Competition between π Donation and α-C−H Agostic Interactions in Complexes of the Type Tp′Ta(=CH-*t*-Bu)(X)(Y) (X = Halide; Y = Halide, NR_2, OR; Tp′ = Hydrotris(3,5-dimethylpyrazolyl)borate)

James M. Boncella,* Mary L. Cajigal, and Khalil A. Abboud

Department of Chemistry and the Center for Catalysis, University of Florida, Gainesville, Florida 32611-7200

Received October 20, 1995[⊗]

The compounds Tp′Ta(CHC$(CH_3)_3$)X_2 (**2** (X = Cl), **3** (X = Br)) (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate), have been synthesized by the reaction of KTp′ with Ta(CHC$(CH_3)_3$)$X_3(thf)_2$ in THF. One Cl ligand in **2** can be substituted with OR^- (R = *i*-Pr, Me) or NMe_2^-. The values of $^1J_{C-H}$ for the alkylidene carbon are uniformly low due to the α-H agostic interaction between the metal center and the alkylidene proton. The magnitude of $^1J_{C-H}$ in these compounds depends upon the π donor properties of the remaining ligands. Attempted synthesis of monoarylamide complexes by displacement of Cl^- from **2** with $N(H)Ar^-$ results in proton transfer from N to C and formation of the imido complexes Tp′Ta($CH_2C(CH_3)_3$)(NAr)Cl (Ar = 2,6-*i*-PrC_6H_3 (**7**), Ph (**8**)). When **2** reacts with KN(Me)Ph, proton transfer occurs from the Me group to the alkylidene carbon giving the imine complex Tp′Ta(η^2-CH_2=NPh)(CH_2CMe_3)Cl (**9**). A single-crystal X-ray diffraction study of **9** confirmed the structure and suggested that **9** is best described as an azametallacyclopropane complex.

Introduction

Over the past several years, our studies of high oxidation state alkylidene complexes that contain polydentate ancillary ligands have focused on compounds that contain group 6 transition metals.[1−5] The use of the hydrotris(pyrazolyl)borate family of ligands has resulted in the formation of kinetically stable six-coordinate complexes.[1−4] The bulky nature of the Tp ligand system combined with formal 18 electron counts on the metal centers has resulted in ligand-centered rather than metal-centered chemistry. We now report the synthesis and characterization of a series of electronically unsaturated, six-coordinate, tantalum neopentylidene complexes containing the hydrotris(3,5-dimethylpyrazolyl)borate (Tp′) ligand.

The use of the Tp and Tp′ ligand systems in Ta chemistry was pioneered by Reger in the mid-1980s.[6] These studies and those of related group 4 complexes[7] demonstrated the sensitivity of the Tp′ ligand system to the powerful Lewis acidity of early transition metal halides. Although functionalization of Tp′ complexes is possible after introduction of the Tp′ ligand,[6c] recent work on the Tp chemistry of early transition metals has focused on coordinating the Tp ligand to the metal center after the desired organometallic functional group has been formed.[8] Thus alkyl and alkyne complexes of Zr, Nb, and Ta containing hydrotris(pyrazolyl)borate ancillary ligands have been synthesized by the reaction of the Tp alkali metal salts with complexes such as $NbCl_3$(DME)(1-phenylpropyne).[9] In a similar fashion, we have used tantalum neopentylidene halide complexes[10] as starting materials for the chemistry described in this paper.

Experimental Section

General Details. All procedures were carried out under an argon atmosphere using Schlenk techniques or under a nitrogen atmosphere in a drybox. Pentane, diethyl ether (Et_2O), tetrahydrofuran (THF), and benzene were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride, and toluene was distilled from sodium metal. All solvents were stored under argon and over molecular sieves. Metal halides were sublimed prior to use. The compounds potassium hydrotris(3,5-dimethylpyrazolyl)borate,[11] $Zn(CH_2CMe_3)_2$,[12] and Me_3CCH_2MgCl[13] were synthesized using published procedures. The *in situ* preparation of Ta(CHC$(CH_3)_3$)$(THF)_2Cl_3$ follows the literature procedure[10] with the modifications described below. NMR spectra were obtained using Varian VXR-300 or GE-QE300 spectrometers. Chemical shifts are reported relative to TMS. Elemen-

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066.
(2) Blosch, L. L.; Gamble, A. S.; Abboud, K.; Boncella, J. M. *Organometallics* **1992**, *11*, 2342.
(3) Gamble, A. S.; Boncella, J. M. *Organometallics* **1993**, *12*, 2814.
(4) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1995**, *14*, 1567.
(5) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378.
(6) (a) Reger, D. L.; Swift, C. A.; Lebioba, L. *Inorg. Chem.* **1984**, *23*, 349. (b) Reger, D. L.; Swift, C. A.; Lebioba, L. *J. Am. Chem. Soc.* **1983**, *105*, 5343. (c) Reger, D. L.; Tarquini, M. E.; Lebioba, L. *Organometallics* **1983**, *2*, 1763.
(7) Bradley, D. C.; Hursthouse, M. B.; Newton, J.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1984**, 188.
(8) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(9) (a) Etienne, M.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3801. (b) Etienne, M.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 4010. (c) Etienne, M. *Organometallics* **1994**, *13*, 410.
(10) (a) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236. (b) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.
(11) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(12) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(13) Schrock, R. R.; Sancho, J.; Pederson, S. F. *Inorg. Synth.* **1989**, *26*, 44.

0276-7333/96/2315-1905$12.00/0

tal analyses were performed by Atlantic Microlabs, Atlanta, GA, or the UF Department of Chemistry Analytical Services. Mass spectrometry was performed by the UF Department of Chemistry Analytical Services.

