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# Synthesis of tantalum and niobium complexes that contain the diamidoamine ligand, $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]^{2-}$ , and the triamidoamine ligand, $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$

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Dedicated to Professor Dr. Dr. h.c. mult. Wolfgang A. Herrmann.

#### Abstract

Several niobium and tantalum compounds were prepared that contain either the diamidoamine ligand,  $[(3,4,5-F_3C_6H_2N-CH_2CH_2)_2NMe]^{2-}$  ( $[F_3N_2NMe]^{2-}$ ), or the triamidoamine ligand,  $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$  ( $[Cl_2N_2NMe]^{3-}$ ). The former include  $[F_3N_2NMe]TaCl_3$ ,  $[F_3N_2NMe]NbCl_3$ ,  $[F_3N_2NMe]TaMe_3$ ,  $[F_3N_2NMe]NbMe_3$ ,  $[(F_3N_2NMe)TaMe_2][MeB(C_6F_5)_3]$ ,  $[F_3N_2NMe]Ta(CHSi-Me_3)(CH_2SiMe_3)$ ,  $[F_3N_2NMe]Ta(CH_2-t-Bu)Cl_2$ ,  $[F_3N_2NMe]Ta(CH-t-Bu)(CH_3)$ , and  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$ . The latter include  $[Cl_2N_2NMe]TaCl_2$ ,  $[Cl_2N_2NMe]TaMe_2$ ,  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)$ , and  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$ . The latter include  $[Cl_3N_2NMe]Ta(CHSiMe_3)(CH_2SiMe_3)$ ,  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)$ , and  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_2)$ .X-ray diffraction studies were carried out on  $[F_3N_2NMe]Ta(CHSiMe_3)(CH_2SiMe_3)$ ,  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$ , and  $[Cl_2N_2NMe]TaMe_2$ . © 2006 Elsevier B.V. All rights reserved.

Keywords: Tantalum; Niobium; Amide; Alkylidene

#### 1. Introduction

In the last several years various multidentate amido ligands have helped uncover much new chemistry involving metals in groups 4, 5, and 6 [1,2]. We have focused on triamidoamine [3] ligands for metals in group 5 and group 6 and diamido/donor ligands primarily for metals in group 4 [4,5], but also to some extent for metals in group 5 and group 6 [6–9]. We have been attracted to ligands that contain aryl substituents on the amido nitrogens, especially aryls that are not as electron-withdrawing as pentafluorophenyl and that have no ortho substituents that can lead to side reactions or other complications. Examples are sterically demanding 3,5-terphenyl groups in triamidoamine ligands [10] and 3,5-dichlorophenyl [9] and 3,4,5-trifluorophenyl groups [8] groups in diamidoamine ligands. We have published only two papers that concern diamido/ donor ligands on tantalum [9,11]. We report here an exploration of d<sup>0</sup> niobium and tantalum complexes that contain the electron-withdrawing ligands  $[(3,4,5-F_3C_6H_2NCH_2-CH_2)NMe]^{2-}$  or  $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$  complexes.

We undertook this investigation with an interest primarily in alkylidene and olefin complexes, and the possibility that an olefin could be induced to rearrange to an alkylidene. The first reported reaction of this type was conversion of [(Me<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) to [(Me<sub>3</sub>SiNCH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>N]Ta(CHMe) in the presence of catalytic amount of PhPH<sub>2</sub> [12,13]. It was proposed that PhPH<sub>2</sub> attacked [(Me<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) to yield intermediate [(Me<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(CH<sub>2</sub>CH<sub>3</sub>)(PHPh), which then decomposed to yield [(Me<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(CHMe) and PhPH<sub>2</sub>. The strong agostic interaction in [(Me<sub>3</sub>-SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(CHMe) was proposed to be the reason why the ethylidene was favored over the ethylene complex. Wolczanski and coworkers published an extensive study of

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the rearrangement of olefins in  $(t-Bu_3SiO)_3M$  (olefin) (M = Nb or Ta) complexes to yield the tautomeric alkylidene complexes [17]. In the  $(t-Bu_3SiO)_3M$  (olefin) systems the intermediate is also proposed to be an alkyl, but one formed as a consequence of CH activation of a methyl group in the Silox ligand. Although we have not yet observed olefin to alkylidene rearrangement in the new Nb and Ta complexes that we prepared, they nevertheless are inherently interesting examples of d<sup>0</sup> Nb and Ta complexes that contain relatively robust multidentate amido ligands.

# 2. Experimental

#### 2.1. General

All air-sensitive work was carried out in a Vacuum Atmospheres dry box under a dinitrogen atmosphere or by standard Schlenk techniques. Chemicals were purchased from Strem Chemicals, Inc., or Aldrich. Solid reagents were used as received unless otherwise stated. Liquid reagents were distilled from CaH<sub>2</sub> under dinitrogen. Diethyl ether, pentane, toluene, benzene and tetrahydrofuran (THF) were sparged with dinitrogen and passed through columns of activated alumina. Dichloromethane was distilled from calcium hydride. All deuterated solvents were freeze-pump-thaw degassed. All listed solvents were stored over 4 Å molecular sieves. <sup>1</sup>H NMR spectra were obtained on an instrument operating at 300 MHz unless otherwise stated. <sup>13</sup>C NMR spectra were obtained on an instrument operating at 125 MHz, while <sup>19</sup>F NMR spectra were obtained on a 282 MHz instrument. All spectra were recorded at or near 22 °C. <sup>1</sup>H and <sup>13</sup>C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent resonance. <sup>19</sup>F NMR shifts are reported relative to  $C_6F_6$  used as an external reference. Microanalyses were performed by Kolbe Microanalytical Laboratories (Mühlheim an der Ruhr, Germany). TaCl<sub>2</sub>Me<sub>3</sub> [14] and  $H_2[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]$  [8] were prepared as reported in the literature.

# 2.2. Syntheses

# 2.2.1. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]TaCl_3$

TaCl<sub>5</sub> (1.90 g, 5.30 mmol) was added in portions to a cold (-30 °C) solution of H<sub>2</sub>[(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-NMe] (2.00 g, 5.30 mmol) in 25 mL of dichloromethane. To the resulting orange suspension was added 2.2 equiv. of triethylamine (1.63 mL, 11.7 mmol). The reaction mixture was left to stir for 5 h. The volatiles were removed in vacuo and the residue was dissolved in 30 mL of THF. The resulting red-orange suspension was then allowed to cool to -30 °C for 15 min to ensure complete precipitation of triethylammonium chloride. The mixture was then filtered through a bed of Celite. The filtrate was collected and concentrated to 5–10 mL in vacuo, at which point bright orange microcrystals formed in the solution. The solids were collected on a frit, washed with pentane, and dried in vacuo to

give 2.59 g (74%) of orange crystals. The product could be recrystallized from THF or dichloromethane. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.17 (m, 4), 4.14 (m, 2), 3.56 (q, 2), 3.12 (m, 2), 2.09 (s, 3), 1.80(q, 2). <sup>19</sup>F NMR:  $\delta$  –129 (dd, 4), –157 (tt, 2). *Anal.* Calc. for TaN<sub>3</sub>F<sub>6</sub>Cl<sub>3</sub>C<sub>17</sub>H<sub>15</sub>: C, 30.81; H, 2.28; N, 6.34; Cl, 16.05. Found: C, 30.48; H, 2.28; N, 6.26; Cl, 15.96%.

