*t*-Bu)(Me$_2$NCH$_2$CH$_2$N(Me)CH$_2$C$_6$H$_4$).[19]

Further reaction of **10** with EtMgCl affords Cp*Ta(NP*t*-Bu$_3$)(η^2-C$_2$H$_4$)(CH$_2$CH$_3$), **12**, in 60% yield. While the NMR data are consistent with the formulation, the ^{1}H NMR spectrum of **12** is complex. Each of the methylene protons are chemically inequivalent, as they are in **10**. Furthermore, HETCOR and COSY experiments revealed that the resonances for the *tert*-butyl groups overlap with one of the protons of the ethylene fragment. Variable-temperature NMR studies of **12** showed no evidence of proton migration and ethylene−ethyl group interchange. While crystallographic data confirmed the formulation of **12**, the quality of the solution was poor. Repeated attempts to obtain better crystals were unsuccessful.

Cationic Complexes. The generation of a variety of zwitterionic and cationic complexes has been studied (Scheme 2). Reaction of **1** with 1 equiv of B(C$_6$F$_5$)$_3$ results in chloride abstraction and initial generation of the salt [Cp*Ta(NPtBu$_3$)Cl$_2$][ClB(C$_6$F$_5$)$_3$], **13**, as evidenced by a downfield shift in the ^{31}P NMR by 11 ppm. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy are also consistent with formation of **13**. The resulting anion [ClB(C$_6$F$_5$)$_3$]$^-$ is not stable in CD$_2$Cl$_2$ over prolonged periods of time. ^{19}F NMR spectra showed resonances attributable to at least three different species including [B(C$_6$F$_5$)$_4$]$^-$ in solution after 24 h. This is consistent with substituent redistribution affording several borate anions. The analogous reaction with Ph$_3$C[B(C$_6$F$_5$)$_4$] affords the related salt [Cp*Ta(NPtBu$_3$)Cl$_2$][B(C$_6$F$_5$)$_4$], **14**. Decker and co-workers[8] have recently structurally characterized the related salt [Cp*Ta((*i*-PrN)$_2$CMe)Cl$_2$]-SbF$_6$, while Bercaw et al.[22] have examined the chemistry of cationic Ta-imido complex [Cp*$_2$Ta(NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$].

Generation of the zwitterionic species Cp*Ta(NPR$_3$)Me$_2$(MeB(C$_6$F$_5$)$_3$) (R = *t*-Bu **15**, *i*-Pr **16**) via reaction of

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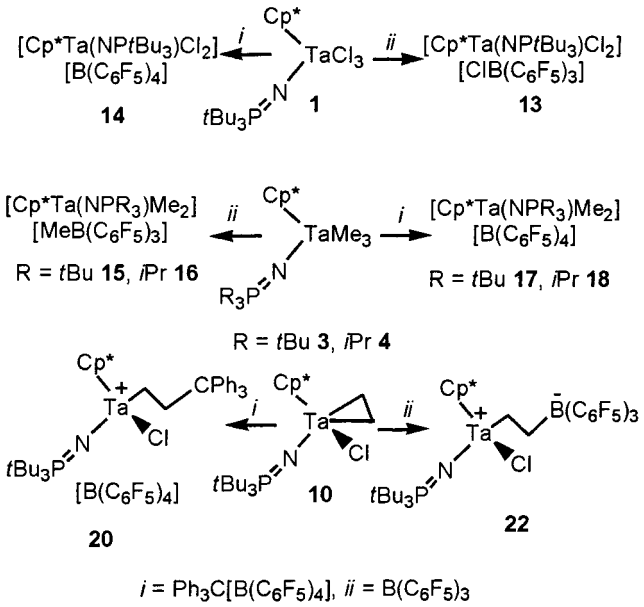
Scheme 2



3 or **4** with $B(C_6F_5)_3$ is consistent with the downfield ^{31}P NMR chemical shifts for **15** and **16**. ^1H NMR data show single resonances attributable to the nine methyl protons. Despite cooling to −80 °C, no appreciable broadening or splitting of these resonances was observed. This suggests a dynamic exchange process that is rapid on the NMR time scale and results in the interchange of Ta and B bound methyl groups. The analogous reaction of **3** and **4** with $Ph_3C[B(C_6F_5)_4]$ affords the related salts $[Cp^*Ta(NPR_3)Me_2][B(C_6F_5)_4]$ (R = *t*-Bu **17**, *i*-Pr **18**). The formation of these products is unequivocally established by NMR spectroscopy. In a similar manner, **17** can be generated by treatment of **6** with $Ph_3C[B(C_6F_5)_4]$. A related Ta-methyl cation, $[Cp^*TaMe(MeN(C_6H_3Me)_2NSiMe_3)]I$, has been recently structurally characterized by Gountchev and Tilley.[23]

The analogous reactions of **5** with $B(C_6F_5)_3$ and $Ph_3C[B(C_6F_5)_4]$ were also performed. In the case of the borane reaction, chloride abstraction results in the formation of the salt $[Cp^*Ta(NPt\text{-}Bu_3)BnCl][ClB(C_6F_5)_3]$, **19**. This is evidenced by NMR spectral data. For example, the benzylic protons of **19** give rise to an AB quartet for the diastereotopic protons. In contrast, the trityl borate attacks the Ta-benzyl bond, affording **14** and Ph_3CCH_2-Ph. The differing reaction pathways for these two reagents are presumably a result of the relative bond strengths of B−Cl versus B−C and C−C versus C−Cl bonds.