Tp′Ta(CHC(CH$_3$)$_3$)Cl$_2$ (2). The dropwise addition of a toluene (10 mL) solution of Zn(CH$_2$C(CH$_3$)$_3$)$_2$ (2.31 g, 11.1 mmol) to a vigorously stirred slurry of freshly sublimed TaCl$_5$ (4.20 g, 11.7 mmol) in 40 mL of toluene was carried out over the course of 10 min. The mixture was stirred for 20 min, and a change from yellow to a bright lemon yellow occurred. The reaction products (ZnCl$_2$ and solutes) were filtered through a glass frit which was washed with toluene (2 × 10 mL). The toluene was removed under reduced pressure from the combined filtrate and extracts. The resulting yellow oil was dissolved in pentane (40 mL) and filtered through Celite. The pentane was removed under reduced pressure giving a yellow oil. The oil was taken into a N$_2$ atmosphere drybox, where it was dissolved in 70 mL of THF and allowed to stir for 1 h resulting in the formation of a deep burgundy solution of Ta(CHC(CH$_3$)$_3$)(THF)$_2$Cl$_3$. To this solution was added KTp′ (3.92 g, 11.7 mmol). The reaction mixture rapidly turned purple. The mixture was left to stir for 3 days in the drybox. The solvent was removed under reduced pressure, and the purple product was dissolved in Et$_2$O (*ca*. 100 mL) and filtered through Celite. The ether solution was reduced in volume to approximately 60 mL, and the solution was stored at −20 °C for 12 h to precipitate the less soluble impurities. The mother liquor was filtered through Celite and the solvent removed under reduced pressure. The product was a dichroic purple powder (5.3 g, 77% yield). It should be noted that sometimes the solid isolated in this step looks green in reflected light, though both solids are identical as observed by proton NMR or MS. The compound may be further purified by recrystallization from diethyl ether. Despite repeated attempts, we were unable to obtain a satisfactory combustion analysis of this compound. Typically, the results for N and H were acceptable while the result for C was *ca*. 1−2% less than the theoretical value. ^{1}H NMR (C$_6$D$_6$, 22 °C; δ): 1.30 (9H, s, CHC(C*H*$_3$)$_3$); 1.92, 2.62(6 H each, s, Tp′ Me), 2.01, 2.91 (3H each, s, Tp′ Me′): 2.51 (1 H, s, C*H*C(CH$_3$)$_3$); 5.41 (2 H′, s, Tp′ ring H), 5.47 (1 H, s, Tp′ ring H). ^{13}C NMR (C$_6$D$_6$, 22 °C; δ): 12.40, 12.71, 15.46, 18.78 (s, Tp′ Me's); 33.64 (CHC(*C*H$_3$)$_3$); 46.27 (CH*C*(CH$_3$)$_3$); 107.95, 108.35 (unsubstituted Tp′ ring C's); 142.93, 145.80, 153.10, 154.20 (substituted Tp′ ring C's); 142.93, 145.80, 153.10, 154.20 (substituted Tp′ ring C's); 248.3 ($^1J_{C-H}$ = 73 Hz; *C*HC(CH$_3$)$_3$). MS (FAB; nitrophenyl octyl ether matrix): M = 619.1677 amu, M$^+$; C$_{20}$H$_{32}$BCl$_2$N$_6$Ta requires 619.1689 amu.

Tp′Ta(CHC(CH$_3$)$_3$)Br$_2$ (3). The same procedure was followed as for **2** using TaBr$_5$ (2.39 g, 4.11 mmol), Zn(CH$_2$C(CH$_3$)$_3$)$_2$ (0.812 g, 3.91 mmol), and KTp′ (1.32 g, 3.91 mmol). The purification procedure was more difficult due to the lower solubility of **3** in ether. A few milliliters of toluene was added to approximately 100 mL of ether to solubilize the product. The mother liquor from two successive precipitations gave 2.16 g (78% yield) of essentially pure product. Compound **3** may be recrystallized from diethyl ether. Despite repeated attempts, we were unable to obtain satisfactory combustion analysis of this compound. Typically, the results for N and H were acceptable while the result for C was *ca*. 1−2% less than the theoretical value. ^{1}H NMR (C$_6$D$_6$, 22 °C; δ): 1.61 (9H, s, CHC(CH$_3$)$_3$); 1.83, 2.61, (6 H each, Tp′ Me's) 2.04, 3.00 (3 H each, Tp′ Me's); 1.88 (1 H, s, C*H*C(CH$_3$)$_3$); 5.36 (2 H, s, Tp′ ring H's); 5.60 (1 H, s, Tp′ ring H's). ^{13}C NMR (C$_6$D$_6$, 22 °C; δ): 12.77, 17.15, 18.90 (Tp′ Me's); 33.55 (CHC(*C*H$_3$)$_3$); 47.44 (CH*C*(CH$_3$)$_3$); 108.16, 108.98 (unsubstituted Tp′ ring C's); 143.26, 146.16, 153.29, 155.36 (substituted Tp′ ring C's); 260.39 ($^1J_{C-H}$ = 69.7 Hz; *C*HC(CH$_3$)$_3$). MS (FAB; nitrophenyl octylether matrix): M = 709.0791 amu, M$^+$; C$_{20}$H$_{33}$BBr$_2$N$_6$Ta requires 709.0620 amu.

Tp′Ta(CHC(CH$_3$)$_3$)(OCH(CH$_3$)$_2$)Cl (4). The combined solids Tp′Ta(CHC(CH$_3$)$_3$)Cl$_2$ (0.300 g, 0.484 mmol) and NaOCH(CH$_3$)$_2$ (0.136 g, 1.65 mmol) were dissolved in 30 mL of THF and heated to reflux for 16 h to give an orange solution. After the solution was allowed to cool to room temperature, the solvent was removed under reduced pressure. The orange oil was dissolved in pentane and filtered through Celite. The volume was reduced to *ca*. 30 mL and stored at −20 °C for 24 h. An orange microcrystalline solid precipitated (0.144 g, 45% yield). ^{1}H NMR (C$_6$D$_6$, 22 °C; δ): 1.06, 1.17 (3H each, d, J_{H-H} = 6.33 Hz, OCH(C*H*$_3$)$_2$); 1.43 (9H, s, CHC(C*H*$_3$)$_3$); 1.99, 2.06, 2.07, 2.52, 2.76, 2.86 (3H each, s, Tp′ Me's); 4.85 (1H, sept, J_{H-H} = 6.33 Hz, C*H*(CH$_3$)$_2$); 5.38, 5.54, 5.64, (1H each, s, Tp′ H's); 5.78 (1H, s, C*H*C(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 22 °C; δ): 12.12, 12.76, 15.32, 18.08, 18.45, 24.46, 24.64, 27.20 (Tp′ methyls and −OCH(*C*H$_3$)$_2$); 35.71 (CHC(*C*H$_3$)$_3$); 43.99 (CH*C*(CH$_3$)$_3$; 79.12 (O*C*H(CH$_3$)$_3$); 107.15, 107.19, 107.72 (unsubstituted Tp′ ring C's); 142.33, 144.51, 145.72, 151.49, 152.05, 153.58 (substituted Tp′ ring C's); 251.91 (*C*HC(CH$_3$)$_3$, $^1J_{C-H}$ = 91.6 H). Anal. Calcd for C$_{23}$H$_{39}$BClN$_6$OTa: C, 42.97; H, 6.11; N, 13.08. Found: C, 42.72; H, 6.23; N, 12.81.