# 2.2.2. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]NbCl_3$

A cold  $(-30 \degree C)$  solution of H<sub>2</sub>[(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>NMe] (2.00 g, 5.30 mmol) in 10 mL toluene was added to a rapidly stirred slurry of NbCl<sub>5</sub> (1.43 g, 5.30 mmol) in 15 mL of toluene. To the resulting orange suspension was added 2.2 equiv. of triethylamine (1.63 mL, 11.7 mmol). The reaction mixture was then heated to 80 °C and left to stir for 6 h. The toluene was removed in vacuo and the residue was dissolved in 50 mL of THF. The resulting red-orange suspension was then allowed to cool to -30 °C for 15 min to ensure complete precipitation of triethylammonium chloride. The mixture was then filtered through a bed of Celite. The filtrate was collected and concentrated to 5-10 mL in vacuo, at which point brick red microcrystals crashed out of solution. The solids were collected on a frit, washed with pentane, and dried in vacuo to give 2.4 g (80%) of the brick red product. The product could be recrystallized from THF: <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  7.26 (m, 4), 3.87 (m, 2), 3.25 (m, 4), 2.08 (s, 3), 1.77 (q, 2); <sup>19</sup>F NMR:  $\delta$  –129 (dd, 4), –155 (tt, 2). Anal. Calc. for NbN<sub>3</sub>F<sub>6</sub>Cl<sub>3</sub>C<sub>17</sub>H<sub>15</sub>: C, 35.54; H, 2.63; N, 7.31; Cl, 18.15. Found: C, 35.63; H, 2.56; N, 7.41; Cl, 18.22%.

# 2.2.3. $[3,4,5-F_3C_6H_2N(CH_2CH_2)_2NMe]TaMe_3$

To a cooled (-30 °C) suspension of 250 mg of  $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]TaCl_3$  (0.380 mmol) in 10 mL diethyl ether was added 3.3 equiv. of methylmagnesium chloride (1.2 mmol, 0.42 mL, 3.0 M in THF). The suspension was allowed to warm at room temperature as it was stirred, during which time the color changed from orange to bright yellow. After 1 h, 1,4-dioxane (0.30 mL) was added. The mixture was filtered through Celite, and the filtrate was concentrated to dryness in vacuo. The yellow residue was rinsed with pentane (15 mL) and dried in vacuo to yield a yellow powder; yield 0.14 g (60%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.37 (m, 4), 3.05 (m, 2), 2.13 (q, 2), 1.93 (s, 3), 1.79 (q, 2), 0.93 (s, 9). <sup>19</sup>F NMR:  $\delta$  –131 (dd, 4), –164 (tt, 2). *Anal.* Calc. for TaN<sub>3</sub>F<sub>6</sub>C<sub>20</sub>H<sub>24</sub>: C, 39.95; H, 4.02; N, 6.99. Found: C, 40.06; H, 3.95; N, 6.87%.

# 2.2.4. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]NbMe_3$

To a suspension of 200 mg (0.348 mmol) of  $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]NbCl_3$  in 10 mL of ether was added dropwise 1.2 mL (1.2 mmol, 3.3 equiv.) of 1.0 M methylmagnesium chloride in diethyl ether. The mixture was allowed to warm to room temperature and stir for 60 min. To the resulting dark red brown solution was added 0.24 mL 1,4-dioxane. The resulting suspension was filtered through Celite and diethyl ether was removed from the filtrate in vacuo. The product was obtained as maroon powder in 61% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.29 (m, 4), 3.08 (m, 2), 2.18 (m, 2), 1.93 (s, 3), 1.80 (q, 2), 1.48 (bs, 9). <sup>19</sup>F NMR:  $\delta$  -131 (dd, 4), -164 (tt, 2). *Anal.* Calc. for NbN<sub>3</sub>F<sub>6</sub>C<sub>20</sub>H<sub>24</sub>: C, 46.80; H, 4.71; N, 8.19. Found: C, 46.94; H, 4.68; N, 8.08%.

# 2.2.5. $\{[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]TaMe_2\}-$ [ $MeB(C_6F_5)_3$ ]

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (170 mg, 0.333 mmol) was added to cooled (-30 °C) solution of 200 mg [(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-NMe]TaMe<sub>3</sub> (0.333 mmol) in 5 mL dichloromethane. The mixture was allowed to warm to room temperature while it was stirred. After 15 min, the solvent was removed in vacuo. The residue was triturated with pentane and filtered off and dried in vacuo to give a pale yellow powder in quantitative yield (363 mg). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.13 (m, 4), 4.72 (m, 2), 4.33 (m, 2), 3.61 (q, 4), 2.65 (s, 3, NMe), 1.35 (s, 3, TaMe), 1.15 (s, 3, TaMe), 0.468 (broad s, 3, BMe). <sup>19</sup>F NMR: -126.35 (dd, 4), -129.65 (d, 6), -154.32 (tt, 2), -161.48 (t, 3), -164.17 (t, 6). Anal. Calc. for TaN<sub>3</sub>F<sub>21</sub>BC<sub>38</sub>H<sub>24</sub>: C, 40.99; H, 2.17; N, 3.77. Found: C, 41.11; H, 2.21; N, 3.73%.

# 2.2.6. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]$ - $Ta(CHSiMe_3)(CH_2SiMe_3)$

Trimethylsilylmethylmagnesium chloride (1.00 mL)0.997 mmol) was added dropwise to a stirred suspension of [(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe]TaCl<sub>3</sub> (200 mg, 0.302 mmol) in 10 mL of diethyl ether at -30 °C. The reaction mixture slowly turned vellow-orange. After 60 min, 0.24 mL (3.0 mmol) of 1,4-dioxane was added. The mixture was stirred for an additional 10 min and filtered. The solid was rinsed with  $(3 \times 2 \text{ mL})$  ether. The filtrate was concentrated to dryness in vacuo. The oily yellow-orange residue was dissolved in 5-10 mL toluene and the solution was heated to 50 °C for 3 h. Volatile components were then removed in vacuo. The residue was triturated with pentane (5 mL), and the solid was filtered off, rinsed with pentane (5 mL), and dried in vacuo to yield a yellow powder; yield 0.15 g (67% yield). X-ray quality crystals were grown from toluene at -30 °C over a period of two days. <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  7.05 (m, 4), 5.82 (s, 1), 3.22 (m, 2), 2.93 (q, 2), 2.23 (q, 2), 1.77 (q, 2), 1.28 (s, 3), 0.28 (s, 2), -0.007 (s, 9), -0.19 (s, 9); <sup>19</sup>F NMR:  $\delta$  -134 (dd, 4), -169 (tt, 2). <sup>1</sup>H-coupled <sup>13</sup>C NMR: 243 (d,  $J_{CH} = 97$ ), 155 (s), 151 (d), 135 (d), 105 (d), 60 (t), 58 (t), 54 (t), 37 (q), 3.5 (q), 3.3 (q). Anal. Calc. for TaN<sub>3</sub>F<sub>6</sub>Si<sub>2</sub>C<sub>25</sub>H<sub>36</sub>: C, 41.15; H, 4.97; N, 5.76. Found: C, 41.23; H, 5.06; N, 5.78%.

## 2.2.7. [(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe]Ta(CH<sub>2</sub>-t-Bu)Cl<sub>2</sub>

To a cooled suspension of 250 mg (0.380 mmol) [(3,4,5- $F_3C_6H_2NCH_2CH_2$ )<sub>2</sub>NMe]TaCl<sub>3</sub> in 10 mL ether was added 0.31 mL of 4.0 M neopentylmagnesium chloride (in diethyl ether; 1.2 mmol). The mixture was allowed to warm to room temperature and was stirred for 3 h. 1,4-Dioxane (0.30 mL) was added and the mixture was left to stir for 10 more minutes before it was filtered through Celite.

