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The synthesis and structures of tantalum complexes that contain a triamido or a diamidoamine ligand

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Abstract

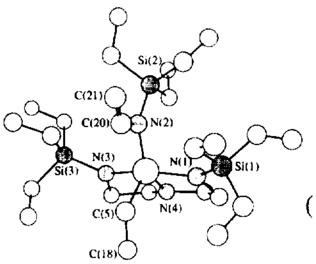
Addition of $(Me_3SiNHCH_2CH_2)_2NH$ ($H_3[N_3(TMS)]$) or $(Me_3SiNH$-*o*-$C_6H_4)_2NH$ ($H_3[ArN_3(TMS)]$) to a solution of $TaMe_5$ yields $[N_3(TMS)]TaMe_2$ or $[ArN_3(TMS)]TaMe_2$, respectively. An X-ray study of $[ArN_3(TMS)]TaMe_2$ showed it to have an approximate trigonal bipyramidal structure in which the two methyl groups are in equatorial positions and the triamido ligand is approximately planar. Addition of $(C_6F_5NHCH_2CH_2)_2NH$ ($H_3[N_3(C_6F_5)]$) to $TaMe_5$ yields first $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$, which then decomposes to $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$. An X-ray study of $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$ shows it to be approximately a trigonal bipyramid, but the C_6F_5 rings are oriented so that they lie approximately in the TaN_3 plane and two *ortho* fluorines interact weakly with the metal. Trimethylaluminum attacks the central nitrogen atom in $[N_3(TMS)]TaMe_2$ to give $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$, an X-ray study of which shows it to be a trigonal bipyramidal species similar to the first two structures, except that the C–Ta–C bond angle is approximately 30° smaller (106.6(12)°). Addition of $B(C_6F_5)_3$ to $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$ yields $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+\{B(C_6F_5)_3Me\}^-$, the structure of which most closely resembles that of $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ in that the C–Ta–C angle is 102.0(6)°. The C_6F_5 rings in $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$ are turned roughly perpendicular to the TaN_3 plane, i.e. *ortho* fluorines do not interact with the metal in this molecule. © 1998 Elsevier Science S.A.

Keywords: Crystal structures; Tantalum complexes; Triamido ligand complexes; Diamidoamine ligand complexes

1. Introduction

Certain tantalum complexes that contain an $[(R_3SiNCH_2CH_2)_3N]^{3-}$ ligand (R = Me or Et) decompose to yield approximately trigonal bipyramidal Ta(V) complexes that contain the planar triamido ligand, $[(R_3SiNCH_2CH_2)_2N]^{3-}$ (e.g. $[N_3N^*]$ when $R_3Si = Et_3Si$, Eq. (1)) [1,2].

$$[N_3N^*]Ta(C_2H_4) \xrightarrow[110\ ^\circ C]{toluene\text{-}d_8}$$



(1)

In the reaction shown in Eq. (1) a β hydride has moved from C(20) to the ethylene ligand to give an ethyl ligand (C(5)–C(18)) and the N(4)–C(21) bond has been cleaved, leaving a vinyl-substituted amido ligand (N(2)) in the equatorial position of a trigonal bipyramidal complex. The resulting planar triamido ligand (N(1), N(3), N(4)) spans the two axial positions and one equatorial position. Planar triamido ligands are related to planar, substituted pyridine ligands of the type $[2,6\text{-}(RNCH_2)_2C_5H_3N]^{2-}$ that have been employed to prepare trigonal bipyramidal complexes of Ti [3], Zr [4], Ta [5] and W [6]. The synthesis of one substituted diethylenetriamine, $(Me_3SiNHCH_2CH_2)_2NH$ ($H_3[N_3(TMS)]$), has been reported in the literature [7]. However, since no other complexes (other than those we reported [1,2]) that contain a trianionic triamido ligand of this general type have appeared in the literature (to the best of our knowledge), we set out to prepare several such ligands and complexes of them that contain tantalum.

2. Experimental

2.1. General

All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox, using standard Schlenk tech-

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niques, or on a high vacuum line ($<10^{-4}$ Torr). Pentane was washed with HNO_3/H_2SO_4 (5/95 vol./vol.), sodium bicarbonate, water, stored over $CaCl_2$, and then distilled from sodium benzophenone under nitrogen. Reagent grade ether, tetrahydrofuran and benzene were distilled from sodium benzophenone under nitrogen. Toluene was distilled from molten sodium. Methylene chloride was distilled from CaH_2. All solvents were stored in the drybox over activated 4 Å molecular sieves. Deuterated solvents were freeze–pump–thaw degassed and vacuum transferred from an appropriate drying agent. NMR spectra are recorded in C_6D_6 unless noted otherwise. ^1H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent peak. ^{19}F NMR are listed in parts per million downfield of $CFCl_3$ as an external standard. Coupling constants are given in Hertz, and routine couplings usually are not listed. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer in our own laboratory. $(Me_3SiNHCH_2CH_2)_2NH$ [7] and $TaMe_5$ [8] were prepared as reported in the literature.