Tp′Ta(CHC(CH$_3$)$_3$)(OCH$_3$)Cl (5). The combined solids Tp′Ta(CHC(CH$_3$)$_3$)Cl$_2$ (0.250 g, 0.404 mmol) and NaOCH$_3$ (0.033g, 0.611 mmol) were dissolved in 30 mL of THF and vigorously stirred for 24 h to give a dusky orange-red solution. The solvent was removed under reduced pressure, and the orange oil was extracted into pentane and filtered through Celite. The volume was reduced to 5 mL and stored at −20 °C for 24 h. An orange microcrystalline solid precipitated (0.10 g, 40% yield). ^{1}H NMR (C$_6$D$_6$, 22 °C; δ): 1.45 (9H, s, CHC(C*H*$_3$)$_3$; 1.99, 2.04, 2.07, 2.46, 2.65, 2.85 (3H each, s, Tp′ methyls); 3.96 (3H, s, OCH$_3$); 5.36, 5.53, 5.62 (1H each, s, Tp′ ring H's); 6.08 (1H, s, C*H*C(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 22 °C; δ): 12.11, 12.72, 14.36, 17.63, 17.92 (Tp′ methyls, note that the resonance at δ 12.72 is twice the intensity of the others and probably consists of two overlapped peaks); 35.87 (CHC(*C*H$_3$)$_3$); 44.01 (CH*C*(CH$_3$)$_3$; 63.71 (O*C*H$_3$); 107.00, 107.27, 107.80 (unsubstituted Tp′ ring C's); 142.72, 144.78, 145.63, 151.12, 152.10, 153.75 (substituted Tp′ ring C's); 256.62 (*C*HC(CH$_3$)$_3$, $^1J_{C-H}$ = 94.6 Hz). Anal. Calcd for C$_{21}$H$_{35}$BClN$_6$OTa: C, 41.03; H, 5.74; N, 13.67. Found: C, 40.78; H, 5.81; N, 13.50.

Tp′Ta(N(CH$_3$)$_2$)(CHC(CH$_3$)$_3$)Cl (6). The solids, Tp′Ta(CHC(CH$_3$)$_3$Cl$_2$ (0.198 g; 0.320 mmol) and LiN(CH$_3$)$_2$ (0.018 g; 0.353 mmol), were dissolved in 40 mL of THF at −78 °C causing a rapid color change from purple to blue. The flask was removed from the cold bath after 5 min and was allowed to warm to room temperature. Within 20 min, the solution had turned orange. The solution was allowed to stir for 1 day. The THF was removed under reduced pressure, and the resultant orange oil was extracted with pentane and the extract filtered through Celite. The filtrate was reduced in volume and stored at −20 °C to give yellow crystals. ^{1}H NMR (CD$_2$Cl$_2$, −40 °C; δ): 1.17 (9H, s, CHC(C*H*$_3$)$_3$); 1.68 (1 H, s, C*H*C(CH$_3$)$_3$); 2.22, 2.31, 2.38, 2.46, 2.72 (3:6:3:3:3 H, s, Tp′ Me's); 2.49, 4.17 (3 H each, s, N(*C*H$_3$)$_2$); 5.78, 5.89, 5.98 (1H each, s, Tp′ ring H's). ^{13}C NMR (CD$_2$Cl$_2$, 25 °C; δ): 12.74, 13.03, 13.22, 15.24, 16.90, 17.93 (Tp′ ring Me's); 18.60, 33.27 (N(*C*H$_3$)$_2$); 34.24 (CHC(*C*H$_3$)$_3$); 47.38 (CH$_2$*C*(CH$_3$)$_3$); 107.33, 107.68, 108.14 (unsubstituted Tp′ ring C's); 144.37, 145.55, 146.05, 152.70, 153.76, 154.07 (substituted Tp′ ring C's); 236.89 ($^1J_{C-H}$ = 69.7 Hz; *C*HC(CH$_3$)$_3$). Anal. Calcd for C$_{22}$H$_{38}$BClN$_7$Ta: C, 42.08; H, 6.10; N, 15.62. Found: C, 41.77; H, 6.27; N, 15.24.

Tp′Ta(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CH$_2$C(CH$_3$)$_3$)Cl (7). Ta(CH$_2$C(CH$_3$)$_3$)$_2$Cl$_3$ was prepared as described above and was isolated by removing the THF from the reaction mixture in a tared Schlenk flask. The crude Ta(CH$_2$C(CH$_3$)$_3$)$_2$Cl$_3$ (4.46 g, 10.4 mmol) was dissolved in 30 mL of THF and cooled to −78 °C. The solution was vigorously stirred while (Me$_3$Si)N(H)-2,6-*i*-Pr$_2$C$_6$H$_3$ (5.1 mL, 20.9 mmol) was added dropwise via syringe. After the solution was allowed to stir for 1 day at room temperature, a THF solution of KTp′ (3.67 g, 10.9 mmol) was added to the resultant yellow solution. No further color change was observed. After the solution was stirred vigorously for 1 day, the solvent was removed under reduced pressure. The

yellow oil was extracted with Et_2O and filtered through Celite. Yellow crystals were isolated by concentrating the Et_2O solution to saturation at room temperature followed by cooling to −20 °C. The crystals were washed with cold (−78 °C) pentane to remove oily impurities. ^{1}H NMR (C_6D_6, 22 °C; δ): 0.58, 1.00 (3 H each, d, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$); 0.967, 2.56 (1H each, d, $^2J_{HH}$ = 16 Hz, CH_2C(CH_3)$_3$); 1.55 (9H, s, CHC(CH_3)$_3$); 1.69, 1.71 (3 H each, d, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$); 1.97, 1.98, 2.12, 2.33, 2.55, 2.88 (3H each, s, Tp′ Me's); 3.07, 5.30 (1 H each, sept, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$); 5.27, 5.51, 5.60 (1H each, s, Tp′ ring H's); 6.89 (1 H, t, $^3J_{H-H}$ = 7.6 Hz *para* H of arylimido); 7.08, 7.35 (1 H each, d, $^3J_{H-H}$ = 7.2 Hz, *meta* H's of arylimido). ^{13}C NMR (C_6D_6, 22 °C; δ): 12.38, 12.70, 12.97, 18.67, 24.06, 24.26, 25.87, 26.45, 28.24, 28.62 (Tp′ ring and isopropyl Me's); 16.37, 16.43 (CH(CH_3)$_2$); 35.64 (CH_2C(CH_3)$_3$); 36.32 (CH_2C(CH_3)$_3$); 94.79 ($^1J_{C-H}$ = 108.4 Hz; CH_2C(CH_3)$_3$); 107.86, 108.62 (coincidentally overlapping unsubstituted Tp′ ring C's); 122.94, 123.80, 124.91 (unsubstituted ring C's of arylimido); 143.39, 144.71, 145.34, 147.62, 148.88, 150.35, 153.36, 153.51, 154.27 (quarternary ring C's of arylimido and Tp′). Anal. Calcd for $C_{32}H_{50}BClN_7Ta$: C, 50.57; H, 6.63; N, 12.90. Found: C, 50.61; H, 6.59; N, 12.96.