The yellow residue was washed with diethyl ether. The filtrate was collected and the solvent was removed in vacuo. The residue was triturated with 3 mL of pentane and the solid was collected on a frit, washed with  $(3 \times 2 \text{ mL})$  pentane, and dried in vacuo; yield 0.121 g (46%) of a yellow powder. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.22 (m, 4), 3.92 (m, 2), 3.60 (q, 2), 2.80 (m, 2), 2.16 (s, 2), 1.95 (s, 3), 1.60 (q, 2), 0.61 (s, 9). <sup>19</sup>F NMR:  $\delta$  –130 (dd, 4), –158 (tt, 2). *Anal.* Calc. for TaN<sub>3</sub>F<sub>6</sub>Cl<sub>2</sub>C<sub>22</sub>H<sub>26</sub>: C, 37.84; H, 3.75; N, 6.02; Cl, 10.15. Found: C, 38.05; H, 3.68; N, 5.88; Cl, 10.25%.

#### 2.2.8. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]$ -Ta(CH-t-Bu)(CH<sub>3</sub>)

Methylmagnesium chloride (0.13 mL, 3.0 M in THF, 0.38 mmol) was added dropwise to a stirred suspension  $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]Ta(CH_2-t-Bu)Cl_2$ of (120 mg, 0.174 mmol) in 3 mL diethyl ether at -30 °C. The reaction mixture slowly became yellow-brown over a period of 1 h. 1,4-Dioxane (0.20 mL) was added and the mixture was stirred for an additional 10 min. The mixture was filtered and the solid was rinsed with ether  $(3 \times 2 \text{ mL})$ . The filtrate was concentrated to dryness and the residue was triturated with pentane (5 mL). The solid was filtered off, rinsed with pentane (5 mL), and dried in vacuo to yield a pale yellow powder; 81 mg (73% yield). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  6.90 (m, 4), 3.30 (m, 2), 2.83 (m, 2), 2.40 (s, 1), 2.14 (m, 2), 1.75 (m, 2), 1.32 (s, 3), 0.72 (s, 9), 0.49 (s, 3); <sup>19</sup>F NMR:  $\delta$  –134 (dd, 4), 169 (tt, 2). <sup>1</sup>H-coupled <sup>13</sup>C NMR:  $\delta$  242 (d,  $J_{CH} = 90$ ), 178 (s), 151(d), 135 (d), 105 (d), 58 (t), 54 (t), 45 (s), 40 (t), 34 (q), 33 (q). Anal. Calc. for TaN<sub>3</sub>F<sub>6</sub>C<sub>23</sub>H<sub>28</sub>: C, 43.07; H, 4.40; N, 6.55. Found: C, 42.88; H, 4.38; N, 6.45%.

# 2.2.9. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]$ - $Ta(CH-t-Bu)(CH_2-t-Bu)$

To a cooled suspension of 250 mg (0.380 mmol) [(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe[TaCl<sub>3</sub> in 10 mL ether was added 0.31 mL of 4.0 M neopentylmagnesium chloride (in ether) (1.2 mmol). The mixture was allowed to warm to room temperature and was stirred for 6 h. 1,4-Dioxane (0.20 mL) was added and the mixture was left to stir for 10 more minutes before being filtered through Celite. The yellow residue was washed with ether (5 mL). The filtrate was collected and the ether was removed in vacuo. The residue was triturated with 3 mL pentane and the solid was collected on a frit, washed with pentane  $(3 \times 2 \text{ mL})$ , and dried in vacuo to give 0.57 g (22%) of a yellow powder. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  6.73 (m, 4), 3.13 (m, 2), 2.95 (m, 2), 2.12 (m, 2), 1.83 (m, 2), 1.80 (s, 3), 1.35 (s, 9), 0.82 (s, 2), 0.75 (s, 9), 0.39 (s, 1);  $^{19}$ F NMR:  $\delta - 134$  (dd, 4), 168 (tt, 2). <sup>1</sup>H-coupled <sup>13</sup>C NMR:  $\delta$ 228 (d,  $J_{CH} = 74$ ), 157 (s), 151 (d), 136(d), 107 (d), 67 (t), 66 (t), 46 (s), 45 (q), 38 (s), 36 (t), 35 (q), 33 (q).

# 2.2.10. $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]$ - $Ta(\eta^2-CH_2CH_2)(CH_2CH_3)$

Ethylmagnesium bromide (1.00 mL, 0.997 mmol) was added dropwise to a stirred solution of 200 mg of  $[(3,4,5-F_3C_6H_2NCH_2CH_2)_2NMe]TaCl_3$  (0.302 mmol) in

10 mL of THF at -30 °C. The bright orange solution immediately became pale orange, then slowly turned red-orange as more ethylmagnesium bromide was added. The mixture was allowed to warm to room temperature as it was being stirred. After 2 h, all solvents were removed in vacuo. Diethyl ether (10 mL) was added to the brown residue, followed by 0.20 mL of 1,4-dioxane. The mixture was stirred for 10 more minutes and filtered. The solid was rinsed with diethyl ether  $(3 \times 2 \text{ mL})$ and the brown filtrate was concentrated to dryness in vacuo. The brown residue was triturated with 3 mL pentane and the solid was collected on a frit, rinsed with  $(3 \times 2 \text{ mL})$  pentane, and dried in vacuo to give 91 mg of brown powder which is  $\sim 80\%$  pure by NMR. <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  5.98 (m, 4), 3.31 (m, 2), 2.61 (m, 4), 2.35 (s, 3), 2.05 (m, 2), 1.81 (q, 2), 1.69 (t, 3), 1.53 (s, 4). <sup>19</sup>F NMR:  $\delta$  -131 (dd, 4), 164 (tt, 2). <sup>1</sup>H-coupled <sup>13</sup>C NMR:  $\delta$  151 (d), 145 (s), 137 (d), 105 (d), 67 (t), 56 (t), 55 (t), 54(t), 48 (q), 13 (q).

#### 2.2.11. $H_3[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]$

The dichloromethane and hexane used in this reaction were analytical grade and used as obtained from the supplier. The Pd catalyst was pre-formed by dissolving 1.5 g (2.4 mmol) rac-BINAP in 80 mL toluene with vigorous stirring and heating. Pd<sub>2</sub>DBA<sub>3</sub> (0.82 g, 0.90 mmol) was added to the solution, the solution was stirred for 60 min, and the mixture was filtered to remove Pd(0). The red-orange solution was then added to a 350-mL Schlenk tube charged with 8.77 g (60.0 mmol) (H<sub>2</sub>N-CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N, 1-bromo-3,5-dichlorobenzene (40.7 g, 180 mmol), sodium tert-butoxide (20.2 g, 210 mmol) and 150 mL toluene. The reaction mixture was heated to 90 °C under a dinitrogen atmosphere for 16 h. The mixture was then cooled to room temperature and filtered through Celite, and volatiles were removed from the filtrate on a rotary evaporator. The resulting brown residue was taken up in 100 mL of dichloromethane. The solution was washed with water  $(2 \times 100 \text{ mL})$  and saturated NaCl solution  $(2 \times 100 \text{ mL})$  and dried over MgSO<sub>4</sub>. MgSO<sub>4</sub> was filtered off, and the filtrate was concentrated in vacuo to leave a red-brown oil. The oil was redissolved in 100 mL dichloromethane and 100 mL hexane was added. The flask was stored at 0 °C for several days over which time solids formed. Two crops of pale yellow powder were obtained to give a combined yield of 17 g (50%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  6.78 (t, 3), 6.21 (d, 6), 3.52 (t, 3), 2.32 (q, 6), 1.90 (t, 6). Anal. Calc. for C<sub>24</sub>H<sub>24</sub>Cl<sub>6</sub>N<sub>4</sub>: C, 49.60; H, 4.16; Cl, 36.60; N, 9.64. Found: C, 49.65; H, 4.21; Cl, 36.56; N, 9.49%.