2.2. Syntheses

2.2.1. 2,2′-Diaminodiphenylamine

2,2′-Dinitrodiphenylamine (21.2 g, 81.9 mmol), zinc dust (65.1 g, 996 mmol) and NH_4Cl (39.4 g, 737 mmol) were added to 400 ml of THF. The mixture was refluxed under nitrogen until the color became pale yellow (~24 h). The mixture was allowed to cool to room temperature and was filtered through a bed of Celite. The solvent was removed from the pale-orange filtrate and the residual solid was partially dissolved in 70 ml of dichloromethane. Diethyl ether was added (90 ml) and the off-white solid product was filtered off; yield 11.89 g (73%). ^1H NMR ($CDCl_3$): δ 6.75–6.95 (m, 8, ArH); 5.01 (br s, 1, NH), 3.64 (br s, 4, NH_2).

2.2.2. 2,2′-Bis(trimethylsilylamino)diphenylamine

2,2′-Diaminodiphenylamine (1.08 g, 5.42 mmol), triethylamine (1.37 g, 3.95 mmol) and trimethylchlorosilane (1.24 g, 11.4 mmol) were added to 60 ml of pentane. The reaction mixture was stirred at room temperature for 3 days and filtered. The pale-orange filtrate was concentrated in vacuo to yield a pale-yellow oil that crystallized at −30°C; yield 1.59 g (85%). ^1H NMR (C_6D_6): δ 6.93 (m, 4, ArH), 6.73 (m, 4, ArH), 4.46 (br s, 1, NH), 3.54 (br s, 2, N*H*(TMS)), 0.13 (s, 18, $SiMe_3$).

2.2.3. $(C_6F_5NHCH_2CH_2)_2NH$

Hexafluorobenzene (43.7 g, 234 mmol) was added to a 60 ml CH_3CN solution of 7.34 g of diethylene triamine (71.2 mmol) and 21.6 g of K_2CO_3 (156 mmol). The mixture was heated to reflux for 20 h. The reaction mixture was then cooled to room temperature and 450 ml of water were added. The aqueous suspension was extracted with chloroform (3×200 ml). The pale-yellow extract was dried over $MgSO_4$ and concentrated to give a yellow oil. The oil was added to an alumina column and eluted with diethyl ether. The first 400 ml of eluent was collected and the ether was removed in vacuo. The thick yellow oil thus obtained is >95% pure by NMR; yield ~40%. It solidifies at −35°C. ^1H NMR ($CDCl_3$): δ 4.15 (s, 2, ArNH), 3.41 (t, 4, CH_2), 2.89 (t, 4, CH_2), 1.07 (s, 1, NH). ^{19}F NMR ($CDCl_3$): δ −160.45 (d, 4, *ortho*), −165.21 (t, 4, *meta*), −172.40 (t, 2, *para*).

2.2.4. $[(Me_3SiNCH_2CH_2)_2N]TaMe_2$

A solution of 9.00 mmol of $TaMe_5$ in 8 ml of diethyl ether that had been prepared at −35°C and kept at that temperature was added to a solution of $H_3[N_3(TMS)]$ (2.19 g, 8.94 mmol) in 50 ml of diethyl ether and the reaction mixture was allowed to warm to 20°C over a period of 1 h. The reaction mixture was filtered through a bed of Celite and the solvent was removed from the bright-yellow filtrate to give a yellow powder. This crude product was recrystallized from pentane to yield 2.18 g of yellow blocks (56% yield). ^1H NMR (C_6D_6): δ 3.88 (br t, 4, CH_2), 3.78 (br t, 4, CH_2), 0.40 (s, 6, Me), 0.14 (s, 18, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 67.63 (t, $J_{CH}=134$, CH_2), 58.80 (q, $J_{CH}=117$, Ta–Me), 55.79 (t, $J_{CH}=134$, CH_2), 0.78 (q, $J_{CH}=119$, $SiMe_3$).