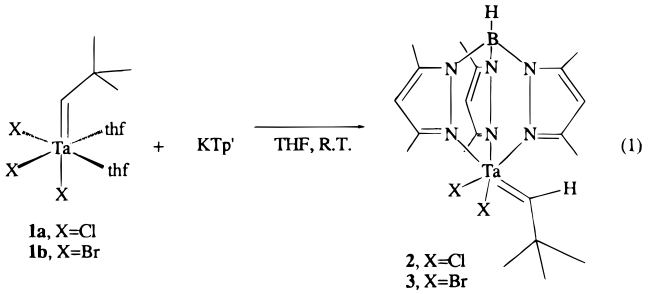
Tp′Ta(NPh)(CH_2C(CH_3)$_3$)Cl (8). The solids, Tp′Ta(CHC(CH_3)$_3$)Cl$_2$ (0.200 g; 0.323 mmol) and KHNPh (0.051g; 0.388 mmol), were dissolved in 40 mL of THF in a Schlenk flask and stirred at room temperature for 2 days. The THF was removed under reduced pressure giving a yellow oil. The yellow oil was dissolved in ether and filtered through Celite. The volume was reduced and the solution stored at −20 °C. A small amount of powder precipitated. The mother liquor was filtered and concentrated to *ca*. 4 mL, and 1 mL of pentane was added. This solution was stored at −78 °C until clear yellow crystals formed (2−3 days). The crystalline solid was washed with 20 mL pentane at −78 °C. ^{1}H NMR (C_6D_6, 25 °C; δ): 0.91, 2.39 (1H each, d, $^2J_{HH}$ = 16 Hz, CH_2C(CH_3)$_3$); 1.58 (9H, s, CH_2C(CH_3)$_3$); 1.86, 1.93, 2.10, 2.32, 2.59, 2.85 (3H each, s, Tp′ Me's); 5.21, 5.42, 5.61 (1H each, s, Tp′ ring H's); 6.71 (1 H, t, $^3J_{H-H}$ = 7.2 Hz *para* H of phenylimido); 7.12 (2 H, t, $^3J_{H-H}$ = 7.2 Hz *meta* H of phenylimido), 7.24 (2 H, d, $^3J_{H-H}$ = 7.2 Hz *ortho* H of phenylimido). ^{13}C NMR (C_6D_6, 25 °C; δ): 12.12, 12.52, 12.73, 15.26, 16.30, 16.46 (Tp′ ring Me's); 35.22 (CH_2C(CH_3)$_3$); 36.48 (CH_2C(CH_3)$_3$); 94.24 ($^1J_{C-H}$ = 109.1 Hz; CH_2C(CH_3)$_3$); 107.35, 107.72, 108.51 (unsubstituted Tp′ ring C's); 123.94, 127.81, 128.29 (substituted ring C's of phenylimido); 143.51, 144.83 145.50, 153.39, 154.26, 154.82, 156.18 (quarternary ring C's of phenylimido and Tp′). Anal. Calcd for $C_{26}H_{38}BClN_6Ta$: C, 46.20; H, 5.67; N, 14.51. Found: C, 46.01; H, 5.83; N, 14.33.

Tp′Ta($\eta^2$$CH_2$=NPh)($CH_2$C($CH_3$)$_3$)Cl (9). A solution of KN(Me)Ph (0.048 g; 0.388 mmol) in 20 mL of THF was cooled to −78 °C and added to a cold (−78 °C) solution of Tp′Ta(CHC(CH_3)$_3$)Cl$_2$ (0.200 g; 0.323 mmol) in THF (10 mL). The cold bath was removed, and the reaction mixture was allowed to warm to room temperature. As the reaction mixture warmed, the color changed from red to yellow and the formation of a white precipitate was observed. The reaction was stirred at room temperature for *ca*. 24 h. The THF was removed under reduced pressure, and the yellow-brown residue extracted with pentane (2 × 20 mL). After filtration, the combined pentane extracts were concentrated to *ca*. 5 mL under reduced pressure. Cooling of the yellow solution to −20 °C initially gave a yellow oil which crystallized upon standing in the mother liquors at −20 °C for 2 weeks. The total yield was 0.11 g, 50%. ^{1}H NMR (C_6D_6, 22 °C; δ): 0.78 (s, 9 H, CH_2C(CH_3)$_3$); 0.78 3.40. (d, $^2J_{HH}$ = 14.6 Hz, 1 H each, CH_2(CH_3)$_3$); 1.72, 1.79, 1.93, 2.10, 2.12, 2.82 (s, 3 H each, 3,5-pyrazole methyls); 3.51, 4.40 (d, $^2J_{HH}$ = 6.2 Hz, 1 H each, CH_2NPh); 5.30, 5.50, 5.63 (s, 1 H each, 4-pyrazole protons); 5.61 (d, 1 H, *o*-phenyl ring); 6.66 (overlapped triplets, 2 H, *m*- and *p*-phenyl ring); 7.22 (d, 1 H, *o*-phenyl ring); 7.33 (t, 1 H, *m*-phenyl ring). ^{13}C NMR (δ): 156.0, 153.6, 153.0, 144.5, 144.4, 144.0 (3-, 5-pyrazole carbons); 129.3, 128.2, 122.7, 122.3, 120.2 (phenyl carbons, 1 missing due to overlap); 120.7 (CH_2C(CH_3)$_3$, $^1J_{CH}$ = 112 Hz); 109.1, 108.4, 108.0 (4-pyrazole carbons); 86.2 (CH_2NPh, $^1J_{CH}$ = 162 Hz); 38.0 (CH_2C(CH_3)$_3$); 34.9 (CH_2C(CH_3)$_3$); 34.4, 22.7, 14.2 (C_5H_{12}); 18.1, 15.8, 14.9, 12.8, 12.7, 12.4 (3-, 5-pyrazole methyls). Anal. Calcd for $C_{27}H_{40}ClN_7Ta$: C, 47.76; H, 5.94; N, 14.44. Found: C, 47.31; H, 5.85; N, 14.23.

X-ray Experimental Details. Data were collected at room temperature on a Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). A total of 30 reflections with 20.0° ≤ 2θ ≤ 22.0° were used to refine the cell parameters. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum corrections on *I* was 7%). Empirical absorption corrections were applied using 210 (ψ-scan) reflections (SHELXTL plus[14]). The structure was solved by the heavy-atom method in SHELXTL plus from which the location of the Ta atom was obtained. The rest of the non-hydrogen atoms were obtained from subsequent difference Fourier maps. The structure was refined in SHELXTL plus using full-matrix least squares, and all of the non-H atoms were refined anisotropically. The positions of the H-atoms were calculated in ideal positions, and their isotropic thermal parameters were fixed. The lattice contains a disordered pentane molecule in a ratio of 4:1 complex-to-pentane; the asymmetric unit contains the complex and half a pentane molecule (disordered around a center of inversion) in 50% occupancy. The linear absorption coefficients, scattering factors, and anomalous-dispersion corrections were taken from ref 15.

Results and Discussion

Synthesis and Characterization. The addition of 1 equiv of KTp′ to the Ta neopentylidene complexes, **1**, results in the displacement of one halide and both THF ligands to give the complexes Tp′Ta(CHC(CH_3)$_3$)X$_2$, **2** (X = Cl) and **3** (X = Br), eq 1. These compounds are



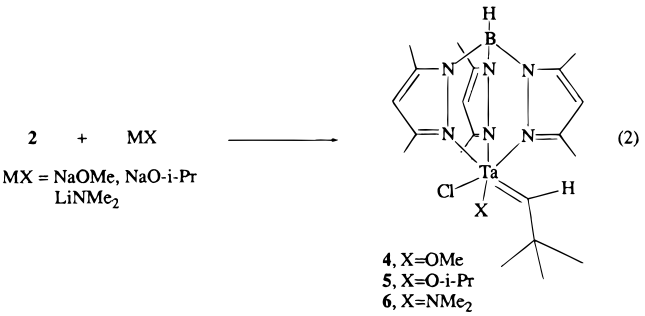
(1)

isolated as purple crystalline materials that are soluble in toluene and diethyl ether. Unlike the related group 6 compounds, they are air sensitive in solution and in the solid state. The proton and carbon NMR spectra are consistent with a pseudooctahedral structure in which a mirror plane renders two of the dimethylpyrazole rings chemically equivalent. These compounds do not react with olefins or acetylenes in the absence of a cocatalyst. In the presence of Al_2Cl_6 they are catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene and cyclooctene. Compounds **2** and **3** react with lithium alkyls, Grignard, or other alkylating agents but do not give tractable products.