# 2.2.12. $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]TaCl_2$

To a rapidly stirred suspension of TaCl<sub>5</sub> (1.23 g, 3.44 mmol) in 100 mL dichloromethane at -30 °C was added (in portions) 2.00 g of solid H<sub>3</sub>[(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]. The mixture, which turned orange immediately, was stirred for 15 min before adding 2.4 mL

(17 mmol) of triethylamine. The resulting deep red-orange mixture was left to stir at room temperature for 16 h. The volatiles were removed in vacuo and the residue was taken up in 50 mL THF. The suspension was cooled to -30 °C before filtering off the triethylammonium chloride. The deep red filtrate was then concentrated until the volume was 5–10 mL. The solids that precipitated out of solution was collected on a frit, washed with diethyl ether (10 mL) and pentane (10 mL), and dried in vacuo. The product was obtained as brick red microcrystals (1.8 g) in 70% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.04 (d, 6), 6.83 (t, 3), 3.47 (t, 6), 2.26 (t, 6). *Anal.* Calc. for C<sub>24</sub>H<sub>21</sub>N<sub>4</sub>Cl<sub>8</sub>Ta: C, 34.73; H, 2.55; Cl, 34.17; N, 6.75. Found: C, 34.51; H, 2.64; Cl, 34.05; N, 6.73%.

#### 2.2.13. $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]Ta(C_2H_4)$

Method A: Ethylmagnesium chloride (0.38 mL, 2.0 M in THF) was added dropwise to a cooled ( $-30 \,^{\circ}$ C) solution of 300 mg (0.361 mmol) [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]TaCl<sub>2</sub> in 10 mL THF. The reaction mixture was stirred for 6 h at room temperature. All volatiles were then removed in vacuo. The product was taken up in 5 mL toluene and the solution filtered through a bed of Celite. The filtrate was concentrated to dryness, and the red brown residue was triturated within pentane, collected on a frit, and dried in vacuo. The product was obtained as an orange-brown powder in 84% yield (240 mg).

Method B: A solution of 100 mg (0.172 mmol)  $H_2[(3.5 Cl_2C_6H_3NCH_2CH_2)_3N$  in 3 mL toluene was cooled to -30 °C, and 61.6 mg (0.172 mmol) of TaCl<sub>5</sub>was added. The reaction mixture was stirred for 15 min at room temperature and cooled to -30 °C. Ethylmagnesium chloride (0.44 mL, 2.0 M in diethyl ether) was then added dropwise. The reaction mixture was stirred for 6 h at room temperature. The resulting deep red-brown mixture was filtered through Celite, and the filtrate was concentrated to dryness. The residue was triturated with pentane and the solids were collected on a frit and dried in vacuo to give 108 mg (80% yield) of orange-brown powder. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.84 (t, 3), 6.57 (d, 6), 3.29 (t, 6), 2.28 (t, 6), 1.66 (s, 4). <sup>1</sup>H-coupled <sup>13</sup>C NMR:  $\delta$  157 (s), 135 (m), 124 (dt), 123 (dt), 73 (t,  $J_{CH} = 143$ ), 58 (t), 54 (t). Anal. Calc. for TaN<sub>4</sub>Cl<sub>6</sub>C<sub>26</sub>H<sub>25</sub>: C, 39.67; H, 3.20; Cl, 27.02; N, 7.12. Found: C, 39.38; H, 3.24; Cl, 27.18; N, 6.97%.

### 2.2.14. $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]TaMe_2$

Method A: To a cooled (-30 °C) suspension of 100 mg (0.120 mmol) [ $(3,5\text{-}Cl_2C_6H_3NCH_2CH_2)_3N$ ]TaCl<sub>2</sub> in 3 mL toluene was added 2.1 equiv. of MeMgCl (0.08 mL, 3 M in THF). The reaction mixture was allowed to warm to room temperature as it was stirred, during which time it changed from a brick-red to a brown-yellow color. After 60 min, the mixture was filtered through Celite, and the filtrate was then taken to dryness in vacuo. The residue was rinsed with diethyl ether (3 × 2 mL) and pentane

 $(3 \times 2 \text{ mL})$ , then dried to give 75 mg of bright yellow powder in 79% yield.

Method B: A solution of 100 mg (0.172 mmol)  $H_3[(3.5 Cl_2C_6H_3NCH_2CH_2)_3N$  in 3 mL toluene was cooled to -30 °C, and 61.6 mg (0.172 mmol) TaCl<sub>5</sub> was added. The reaction mixture was stirred for 15 min at room temperature then cooled to -30 °C. Methyl lithium (0.63 mL, 1.4 M in diethyl ether) was added dropwise to the reaction mixture, which was then left to stir at room temperature for 60 min. The resulting suspension of dark precipitate in a vellow-brown liquid was filtered through Celite, and the filtrate was concentrated to dryness. The residue was triturated with pentane, collected on a frit, and dried in vacuo to give 88 mg (65% yield) of yellow powder. Single crystals suitable for X-ray diffraction were grown from concentrated toluene solution at -30 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 6.90 (t, 3), 6.80 (d, 6), 3.22 (t, 6), 2.09 (t, 6), 1.23 (s, 6). Anal. Calc. for TaN<sub>4</sub>Cl<sub>6</sub>C<sub>26</sub>H<sub>27</sub>: C, 39.57; H, 3.45; N, 7.10. Found: C, 39.46; H, 3.41; N, 7.16%.

#### 2.2.15. $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]Ta(\eta^2-C_2H_2)$

To a rapidly stirred solution of [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>N]TaCl<sub>2</sub> (100 mg, 0.120 mmol) in 10 mL THF (-30 °C) was added dropwise 0.25 mL of vinylmagnesium bromide (0.25 mmol, 1.0 M in THF). After stirring the mixture for 3 h, 0.25 mL of 1,4-dioxane was added, and the reaction mixture was allowed to stir for additional 15 min. The volatile components were removed in vacuo and the residue was taken up in 5 mL toluene. The solution was filtered through Celite and the filtrate was concentrated to dryness. The residue was triturated in 3 mL pentane, collected on frit, and dried to give the product in 68% yield (64 mg). <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  11.90 (s, 2), 6.82 (t, 3), 6.53 (d, 6), 3.25 (t, 6), 2.23 (t, 6). <sup>1</sup>H-coupled <sup>13</sup>C NMR:  $\delta$  226 (d,  $J_{\rm CH} = 181$  Hz), 161 (s), 135 (t), 123 (dt), 123 (dt), 57 (t), 53 (t).