Treatment of **10** with $[Ph_3C][B(C_6F_5)_4]$ results in a downfield shift of about 16 ppm in the ^{31}P NMR resonance. The new species **20** also exhibits downfield shifts for the Cp*, *t*-Bu, and ethylene resonances in the ^1H NMR spectrum. The ethylene carbons are also shifted, one being 15 ppm downfield and the other 3 ppm upfield from the corresponding resonances in **10**. ^{11}B, ^{19}F, ^1H-NOESY, COSY, HETCOR, and gradient HMBC provided data that confirmed the long-range carbon−hydrogen connectivities, establishing that the ethylene protons are adjacent to the trityl group. This is consistent with the formulation of **20** as the cationic complex $[Cp^*Ta(NPt\text{-}Bu_3)(Cl)(CH_2CH_2CPh_3)][B(C_6F_5)_4]$. In a similar manner $[Cp^*Ta(NPt\text{-}Bu_3)(Cl)(CH_2CH_2\text{-}CPh_3)][BF_4]$, **21**, is formed via reaction of **10** with Ph_3CBF_4.

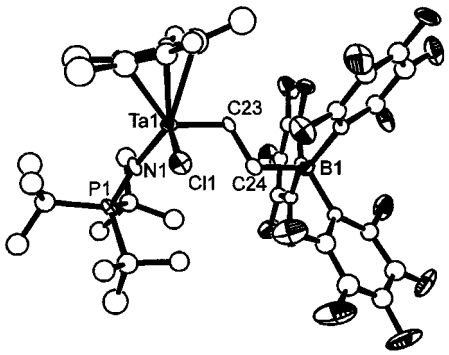


Figure 9. ORTEP drawings of **22**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta(1)−N(1) 1.818(16); Ta(1)−C(23) 2.10(3); Ta(1)−C(2) 2.32(4); Ta(1)−Cl(1) 2.342(4); Ta(1) C(1) 2.37(3); Ta(1)−C(3) 2.47(3); Ta(1)−C(5) 2.46(3); Ta(1)−C(4) 2.54(3); P(1)−N(1) 1.639(18); N(1)−Ta(1)−C(23) 100.5(10); N(1)−Ta(1)−Cl(1) 102.5(5); C(23)− Ta(1)−Cl(1) 112.4(9); P(1)−N(1)−Ta(1) 171.2(11); C(24)−C(23)−Ta(1) 103(2); C(23)−C(24)−B(1) 115(2).

In an analogous manner, treatment of **10** with 1 equiv of $B(C_6F_5)_3$ in CD_2Cl_2 results in the formation of a new species **22**. ^{31}P, ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra are consistent with the formation of a zwitterionic complex. Small yellow crystals were obtained upon standing of the solution. X-ray crystallographic study confirmed the formulation of **22** as the zwitterionic species $[Cp^*Ta(NPt\text{-}Bu_3)(Cl)(CH_2CH_2B(C_6F_5)_3)]$ (Figure 9). Attack of the metallocyclopropane ring of **10** by the borane results in an ethylene tether between the anionic borate and cationic tantalum centers, which are 4.427 Å apart. While the remaining metric parameters are unexceptional, it is noteworthy that one of the hydrogen atoms on the β-methylene carbon is 2.728 Å from Ta in the plane of the chloride and C(23). Although this approach in the solid state suggests a weak agostic interaction, NMR data show that this interaction does not persist in solution. This is in contrast to the strong α-agostic interactions observed in the related complexes $Cp_2TaMe(CH_2B(C_6F_5)_3)$ and $[Cp_2Zr(PPh_2Me)CH_2CH_2B(C_6F_5)_3]$ recently described by Piers et al.[21,24] Analogous β-interactions are thought to precipitate β-hydrogen elimination in related group IV metal species.

Consideration of the above chemistry of pentamethylcyclopentadienyl−tantalum−phosphinimide complexes affords some general observations regarding the effect of the use of phosphinimide ligands. In the present Ta chemistry, Ta-alkyl and -alkylidene species appear less reactive than the corresponding tantalocene analogues. This is attributed to greater Lewis acidity at the metal center as a result of replacement of a cyclopentadienyl ligands with a bulky phosphinimide ligand. However, it is interesting to contrast the absence of β-agostic-H interactions with the metal center in zwitterionic and cationic alkyl Ta phosphinimide complexes with the

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(24) Sun, Y. M.; Piers, W. E.; Rettig, S. J. *Chem. Commun.* **1998**, 127−128.

presence of such interactions in analogous tantalocene and zirconocene species. This apparently conflicting observation suggests the LUMO responsible for the Lewis acidity is not appropriately directed for interaction with groups in the plane orthogonal to the CpM(NPR$_3$) fragment. This view is consistent with recent solid state EPR studies of [CpTi(NPR$_3$)μ-Cl]$_2$, which suggest the LUMO of the CpTi(NPR$_3$) fragments is primarily $d_{z^2-x^2}$ in character in contrast with the corresponding LUMO of the Cp$_2$M fragments, which is principally d_{z^2} in nature.[7]

Summary

A series of neutral tantalum phosphinimide complexes have been prepared and characterized. These compounds have been employed to synthesize a number of zwitterionic and cationic complexes. Reactivity of these species as well as the effect of phosphinimide ligands on the chemistry of other metals continue to be subjects of study.

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Supporting Information Available: Crystallographic and ^{1}H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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