(14) Sheldrick, G. M. SHELXTL plus, version 4.21/V, Siemens XRD, Madison, WI, 1990.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 55 (present distributor: D. Reidel, Dordrecht, The Netherlands.

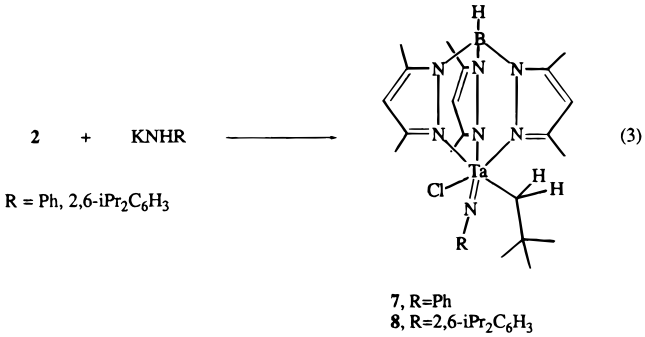
The reaction of **2** with alkoxides or $LiNMe_2$ proceeds with facile displacement of one of the chloride ligands as shown in eq 2. The resulting compounds are yellow,



crystalline materials that are readily soluble in pentane. The ^1H NMR spectra of **4**−**6** display six inequivalent methyl groups and three inequivalent pyrazole ring protons as expected for compounds of the stoichiometry Tp′M(X)(Y)(CHC$(CH_3)_3$). The isopropoxide methyl groups in **5** are diastereotopic as is predicted by the proposed chiral structure. Each of the compounds **2**−**6** has a low-field resonance in the ^{13}C NMR spectrum that appears as a doublet in the gated-decoupled ^{13}C spectrum that is assigned to the alkylidene carbon atom. As discussed in more detail below, the chemical shift of the alkylidene proton and the value of $^1J_{C-H}$ for the alkylidene vary depending upon the nature of the remaining substituents on tantalum.

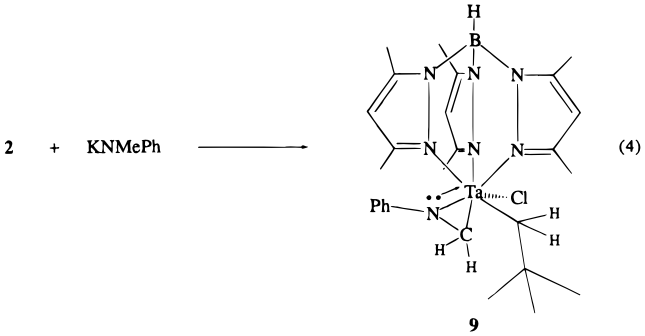
The room-temperature proton NMR spectrum of complex **6** (C_7D_8) has broad resonances at 4.16 and 2.55 ppm that integrate to three protons each and are assigned to the NMe_2 group. When an NMR sample of **6** is warmed to 69 °C, these broad peaks coalesce into one peak at 3.35 ppm indicating that rotation of the NMe_2 group is rapid on the NMR time scale. The two site exchange equation[16] and a coalescence temperature of 342 K can be used to estimate a value for $\Delta G^{\ddagger}$ of 15.4 kcal·mol^{-1} for the rotation of the NMe_2 group in **6**. The observed activation barrier for rotation in **6** is comparable to rotational barriers in other electronically unsaturated dialkylamido complexes[17] and indicates that the NMe_2 group functions as a π donor toward the Ta center.

The reaction between **2** and KNHR (R = Ph, 2,6-*i*-$Pr_2C_6H_3$) does not lead to simple substitution of a chloride ligand. In this case, substitution is followed by α-H transfer from the unobserved amido N−H to the alkylidene carbon atom. The final products of the reaction are the imido neopentyl complexes Tp′Ta(=NAr)Cl(CH_2CMe_3), **7** (R = Ph) and **8** (R = 2,6-*i*-$Pr_2C_6H_3$), eq 3. The reaction proceeds in good yield when R = Ph but in poor yield when R = 2,6-*i*-$Pr_2C_6H_3$. A more efficient synthesis of compound **8** involves the one-pot reaction of **1** with Me_3SiNH(2,6-*i*-$Pr_2C_6H_3$) followed by addition of KTp′ as described in the Experimental Section.



The ^1H NMR spectra of compounds **7** and **8** display inequivalent resonances for the pyrazole rings and a pair of peaks for the diastereotopic protons of the CH_2 groups of the neopentyl ligands as is consistent with six-coordinate, trisubstituted Tp′ complexes. The $^1J_{C-H}$ values of the neopentyl CH_2 groups of 108 and 109 Hz are in the range observed for electronically unsaturated early transition metal alkyl complexes.[18a] Whether or not these values are an average of $^1J_{C-H}$ values of one α-agostic M−C−H interaction and one "normal" $^1J_{C-H}$ is not known at this time. Given that the difference in chemical shifts of the CH_2 protons in the ^1H NMR spectra (2.40 and 0.58 ppm for **8**) may indicate significantly different environments for these protons, the observed $^1J_{C-H}$ of 108 Hz may be a result of time-averaged α-agostic interaction though these data are not in themselves definitive.[18b]

Addition of the bulkier secondary amide KN(Me)Ph to **2** results in the formation of Tp′Ta(η^2-CH_2=NPh)(CH_2-CMe_3)Cl, **9**, eq 4. The η^2-imine group is apparently



formed by transfer of a proton from the methyl group of an *N*-methylanilide complex to the alkylidene carbon atom. The ^1H NMR spectrum of **9** displays resonances due to inequivalent pyrazole rings as well as doublets at 4.40 and 3.51 ppm for the imine methylene protons. The neopentyl methylene protons give rise to a pair of doublets at 3.40 and 0.78 ppm and confirm the lack of symmetry in the molecule. The phenyl protons of the imine appear as four separate peaks between 5.61 and 7.33 ppm. Three of the phenyl peaks are due to a single proton while the fourth is a two proton peak that is a pair of overlapping triplets. This pattern of peaks from the phenyl group is indicative of hindered rotation

(16) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press, Inc.: San Diego, CA, 1988; pp 179−189.

(17) (a) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 2, p 161. (b) Le Ny, J. P.; Youinou, M. T.; Osborn, J. A. *Organometallics* **1992**, *11*, 2413. (c) Perez, P. J.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 7928. (d) Powell, K. R.; Perez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851. (e) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 8613.