#### 3. Results and discussion

3.1. Complexes that contain the  $[(3,4,5-F_3C_6H_2NCH_2CH_2)NMe]^{2-}$  ligand

Reduction of  $(C_6F_5NHCH_2CH_2)_2NMe$  with LiAlH<sub>4</sub> produces  $(3,4,5-F_3C_6H_2NHCH_2CH_2)_2NMe$   $(H_2[F_3NMe])$ in good yield [8]. The reaction between  $H_2[F_3N_2NMe]$ and TaCl<sub>5</sub> in the presence of triethylamine in dichloromethane at room temperature gave  $[F_3N_2NMe]TaCl_3$  as bright orange microcrystals (Eq (1)). The presence of only two resonances at -129 ppm and -157 ppm in the <sup>19</sup>F NMR spectrum in  $C_6D_6$  and the sharp multiplet in the aromatic region of the <sup>1</sup>H NMR spectrum are consistent with equivalent, rapidly rotating trifluorophenyl rings. On the basis of an X-ray structure of  $[(3,5-C_6Cl_2H_3NCH_2-CH_2)_2NMe]TaMe_3$  [9], we assume that the ligand adopts (approximately) the *mer* configuration, as shown in Eq (1). The analogous niobium species,  $[F_3N_2NMe]NbCl_3$ , could be synthesized similarly and isolated as brick-red microcrystals



The reaction between  $[F_3N_2NMe]TaCl_3$  and 3.3 equiv. of methylmagnesium chloride afforded the trimethyl species,  $[F_3N_2NMe]TaMe_3$ . An alternate route to  $[F_3N_2NMe]$ -TaMe\_3 consists of the reaction between K<sub>2</sub>[F<sub>3</sub>N<sub>2</sub>NMe] and TaCl<sub>2</sub>Me<sub>3</sub> [14], as shown:



<sup>1</sup>H NMR spectrum The room temperature of [F<sub>3</sub>N<sub>2</sub>NMe]TaMe<sub>3</sub> reveals that the methyl ligands are magnetically equivalent on the <sup>1</sup>H NMR timescale, giving rise to a singlet at 0.93 ppm in toluene- $d_8$ . At -80 °C the methyl ligands are all distinguishable as singlet resonances at 1.45, 0.97, and 0.61 ppm, similar to what has been observed in [(C<sub>6</sub>F<sub>5</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe]TaMe<sub>3</sub> [11] and  $[(3,5-Cl_2C_6H_3NCH_2CH_2)_2NMe]TaMe_3$ [9]. At -50 °C only two resonances are observed at 1.15 and 0.59 ppm with relative areas of 6:3. Therefore, we propose that [F<sub>3</sub>N<sub>2</sub>NMe]TaMe<sub>3</sub> assumes the mer configuration at low temperatures, as shown in Eq. (2), and that two of the three methyl groups equilibrate before all three become equivalent on the NMR time scale. Details of the equilibration process are not known and we cannot rule out dissociation of the amine donor to give a fluxional five-coordinate intermediate. [F<sub>3</sub>N<sub>2</sub>NMe]TaMe<sub>3</sub> is relatively stable at room temperature, unlike [(C<sub>6</sub>F<sub>5</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH]TaMe<sub>3</sub> [11], which evolves methane even in the solid state to give the triamido complex, [(C<sub>6</sub>F<sub>5</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N]TaMe<sub>2</sub>.

The analogous niobium compound,  $[F_3N_2NMe]NbMe_3$ , was prepared by treating  $[F_3N_2NMe]NbCl_3$  with 3 equiv. of methylmagnesium chloride.  $[F_3N_2NMe]NbMe_3$  is also fluxional at room temperature with the three methyl ligands giving rise to a broad singlet at 1.36 ppm in the <sup>1</sup>H NMR spectrum at room temperature in toluene-*d*<sub>8</sub>. The variable-temperature behavior of  $[F_3N_2NMe]NbMe_3$ is similar to that observed for  $[F_3N_2NMe]TaMe_3$ . The methyl resonances in  $[F_3N_2NMe]NbMe_3$  are broader than they are in  $[F_3N_2NMe]TaMe_3$ , a typical consequence of the onset of coupling of the methyl protons to Nb.

A methyl ligand can be abstracted from  $[F_3N_2NMe]$ -TaMe<sub>3</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to yield  $[(F_3N_2NMe)TaMe_2]$ -[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (Eq. (3)) as a yellow powder in 100% yield

Tabla 1



The <sup>1</sup>H and <sup>19</sup>F NMR spectra of [(F<sub>3</sub>N<sub>2</sub>NMe)TaMe<sub>2</sub>]- $[MeB(C_6F_5)_3]$  are consistent with the proposed mirror symmetry of the trigonal bipyramidal structure. The trifluorophenyl rings are equivalent and rotating rapidly on the NMR time scale at room temperature. The methyl ligands are observed as two singlets at 1.35 and 1.15 ppm in CD<sub>2</sub>Cl<sub>2</sub>. The observed high field shift for the meta- and para-fluorine substituents of the anion, as well as the small  $\Delta\delta$  ( $\delta_m - \delta_n$ ) of 2.69 ppm in the <sup>19</sup>F NMR spectrum are indicative of solvent-separated, relatively non-coordinating  $[MeB(C_6F_5)_3]^-$  ion in solution [15,16]. A similar cationic complex, { $[(C_6F_5NCH_2CH_2)_2NH]TaMe_2$ }[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>], has been synthesized and structurally characterized [11]. The  $[MeB(C_6F_5)_3]^-$  anion is clearly separated from  $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$  in  $\{[(C_6F_5NCH_2CH_2)_2-$ NH]TaMe<sub>2</sub>}[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>].

The reaction between  $[F_3N_2NMe]TaCl_3$  and trimethylsilylmethylmagnesium chloride afforded  $[F_3N_2NMe]$ -Ta(CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>) as a yellow powder



It is not clear whether the reaction proceeds via  $\alpha$ -hydrogen abstraction in putative  $[F_3N_2NMe]Ta(CH_2SiMe_3)_3$  or  $[F_3N_2NMe]Ta(CH_2SiMe_3)_2Cl$ , or whether  $[F_3N_2NMe]$ -Ta $(CH_2SiMe_3)_2Cl$  is dehydrohalogenated by the third equivalent of lithium reagent. Mechanistic questions of this type typically have not been answered in any tantalum alkylidene system, including the first of its type, Ta(CHCMe\_3)(CH\_2CMe\_3)\_3 [17]. The alkylidene carbon resonance in  $[F_3N_2NMe]Ta(CHSiMe_3)(CH_2SiMe_3)$  is observed at 243 ppm with  ${}^1J_{CH} = 97$  Hz and the corresponding proton resonance is found at 5.82 ppm, both in C<sub>6</sub>D<sub>6</sub>. The high-field chemical shift for H<sub> $\alpha$ </sub> combined with a low value for  ${}^1J_{CH}$  suggests that there is a significant agostic interaction between the tantalum and the C<sub> $\alpha$ </sub>-H<sub> $\alpha$ </sub> bond [17–19].

An X-ray diffraction study of  $[F_3N_2NMe]Ta(CHSi-Me_3)(CH_2SiMe_3)$  revealed the structure shown in Fig. 1. Selected distances and angles are listed in Table 1. The complex is best described as a distorted square pyramid in which the alkyl group (C(5)) occupies the axial position. The  $[F_3N_2NMe]^{2-}$  ligand coordinates to the metal in the basal positions and the amido nitrogen atoms are essentially planar, consistent with  $\pi$ -donation to the metal. The alkylidene  $\alpha$  carbon atom C(1) is in a basal



Fig. 1. The solid-state structure of [F<sub>3</sub>N<sub>2</sub>NMe]Ta(CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>).

1 abic 1								
Selected	intramolecular	distances	(Å)	and	bond	angles	(°)	of
[F <sub>3</sub> N <sub>2</sub> NN	IeTa(CHSiMe <sub>3</sub> )	CH <sub>2</sub> SiMe <sub>3</sub>	)					

[- ]7](			
Ta-C(1)	1.906(13)	C(1)-Ta-N(3)	136.4(5)
Ta-C(5)	2.124(12)	N(2)-Ta-C(5)	101.6(4)
Ta-N(1)	2.116(11)	N(1)-Ta-C(5)	100.5(4)
Ta-N(2)	2.094(10)	C(5)-Ta-N(3)	115.5(5)
Ta-N(3)	2.239(11)	N(2)-Ta-N(1)	146.9(4)
Si(1)-C(1)-Ta	144.8(8)	N(2)-Ta-N(3)	74.1(4)
Si(2)-C(5)-Ta	127.9(6)	N(1)-Ta-N(3)	74.3(4)
C(1)-Ta-C(5)	108.0(5)	C(14)-N(1)-Ta	133.4(9)
C(1)-Ta-N(1)	100.3(5)	C(20)-N(2)-Ta	127.1(8)
C(1)-Ta-N(2)	95.8(5)		

position with the substituent (Si(1)) pointing away from C(5). The alkylidene ligand lies approximately in the C(1)/Ta/C(5)/N(3) plane. The difference between the Ta-C(1) (1.906(13) Å) and Ta-C(5) (2.124(12) Å) bonds is typical of that between an alkyl and an alkylidene [17,19]. The relatively short Ta–C(1) (Ta= $C_{\alpha}$ ) bond distance (1.906(13) Å) and large Si(1)–C(1)–Ta (Ta= $C_{\alpha}$ –Si) bond angle  $(144.8(8)^{\circ})$  are consistent with a significant agostic interaction between the metal and  $H_{\alpha}$ . These metrical parameters should be compared with those in two previously crystallographically characterized tantalum trimethylsilylmethyl trimethylsilylmethylidene complexes [20,21]. The three *n*d orbitals that could be involved in  $\pi$ -bonding framework of the complex are illustrated in Fig. 2. The Ta=C  $\pi$ -bond employs the  $d_{xy}$  orbital, while overlap with the imido nitrogen out of phase p-orbitals employs the  $d_{xz}$  orbital. From this analysis the CH<sub>a</sub> agostic interaction would seem to most likely involve the metal  $d_{\nu z}$  orbital.

Initial attempts to synthesize the neopentyl/neopentylidene complex in an analogous fashion gave instead the



Fig. 2. Qualitative analysis of the  $\pi$ -bonding framework of  $[F_3N_2NMe]Ta(CHSiMe_3)(CH_2SiMe_3)$ .

mononeopentyl complex,  $[F_3N_2NMe]Ta(CH_2-t-Bu)Cl_2$ , as a yellow powder (Eq. (5)), even in the presence of 3.3 equiv. of neopentylmagnesium chloride. No additional alkylation took place in 3 h under the conditions employed. Steric congestion at the metal center caused by the more bulky neopentyl ligand is believed to hinder further substitution. After 6 h, however,  $[F_3N_2NMe]Ta(CH-t-Bu)(CH_2-t-Bu)$ could be isolated in low yield (22%). The neopentylidene proton was observed by <sup>1</sup>H NMR in C<sub>6</sub>D<sub>6</sub> at 0.39 ppm, and the carbon atom was observed as a doublet at 228 ppm ( $J_{CH} = 74$  Hz) in the <sup>1</sup>H-coupled <sup>13</sup>C NMR spectrum. The chemical shift for the alkylidene proton and the extremely low value for  $J_{CH}$  again are characteristic of a significant agostic interaction of the CH<sub> $\alpha$ </sub> electrons with the metal



Further alkylation of  $[F_3N_2NMe]Ta(CH_2-t-Bu)Cl_2$  with 2.2 equiv. of methylmagnesium chloride afforded a species whose <sup>1</sup>H NMR spectrum is consistent with it being  $[F_3N_2NMe]Ta(CH-t-Bu)(CH_3)$  (Eq. (6)). In addition to the diamidoamine resonances, three singlets were observed at 2.40, 0.72, and 0.49 ppm in a ratio of 1:9:3, corresponding to the neopentylidene  $H_{\alpha}$ , *t*-butyl, and methyl resonances, respectively. The alkylidene  $C_{\alpha}$  resonance was found as a doublet at 242 ppm (<sup>1</sup> $J_{CH} = 90$  Hz) in the <sup>1</sup>Hcoupled <sup>13</sup>C NMR spectrum



The neopentylidene ligand could form via dehalogenation of  $[F_3N_2NMe]Ta(CH_2-t-Bu)Cl_2$  to give  $[F_3N_2NMe]-Ta(CH-t-Bu)Cl$ , followed by its rapid reaction with additional methylating agent to give the observed product. If  $\alpha$ -hydrogen abstraction were to take place in an intermediate such as  $[F_3N_2NMe]Ta(CH_2-t-Bu)Me_2$ , we would expect a neopentylidene to be formed instead of a methylene. Typically neopentyl  $\alpha$ -hydrogens are more activated as a consequence of an increase in the Ta–C $_{\alpha}$ –C $_{\beta}$  angle in a sterically crowded circumstance [17].

The alkylidene proton and carbon resonances of the three alkyl/alkylidene complexes are collected in Table 2. All H<sub> $\alpha$ </sub> resonances are found in the region 0–6 ppm and alkylidene carbon resonances are found in the range 220–245 ppm. The <sup>1</sup>J<sub>CH</sub> values for the alkylidene carbon are uniformly low and well within the range expected for Ta(V) alkylidene complexes exhibiting  $\alpha$ -agostic interactions [22,23]. The variation in <sup>1</sup>J<sub>CH</sub> in the order  $\mathbf{C} < \mathbf{B} < \mathbf{A}$  emphasizes the dramatic tendency for neopentylidenes to engage in  $\alpha$ -agostic interactions and the steric demands of both neopentylidene and neopentyl groups [19].

The reaction between  $[F_3N_2NMe]TaCl_3$  and  $CH_3CH_2$ -MgBr led to formation of  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2-CH_3)$  as a brown powder (Eq. (7)). There is no evidence for formation of any significant amount of  $[F_3NMe]$ -Ta(CHCH<sub>3</sub>)(CH<sub>2</sub>CH<sub>3</sub>)



Although competition between  $\alpha$  hydrogen abstraction and  $\beta$  hydrogen abstraction is known in tantalum chemistry that involves triamidoamine ligands [13,24], steric factors in the intermediate leading to [F<sub>3</sub>NMe]Ta(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>3</sub>) are not likely to be significant enough to block  $\beta$  hydrogen abstraction. NMR studies of F<sub>3</sub>N<sub>2</sub>NMe]Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(CH<sub>2</sub>CH<sub>3</sub>) reveal that all four protons of the

Table 2							
Relevant	alkylidene	$H_{\alpha}$ a	nd C	resonances	of	tantalum	alkyl/alkylidene
complexe	S						

Complex	$^{1}H_{\alpha}$ $(ppm)^{a}$	$^{13}C_{\alpha}$ (ppm) <sup>b</sup>	$^{1}J_{\rm CH}$ (Hz) <sup>c</sup>
$[F_3N_2NMe]Ta(CHSiMe_3)(CH_2SiMe_3)$ (A)	5.82	243	97
$[F_3N_2NMe]Ta(CHCMe_3)(CH_3)$ ( <b>B</b> )	2.40	242	90
$[F_3N_2NMe]Ta(CHCMe_3)(CH_2CMe_3)$ (C)	0.39	228	74

<sup>a</sup> Solvent:  $C_6D_6$  (300 MHz).

<sup>b</sup> Toluene-*d*<sub>8</sub> (125 MHz).

 $^{c \ 1}J_{CH}$  values were determined from the alkylidene doublet in  $^{1}$ H-coupled  $^{13}$ C experiments.

ethylene ligand give rise to a singlet at 1.53 ppm, even at -80 °C. The ethylene carbons are likewise equivalent on the <sup>13</sup>C NMR time scale and give rise to a resonance at 56 ppm.