(18) (a) Poole, A. D.; Williams, D. N.; Kenwright, A. M.; Gibson, V. C.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A. *Organometallics* **1993**, *12*, 2549. (b) As suggested by a reviewer, the large chemical shift differences and reduced values of $^1J_{C-H\alpha}$ are not in and of themselves completely reliable indicators of α-agostic interactions in early transition metal alkyl complexes as demonstrated in the following reference: Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169.

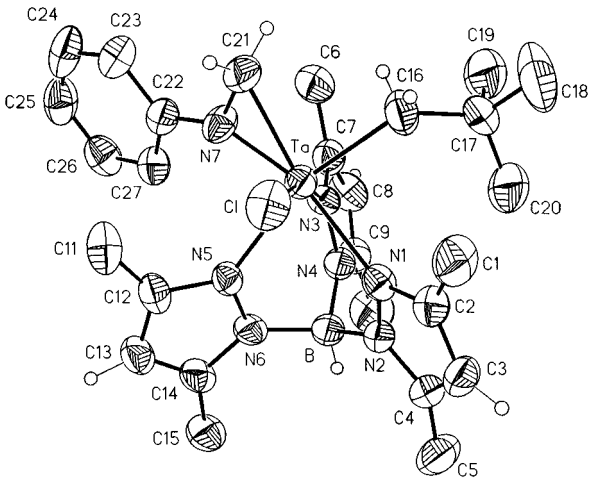


Figure 1. Thermal ellipsoid plot of compound **9**.

caused by the interleaving of the imine phenyl ring with the Tp′ pyrazole rings. The extreme upfield shift of the *ortho* phenyl resonance (5.61 ppm) is undoubtedly caused by the ring currents of the pyrazole groups. This resonance can be assigned to the proton on C27 in the crystal structure of **9**. Extreme shielding of protons that are constrained to occupy positions between the pyrazole rings of polypyrazolyl borate ligands has been previously observed[19] and is consistent with our assignment.

X-ray Crystallography. A single crystal of **9** suitable for an X-ray diffraction study was obtained by cooling a saturated pentane solution of **9** to −20 °C for 2 weeks. A thermal ellipsoid plot of **9** is shown in Figure 1. The data collection parameters are summarized in Table 1, while intramolecular bond lengths and angles are found in Table 2. The structure confirms the presence of an η^2-imine group and that the alkylidene moiety has been transformed into a neopentyl group as indicated by NMR spectroscopy. The coordination geometry is probably best described as a distorted octahedron, with the N atoms of the Tp′ ligand, the midpoint of the imine C−N bond, the Cl, and the neopentyl CH_2 occupying the octahedral positions. The distances between Ta and the N atoms of the Tp′ ligand vary in accord with a *trans* influence of imine > alkyl > Cl.

Even though the geometry of the complex may be best understood in terms of an octahedral structure with an η^2-imine ligand, the bond distances strongly suggest that the η^2-imine ligand adopts an azametallacyclopropane structure.[20] Thus, the Ta−N distance of 1.932(6) Å and the Ta−C21 distance of 2.196(9) Å indicate a highly asymmetric bonding interaction between Ta and the imine ligand. The Ta−N distance indicates considerable multiple bond character suggesting that the N lone pair is engaging in significant π bonding with the Ta as might be expected in an electron-deficient Ta amide complex,[21] while the Ta−C21 distance is identical to the Ta−C16 distance of the alkyl ligand. The N7−C21 distance of 1.360(13) Å suggests considerable C−N single-bond character and is also consistent with an azametallacyclopropane type structure. The geometry of the η^2-imine ligand is also consistent with an azametallacyclopropane type interaction. The phenyl ring is coplanar with Ta−N7−C21, and the bond angles around N7 sum to 360° indicating planarity at N7. The structure of compound **9** is similar to imine complexes of Ti, Zr, Ta, and W that are also best described as azametallacycles that display asymmetric M−C and M−N distances and planar N atoms.[21−24]

Overall, the coordination sphere about the Ta atom is quite congested. The *t*-Bu group of the neopentyl ligand is wedged between two of the pyrazole rings

Table 1. Crystallographic Data for 9

A. Crystal Data (298 K)	
a, Å	10.526(2)
b, Å	12.846(3)
c, Å	13.523(3)
α, deg	89.92(2)
β, deg	67.76(2)
γ, deg	82.85(2)
V, Å^3	1677.3(7)
d_{calc}, g·cm^{-3}	1.402
empirical formula	$C_{27}H_{40}BN_7ClTa\cdot{}^1/_4C_5H_{12}$
fw	707.91
cryst system	triclinic
space group	$P\bar{1}$
Z	2
F(000), electrons	713
cryst size (mm^3)	0.30 × 0.27 × 0.15
B. Data Collection (298 K)	
radiation, *λ* (Å)	Mo Kα, 0.710 73
mode	*ω*-scan
scan range	symmetrically over 1.2° about $K\alpha_{1,2}$ max
bkgd	offset 1.0 and −1.0 in *ω* from $K\alpha_{1,2}$ max
scan rate, deg·min^{-1}	3−6
2*θ* range, deg	3−55
range of *hkl*	$0 \le h \le 13$ $-16 \le k \le 16$ $-17 \le l \le 17$
tot. reflcns measd	8135
unique reflcns	7712
abs coeff *μ*(Mo Kα), cm^{-1}	3.38
min, max transm	0.304, 0.370
C. Structure Refinement	
S, goodness-of-fit	1.33
reflcns used, $I > 2\sigma(I)$	5133
no. of variables	346
R, w*R*,[a]	4.85, 4.89
R_{int}, %	3.07
max shift/esd	0.001
min peak in diff Fourier map, e Å^{-3}	−0.86
max peak in diff Fourier map, e Å^{-3}	2.19

[a] Relevant expressions are as follows, where F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F) + 0.0004F^2]$. $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

(19) (a) Reger, D. L.; Mason, S.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1994**, *33*, 1803. (b) Reger, D. L.; Mason, S.; Reger, L.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1994**, *33*, 1811.

(20) (a) The value of $^1J_{C-H}$ of 161 Hz for the CH_2 group of the imine ligand is also consistent with imine ligand being best described as an azametallacyclopropane and is close to the value of 156 Hz found in cyclopropane.[20b] (b) Silverstein, R. M.; Bassler, G. C.; Morill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley: New York, 1991; p 247.

(21) (a) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579. (b) Chisholm, M. H.; Huffman, J. C.; Tan, L.-S. *Inorg. Chem.* **1981**, *20*, 1859. (c) Chisholm, M. H.; Huffman, J. C.; Tan, L.-S. *J. Am. Chem. Soc.* **1982**, *104*, 4879.

(22) (a) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 7978.