An X-ray study of  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$  revealed the structure shown in Fig. 3. If the bound ethylene is viewed as occupying a single coordination site, the geometry about the tantalum center may be viewed as distorted square pyramid with the ethylene ligand in the apical position. At this stage it is not known if the fluxional process that equilibrates the ethylene protons and carbon atoms consists only of rotation of the ethylene about the Ta-ethylene bond axis, or whether the core itself rearranges at the same time.

Pertinent bond lengths and angles in [F<sub>3</sub>N<sub>2</sub>NMe]Ta- $(\eta^2-C_2H_4)(CH_2CH_3)$  are listed in Table 3. The ethylene moiety has relatively short and essentially equivalent Ta-C bond lengths (2.172(8) Å and 2.174(8) Å). The observed C(1)-C(2) bond distance (1.502 Å) is only slightly shorter than typical C-C single bonds and much longer than typical C=C double bonds [25], indicative of extensive backbonding from the metal to the ethylene ligand. The orientation of the ethylene ligand suggests that the orbital that is used for  $\pi$  backbonding is the orbital normal to that utilized in forming the alkylidene  $\pi$ -bond in [F<sub>3</sub>N<sub>2</sub>NMe]-Ta(CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>). Evidently, these two possible  $\pi$  bonding orbitals (d<sub>xy</sub> and d<sub>yz</sub> in Fig. 2) are relatively close in energy. Exposure of  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$ to 1.5 equiv. of <sup>13</sup>C-labeled ethylene at room temperature gave no evidence of ethylene exchange.

# 3.2. Tantalum (V) complexes that contain the $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]^{3-}$ ligand

A palladium-catalyzed Buchwald–Hartwig C–N coupling reaction [26-28] was employed in order to synthesize  $H_3[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]$  from  $(H_2NCH_2CH_2)_3N$  and 3 equiv. of 1-bromo-3,5-dichlorobenzene in 50% yield without complications. For convenience,  $[(3,5-Cl_2C_6H_3N-1)]$ 

Table 3

Selected intramolecular	distances (Å)	and bond	angles (	°) of [F <sub>3</sub> ]	√2NMe]-
$Ta(n^2-C_2H_4)(CH_2CH_3)$					-

· · - · · ·	/		
Ta-C(1)	2.164(9)	C(1)-Ta-N(3)	130.7(3)
Ta-C(2)	2.166(9)	C(2)-Ta-C(3)	126.5(3)
Ta–C(3)	2.268(8)	N(1)-Ta-C(2)	107.8(4)
C(1) - C(2)	1.508(13)	N(2)-Ta-C(2)	108.1(4)
C(3) - C(4)	1.423(14)	C(2)-Ta-N(3)	90.0(3)
Ta-N(1)	1.997(7)	N(1)-Ta-C(3)	94.3(3)
Ta-N(2)	2.003(7)	N(2)-Ta-C(3)	91.0(3)
Ta–N(3)	2.367(6)	C(3)-Ta-N(3)	143.4(3)
C(4)-C(3)-Ta	110.6(6)	N(1)-Ta-N(2)	130.4(3)
C(1)–Ta–C(2)	40.8(4)	N(1)-Ta-N(3)	74.8(3)
C(1)– $Ta$ – $C(3)$	85.8(3)	N(2)-Ta-N(3)	72.2(2)
N(1)–Ta–C(1)	112.7(3)	C(10)-N(1)-Ta	123.3(6)
N(2)–Ta–C(1)	116.9(4)	C(16)-N(2)-Ta	120.3(5)

 $CH_2CH_2)_3N]^{3-}$  will be abbreviated as  $\left[Cl_2N_2NMe\right]^{3-}$  in discussions below.

The dichloride complex,  $[Cl_2N_2NMe]TaCl_2$ , was prepared in a reaction between  $H_3[(3,5-Cl_2C_6H_3NCH_2-CH_2)_3N]$  and  $TaCl_5$  in the presence of triethylamine (Eq. (8)). The <sup>1</sup>H NMR spectrum of brick red [(3,5-Cl\_2-C\_6H\_3NCH\_2CH\_2)\_3N]TaCl\_2 is consistent with threefold symmetry on the NMR time scale, as found in the related species [(Me\_3SiNCH\_2CH\_2)\_3N]TaCl\_2 [29]

$$(3.5-Cl_2C_6H_3N_{3}NH_2^{+}TaCl_5 \xrightarrow{5 \text{ eq } NEt_3}_{-3 \text{ Et}_3NHCl} \xrightarrow{Ar^{Cl}}_{N} \xrightarrow{Cl}_{Ta} \xrightarrow{Ar^{Cl}}_{N} \xrightarrow{Ar^{Cl}}_$$

The reaction between  $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]$ -TaCl<sub>2</sub> and 2 equiv. of ethylmagnesium chloride gave the ethylene complex,  $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]Ta(\eta^2-C_2H_4)$ , in good yield (Eq. (9)).  $[(3,5-Cl_2C_6H_3NCH_2CH_2)_3-N]Ta(\eta^2-C_2H_4)$  also could be obtained in one step by treating a mixture of  $H_3[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]$  and TaCl<sub>5</sub> with 5 equiv. of ethylmagnesium chloride



Fig. 3. The solid-state structure of  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$ .



In the <sup>1</sup>H NMR spectrum, the proton resonance for bound ethylene is found as a singlet at 1.66 ppm ( $C_6D_6$ , 500 MHz). The ethylene carbons likewise are equivalent on the <sup>13</sup>C NMR time scale and give rise to a resonance at 72.58 ppm ( ${}^{1}J_{CH} = 143$  Hz). All spectroscopic data suggest that  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)$  is C<sub>3</sub>-symmetric on the NMR time scale, as found also for [(Me<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]- $Ta(\eta^2-C_2H_4)$  [24]. We assume that the structure of  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)$  is analogous to that found for  $[(Me_3SiNCH_2CH_2)_3N]Ta(n^2-C_2H_4)$  [24]. In  $[(Me_3SiNCH_2 CH_2$ <sub>3</sub>N]Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) the C–C axis of the ethylene is lined up with one of the amido Ta-N bonds. The ethylene ligand rotates rapidly about the pseudo- $C_3$  axis of the complex on the NMR time scale as a consequence of degeneracy of the  $d_{xz}$  and  $d_{yz}$  orbitals. Comparison of the ethylene <sup>1</sup>H and  $^{13}C$  resonances of [Cl<sub>2</sub>N<sub>2</sub>NMe]Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) with those reported for  $[(R_3SiNCH_2CH_2)_3N]Ta(\eta^2-C_2H_4)$  complexes (R = Me or Et) are summarized in Table 4. Formation  $[(R'NCH_2CH_2)_3N]Ta(\eta^2-C_2H_4)$  (R' = 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, of Me<sub>3</sub>Si, Et<sub>3</sub>Si) complexes is believed to proceed via β-abstraction in intermediate [(R'NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>. Only in the synthesis of [(Et<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]-Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) is  $\alpha$ -abstraction to give [(Et<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>-NTa(CHCH<sub>3</sub>), competitive with  $\beta$ -hydrogen abstraction [13]. It was proposed that the sterically demanding triethylsilyl substituents in [(Et<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(CHCH<sub>3</sub>) force the Ta– $C_{\alpha}$ – $C_{\beta}$  angles in the diethyl intermediate to increase, thereby activating the  $\alpha$  hydrogens toward  $\alpha$ abstraction to give the alkylidene and at the same time preventing activation of  $\beta$  hydrogens toward  $\beta$ -abstraction.