(23) (a) Koschmieder, S. U.; Hussain-Bates, B.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1991**, 2785. (b) Galakov, M. V.; Gomez, M.; Jimenez, G.; Royo, P.; Pellinghelli, M. A.; Tiripiccio, A. *Organometallics* **1995**, *14*, 1901.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Non-H Atoms of Compound 9

1	2	3	1−2	1−2−3
Cl	Ta	N1	2.391(3)	81.4(2)
Cl	Ta	N3		161.53(15)
Cl	Ta	N5		86.4(2)
Cl	Ta	N7		104.2(2)
Cl	Ta	C16		107.4(3)
N1	Ta	N3	2.298(5)	85.3(2)
N1	Ta	N5		77.3(2)
N1	Ta	N7		161.1(3)
N1	Ta	C16		87.2(2)
N1	Ta	C21		160.1(3)
N3	Ta	N5	2.233(8)	78.2(2)
N3	Ta	N7		84.6(3)
N3	Ta	C16		84.5(3)
N3	Ta	C21		111.4(3)
N5	Ta	N7	2.270(6)	84.9(2)
N5	Ta	C16		157.6(3)
N5	Ta	C21		115.6(3)
N7	Ta	C16	1.932(6)	107.8(3)
N7	Ta	C21		37.8(3)
C16	Ta	C21	2.198(8)	83.9(3)
C21	Ta	Cl	2.196(9)	84.3(3)
C21	N7	C22	1.360(13)	127.4(7)
C21	N7	Ta		81.7(4)
C22	N7	Ta	1.423(10)	150.8(6)
C17	C16	Ta	1.526(13)	141.7(7)

causing the N1−Ta−N3 angle to open to 85° (as compared to 77 and 78° for N1−Ta−N5 and N5−Ta−N3). The disposition of the η^2-imine ligand is such that the phenyl substituent lies between the pyrazole rings containing N3 and N5. The observation of restricted rotation about the N7−C22 bond on the NMR time scale at room temperature and the upfield shift of the proton on C27 suggests that the solid-state structure is maintained in solution.

α-Agostic Interactions and π Bonding. The $^1J_{C-H\alpha}$ values for the alkylidene carbon atoms of complexes **2**−**6** are summarized in Table 3 along with two other six-coordinate Ta alkylidene complexes that contain a facial coordinating tridentate ligand.[29] The values are uniformly smaller than would be expected for an "undistorted" alkylidene structure.[25] The extremely low values reported for compounds **2**, **3**, and **6** are essentially identical to the lowest reported values for d^0 alkylidene complexes.[26] The small values of $^1J_{C-H\alpha}$ also correlate well with the chemical shift of the alkylidene proton and suggest that as the coupling constant decreases, the proton is more highly shielded by the metal center. These data indicate the presence of a strong α-agostic interaction between the electronically unsaturated metal center and the alkylidene proton. Infrared spectra of the alkylidene complexes reveal weak absorptions in the 2600−2700 cm^{-1} region and are also consistent with the presence of an α-agostic interaction between the alkylidene α proton and the metal center.[30] We have not yet been able to obtain X-ray diffraction quality single crystals of any of the alkylidenes, but given the small coupling constants, they would be expected to have highly distorted neopentylidene groups with acute Ta−C−H and obtuse Ta=C−C angles.[25] Indeed, the crystal structure of Ta(=CH-*t*-Bu)Cl_2(NCN) (NCN = [*o*-(CH_2-NMe_2)$_2$$C_6H_3$]) has been determined and this compound has a Ta=C−C angle of 170° and a Ta−C−H angle of 71°.[31]

There is also a clear trend in the values of $^1J_{C-H\alpha}$ depending upon the identity of the ancillary ligands in these compounds, with alkoxide complexes **4** and **5** having considerably larger coupling constants than the halide or NMe_2 ligands. This suggests that the α-agostic interaction is stronger in compounds **2**, **3**, and **6** than in the alkoxide derivatives. Given that NMe_2 and OR are both more effective π donors than Cl or Br, it is not simply variation in π donor ability that leads to the observed change in the strength of the α-agostic interaction. The data indicate that the strength of the α-agostic interaction is dependent upon *both* the π donor ability and the number of π donor interactions between the ancillary ligands and the metal center.

Because **2**−**6** are all six-coordinate pseudooctahedral compounds, the complexes will have the usual octahedral σ bonding framework leaving the d_{xy}, d_{xz}, and d_{yz} orbitals available as π acceptor orbitals. One of these orbitals will be involved in the Ta alkylidene π bond freeing the remaining two orbitals for further interactions with the ligands. In the case of the halide ligands, the π donor abilities are not expected to be particularly large, and even though there is potential for a competition between halide π donation and the α-agostic interaction, the agostic interaction dominates and a small $^1J_{C-H\alpha}$ is observed.

The situation in compound **6** and in the alkoxides, **4** and **5**, is not as obvious since both sets of ligands are potent π donors. Idealized orbitals showing the interaction between the amido and alkoxide groups in **4** and **6** are shown in Figure 2. In **6**, the Me_2N and the Ta atom undergo a strong π interaction as is demonstrated by the 15 kcal·mol^{-1} barrier to rotation about the Ta−N bond. The fact that the NMe_2 group has only a single filled p orbital that can interact with the metal center leaves one remaining empty d orbital (d_{xz} in Figure 2) to accommodate an α-agostic interaction between the alkylidene and the metal center. In the case of the alkoxide ligands, the O atom has two lone pairs that are available as π donors. One of these orbitals will, by necessity, be competing with the alkylidene C−H bond for donation into the one remaining empty d orbital (d_{xz} in Figure 2) of Ta. The net result is an attenuated α-agostic interaction and a larger value of $^1J_{C-H\alpha}$ in the alkoxide complexes **4** and **5**.

A similar phenomenon was observed in the complexes Tp′Nb(η^2MeCCPh)(Et)X (X = Cl, OMe).[9c] In this case, an α-agostic interaction was observed between the Et

(24) (a) Durfree, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720. (b) Durfree, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. (c) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486.

(25) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley: New York, 1988.

(26) Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

(27) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (c) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(28) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651.

(29) Abbenhuis, H. C. L.; Rietveld, M. H. P.; Haarman, H. F.; Hogerheide, M. P.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 3259.

(30) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

(31) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; Van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773.

Table 3. Coupling Constant and Chemical Shift Data for Six-Coordinate Alkylidene Complexes with Tridentate Ancillary Ligands[a]

	$^1J_{C-H\alpha}$, Hz	$\delta(^1H_{H\alpha})$, ppm	$\delta(^{13}C)$, ppm	ref
Tp′Ta(=C(H)-*t*-Bu)(Cl)(OMe) (**4**)	95	6.08	256.6	this work
Tp′Ta(=C(H)-*t*-Bu)(Cl)(O-*i*-Pr) (**5**)	92	5.78	251.8	this work
Tp′Ta(=C(H)-*t*-Bu)$(Cl)_2$ (**2**)	73	2.51	248.3	this work
Tp′Ta(=C(H)-*t*-Bu)$(Br)_2$ (**3**)	70	1.88	260.5	this work
Tp′Ta(=C(H)-*t*-Bu)(Cl)(NMe_2) (**6**)[b]	70	1.62	236.9	this work
Ta(=CH-*t*-Bu)$Cl_2(NCN)$[a,c]	78	2.61	253.5	29, 31
Ta(=CHSiMe_3)Cl(O-*t*-Bu)(NCN)[a,c]	111	6.96	238.3	29

[a] C_6D_6 solvent at 25 °C. [b] CD_2Cl_2, 25 °C. [c] NCN = [*o*-$(CH_2NMe_2)_2C_6H_3$].