All attempts to convert  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)$  into  $[Cl_2N_2NMe]Ta=CHMe$  in the presence of a catalytic amount of PhPH<sub>2</sub> were unsuccessful. No observable change was noted when  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)$  was treated with catalytic amounts of PhPH<sub>2</sub> in deuterated benzene or toluene even after several days at room temperature. The mixtures were not heated since  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_4)$  was found to be unstable in solution at elevated temperatures and to decompose in a manner analogous to  $[(R_3SiNCH_2CH_2)_3N]Ta(\eta^2-C_2H_4)$  (R = Me, Et) com-

Table 4

Comparison of ethylene H and C resonances of [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) with reported [(R<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]-Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) complexes

Complex	<sup>1</sup> H (ppm)	<sup>13</sup> C (ppm)	$^{1}J_{\rm CH}$ (Hz)
$[(3,5-Cl_2C_6H_3NCH_2CH_2)_3N]Ta(\eta^2-C_2H_4)$	1.66	72.6	143
$[(\text{Me}_{3}\text{SiNCH}_{2}\text{CH}_{2})_{3}\text{N}]\text{Ta}(\eta^{2}\text{-}C_{2}\text{H}_{4})$ $[(\text{Et}_{3}\text{SiNCH}_{2}\text{CH}_{2})_{3}\text{N}]\text{Ta}(\eta^{2}\text{-}C_{2}\text{H}_{4})$	2.14 2.10	62.6 62.7	144 141

plexes. (Compare with the decomposition of  $[Cl_2N_2NMe]$ -TaMe<sub>2</sub> below.)

Alkylation of  $[Cl_2N_2NMe]TaCl_2$  with 2 equiv. of methylmagnesium chloride in toluene affords  $[Cl_2N_2NMe]$ -TaMe<sub>2</sub> as bright yellow crystals (Eq. (10)).



 $[Cl_2N_2NMe]TaMe_2$  also can be obtained through addition of 5 equiv. of MeMgCl to a mixture of TaCl<sub>5</sub> and H<sub>3</sub>[Cl<sub>2</sub>N<sub>2</sub>NMe]. A resonance for the two methyl groups in  $[Cl_2N_2NMe]TaMe_2$  is found as a singlet at 1.31 ppm in the <sup>1</sup>H NMR spectrum.

Single crystals of [Cl<sub>2</sub>N<sub>2</sub>NMe]TaMe<sub>2</sub> suitable for X-ray crystallographic studies were obtained from toluene solution at -30 °C. The structure obtained (Fig. 4) shows it to be a six coordinate species with the methyl ligands within the bowl-like coordination pocket defined by the ligand. The structure is related to that found for [(Me<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(Et)(Me) [24], in which the alkyl ligands lie approximately in the plane formed by the donor nitrogen, the tantalum center, and one of the imido nitrogen atoms. The Ta-C bond lengths in [Cl<sub>2</sub>N<sub>2</sub>NMe]TaMe<sub>2</sub>  $(\sim 2.22 \text{ Å})$  are essentially the same within experimental error. The Ta-Naxial bond length in [Cl2N2NMe]TaMe2 (2.318(6) Å) is significantly shorter than the Ta-N<sub>axial</sub> bond length in  $[(Me_3SiNCH_2CH_2)_3N]Ta(Et)(Me)$  (2.444(8)Å). A list of selected bond lengths and angles can be found in Table 5.

 $[Cl_2N_2NMe]TaMe_2$  is stable in the solid state at room temperature, but it evolves methane in solution at elevated temperatures. The thermolysis product is believed to be analogous to the thermolysis product of  $[(R_3SiNCH_2CH_2)_3N]$ - $TaMe_2$  (R = Me or Et) [24,13] on the basis of a NMR spectrum of the product analogous to that for MeTa[N-(SiR\_3)(CH=CH\_2)][N(CH\_2CH\_2NSiR\_3)\_2]} where R = Me



Fig. 4. The solid-state structure of [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]TaMe<sub>2</sub>.

Table 5 Selected intramolecular distances (Å) and bond angles (°) of  $[(3,5-Cl_2CH_2NCH_2CH_2)]$ NIT a Me2

Ta-C(1)	2.224(8)	N(2)-Ta-N(1)	96.2(3)				
Ta-C(2)	2.221(7)	N(3)-Ta-N(2)	116.3(3)				
Ta-N(1)	2.085(6)	N(3)-Ta-N(1)	124.4(2)				
Ta-N(2)	2.077(6)	C(9)-N(1)-Ta	125.2(5)				
Ta-N(3)	2.006(6)	C(15)-N(2)-Ta	129.3(5)				
Ta-N(4)	2.318(6)	C(21)-N(3)-Ta	121.7(5)				
C(2)-Ta-C(1)	77.8(3)						

[24] or Et [13], as shown in Eq. (11). Isolation of this product was not pursued



Addition of 2 equiv. of vinylmagnesium chloride to  $[Cl_2N_2NMe]TaCl_2$  produced the acetylene complex,  $[Cl_2N_2NMe]Ta(\eta^2-C_2H_2)$  (Eq. (12))



Proton and carbon NMR established that this molecule has pseudo- $C_3$ -symmetry with the acetylene proton resonance at 11.90 ppm and the corresponding carbon resonances at 226 ppm ( $J_{CH} = 181$  Hz). The structure of this compound is likely to be closely related to that reported for  $[(Me_3SiNCH_2CH_2)_3N]Ta(\eta^2-C_2H_2)$  [24]. Note that in the  $[(Et_3SiNCH_2CH_2)_3N]^{3-}$  system, a dimeric alkylidene complex,  $\{[(Et_3SiNCH_2CH_2)_3N]Ta(=CHCH_2)\}_2$ , was obtained in combination with the [(Et<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]- $Ta(\eta^2-C_2H_2)$  when the reaction was performed at elevated temperatures [13]; most likely the dimeric species is formed through coupling of two d<sup>1</sup> [(Et<sub>3</sub>SiNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]Ta(CH= CH<sub>2</sub>) molecules. An analogous reaction to give the hypothetical  $\{[Cl_2N_2NMe]Ta(=CHCH_2)\}_2$  was not observed when the reaction shown in Eq. (12) was performed at elevated temperatures.

#### 4. Conclusion

The results presented here illustrate the potential of  $[F_3N_2NMe]^{2-}$  as a relatively robust ligand for d<sup>0</sup> organotantalum chemistry. Its attachment to the metal in a "direct" synthesis that begins with the metal halide is especially attractive. The structures of an alkylidene and an olefin complex suggest that the two perpendicular orbitals of the " $[F_3N_2NMe]Ta(R)$ " core available for  $\pi$  bonding (d<sub>xy</sub> and  $d_{yz}$  in Fig. 2) are relatively close in energy and that sterics appear to dictate the orientation of the alkylidene or olefin.

Tantalum complexes that contain the  $[Cl_2N_2NMe]^{3-}$ ligand are also readily prepared in a "direct" method. In general they appear to be quite similar to  $[(Me_3SiN-CH_2CH_2)_3N]^{3-}$  complexes that have been reported, although conversion of the ethylene to the ethylidene complex in the presence of a catalytic amount of PhPH<sub>2</sub> was not observed. Although we had hoped that the backbone would be more stable to N–C bond cleavage reactions than in the  $[(Me_3SiNCH_2CH_2)_3N]^{3-}$  ligand system, that does not appear to be the case.

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#### Appendix A. Supplementary material

Fully labeled thermal ellipsoid drawing, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates are available for  $[F_3N_2NMe]Ta(CHSiMe_3)(CH_2SiMe_3)$  (01199),  $[F_3N_2NMe]Ta(\eta^2-C_2H_4)(CH_2CH_3)$  (02042), and  $[Cl_2N_2NMe]TaMe_2$ . (03047). These data are available to the public at http://www.reciprocalnet.org/. The numbers in parentheses listed above can be used to access each structure at this site. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006. 03.044.

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