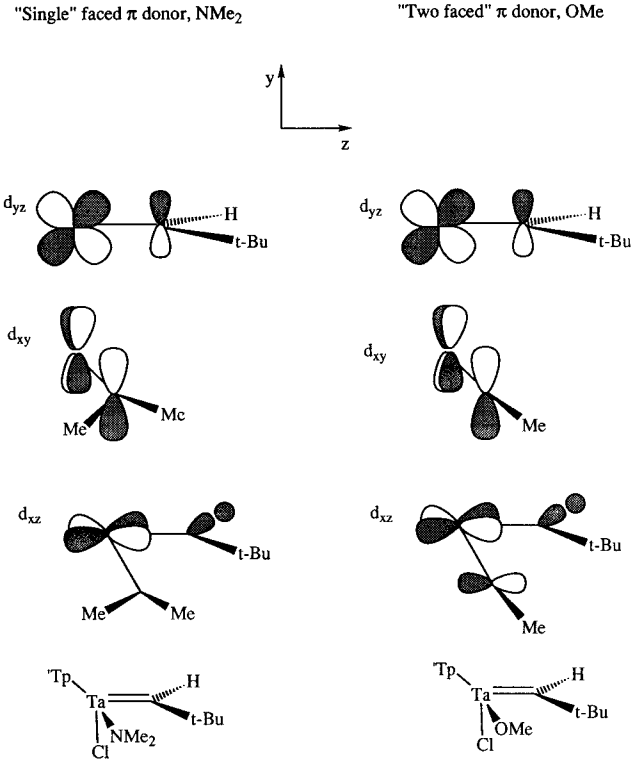


Figure 2. Idealized MO's for the alkylidene and π donor ligand interactions in compounds **6** and **4**.

group and the Nb center when X = Cl. When X = OMe, there was no conclusive evidence for a similar α-agostic interaction, though a weaker α-agostic interaction that was averaged on the NMR time scale could not be ruled out. It was suggested that competition from π-donation from the methoxide ligand weakens the interaction between the metal center and the α-C−H bond.[9c]

It was of interest to determine whether or not the correlation between the number and strength of ancillary π donors and strength of α-agostic interaction is general for other alkylidene complexes. Examination of coupling constant and chemical shift data in six-coordinate Ta alkylidene complexes that contain monodentate ligands reveals a similar (but imprecise) general trend.[30,32] Complexes with more than one efficient π donor interaction have larger values of $^1J_{C-H\alpha}$ and presumably weaker α-agostic interactions. In the monodentate ligand case, the correlation between π donor ability and spectral parameters is not as good as in compounds **2**−**6**. We suspect that the poorer correlation arises because monodentate ligands do not impose as rigid a coordination geometry on the metal center as does the Tp′ ligand. With a less rigid coordination environment, other factors such as ligand sterics or the formation of different isomers will also affect the coupling constants.[30,32]

The reactions between **2** and KN(Me)Ph or KNHAr are related in that they both involve a tautomerization or a rearrangement following halide substitution. In the case of the monosubstituted amides, the tautomerization involves proton migration from N to the alkylidene carbon atom. Presumably, the driving force for this transformation is the formation of a stronger Ta=N interaction at the expense of the Ta=C bond. This type of tautomerization has been observed in the chemistry of group 6 and 7 alkylidene complexes and is usually a base-catalyzed process.[4,27] Such a base-catalyzed process is certainly possible in this case as well, though the experiments to demonstrate this have not been performed. It is interesting to note, however, that because of the electronic unsaturation of the metal center, an intramolecular proton transfer process involving orbitals on the metal is also possible via an α-agostic N−H interaction.

The transfer of a proton from the methyl group of the N(Me)Ph ligand to the alkylidene carbon atom generating an η^2-imine complex, as occurs during the formation of **9**, appears to be more difficult to rationalize. To a first approximation, the formation of **9** from the unobserved amide alkylidene complex involves the breaking and making of one C−H bond, the loss of a Ta−C π bond, and the formation of a Ta−C σ bond. Given that the Ta−N bond in **9** retains a significant π interaction (as judged by the Ta−N bond length), the contribution of the Ta−N π to the bonding should be similar in the two compounds. Viewed from this perspective, the transformation is thermodynamically reasonable since a Ta−C σ bond is expected to be significantly stronger than a Ta−C π bond.

The formation of **9** is similar to the elimination of methane from Cp*Ta$(NMe_2)Me_3$ to generate Cp*Ta(η^2-CH_2=NMe)Me_2.[28] The latter reaction occurs by a unimolecular process and suggests that β-H transfer occurs by a metal-mediated four-center transition state. It is interesting to note that, in order to orient the amido and alkylidene π bonds orthogonal to one another, the preferred alignment of the R groups in any Tp′Ta(NMeR)(X)(=CHR) compound will place the Me group in the same plane as the alkylidene p orbital as shown in Figure 2. It is this alignment of orbitals that will facilitate intramolecular transfer of H from the Me group to the alkylidene.

Summary and Conclusions. The utilization of the sterically demanding Tp′ ligand has resulted in the formation of mononuclear, electronically unsaturated, neopentylidene complexes that display strong α-agostic interactions between the alkylidene C−H bond and the

(32) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.

metal center. The strength of the α-agostic interaction depends upon the ability of the remaining ligands to function as π donors. When weak π donor ligands, *i.e.* halides, are present, the alkylidene C−H bond competes for the vacant metal orbital and a strong α-agostic interaction ensues. If there is one e^- pair that is an effective π donor, *i.e.* NMe_2, a strong α-agostic interaction is still possible, because there is one remaining empty metal orbital that can accommodate the α-agostic interaction. When there are two e^- pairs that are effective π donors, as in the alkoxide complexes, **4** and **5**, competition for the vacant metal orbitals by the alkoxide ligand weakens the α-agostic interaction.

The observation of hindered rotation about the Ph−N single bond in compound **9** which adopts a conformation in which the phenyl ring of the azametallacycle is wedged between the pyrazole rings demonstrates the bulkiness of the Tp′ ligand. The steric influence of Tp′ also tends to shield the Ta atom from attack by external reagents thereby stabilizing the compounds by impeding further chemical reactivity such as nucleophilic substitution or olefin metathesis reactions. Thus, despite the electronic unsaturation, the range of clean chemical transformations observed in these complexes is somewhat limited.

Acknowledgment. We wish to acknowledge the National Science Foundation (Grant DMR9207358) for the support of this work. We also wish to thank a reviewer for bringing the work in ref 19 to our attention.

Supporting Information Available: Tables of bond lengths and angles and positional and thermal parameters (7 pages). Ordering information is given on any current masthead page.

OM950836O