2.2.5. $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2N]TaMe_2$

$[(Me_3SiN\text{-}o\text{-}C_6H_4)_2N]TaMe_2$ was prepared in a similar manner to that described for the synthesis of $[(Me_3SiNCH_2CH_2)_2N]TaMe_2$, except the reaction temperature was kept at −20°C for 10 h. The reaction mixture was then allowed to warm to room temperature and was filtered. The solvent was removed from the deep-red filtrate in vacuo and the red residue was extracted with dichloromethane (3×20 ml). The filtrate was concentrated in vacuo and stored at −35°C for 24 h. Deep-red blocks were filtered off (80% yield). ^1H NMR (C_6D_6): δ 7.66 (m, 2, ArH), 6.82 (m, 4, ArH), 6.67 (m, 2, ArH), 0.71 (s, 6, Me), 0.32 (s, 18, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 150.00 (C_{ipso}), 140.96 (C_{ipso}), 121.58 (CH), 120.94 (CH), 115.58 (CH), 115.33 (CH), 60.22 (TaMe), 1.23 ($SiMe_3$).

2.2.6. $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$

At −35°C, an ether (2 ml) solution of $(C_6F_5NHCH_2CH_2)_2NH$ (336 mg, 0.771 mmol) was added to an ether (6 ml) solution of $TaMe_5$ (0.771 mmol) at −35°C. The reaction mixture was then stirred at room temperature for 10 min. At this point an aliquot showed the product was >95% pure $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$ according to ^1H and ^{19}F NMR spectra. The reaction mixture was filtered through Celite and the solvent was removed in vacuo to afford 504 mg of the pale-yellow crystalline product; yield 99%. ^1H NMR (C_6D_6): δ 3.40 (m, 2, CH_2), 3.04 (m, 2, CH_2), 2.43 (s, br, 1, NH), 2.15 (m, 4, CH_2), 0.96 (s, 9, Me). ^{19}F NMR (C_6D_6): δ −149.86 (d, 4, *ortho*), -162.15 (t, 2, *para*), −165.39 (t, 4, *meta*). ^{13}C {^1H} NMR (CD_2Cl_2): δ 144.41 (d, $^1J_{CF}=244$, *ortho*), 138.76 (d, $^1J_{CF}=253$, *meta*), 138.40 (d, $^1J_{CF}=244$, *para*), 130.00 (s, C_{ipso}), 69.30 (s, CH_2), 60.29 (s, CH_2), 49.20 (s, Me). *Anal.*

Calc. for $C_{19}H_{18}N_3F_{10}Ta$: C, 34.61; H, 2.75; N; 6.37. Found: C, 34.56; H, 2.63; N, 6.38%.

2.2.7. *[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$N]TaMe$_2$*

A 100 ml reaction vessel was charged with a yellow toluene solution (15 ml) of $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$ (975 mg, 1.48 mmol) and the solution was heated at 65°C for 9 h to afford an orange solution that contained > 95% pure $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$ according to ^1H and ^{19}F NMR spectra. Orange, crystalline $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$ was recovered after removal of all solvents in vacuo; yield 886 mg (93%). X-ray quality crystals were obtained from mixtures of ether and toluene at −35°C. ^1H NMR (C_6D_6): δ 3.99 (t, 4, $J=6.6$, CH_2), 3.71 (t, 4, $J=6.6$, CH_2), 0.63 (quintet, 6, $J_{HF}=3.6$, Me). ^{19}F NMR (toluene-d$_8$): δ −150.93 (d, 4, *ortho*), −164.25 (t, 4, *meta*), −164.63 (t, 2, *para*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.33 (d, $^1J_{CF}=248$, *ortho*), 139.17 (d, $^1J_{CF}=254$, *meta*), 138.14 (d, $^1J_{CF}=255$, *para*), 127.44 (s, C_{ipso}), 63.75 (s, br, Me), 63.44 (s, CH_2), 60.31 (s, CH_2). *Anal.* Calc. for $C_{18}H_{14}N_3F_{10}Ta$: C, 33.61; H, 2.19; N; 6.53. Found: C, 33.31; H, 1.97; N, 6.43%.

2.2.8. *[(Me$_3$SiNCH$_2$CH$_2$)$_2$NAlMe$_3$]TaMe$_2$*

Trimethylaluminum (0.145 mmol as a 2.0 M solution in n-hexane) was added to a solution of $[N_3(TMS)]TaMe_2$ (58 mg, 0.145 mmol) in 4 ml of pentane at −30°C. The reaction was stirred at room temperature for 2.5 h and the solution was concentrated to ~1 ml. After the solution was stored at −30°C for several hours, pale-yellow prisms (49 mg; 0.104 mmol) were filtered off; yield 72%. ^1H NMR (C_6D_6): δ 4.40 (br m, 2, CH_2), 3.93 (br m, 2, CH_2), 3.47 (br m, 2, CH_2), 2.63 (br m, 2, CH_2), 0.85 (br s, 3, TaMe), 0.55 (br s, 3, TaMe), 0.31 (br s, 9, $AlMe_3$), 0.18 (br s, 18, TMS).

2.2.9. *{[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NH]TaMe$_2$}$^+${MeB(C$_6$F$_5$)$_3$}$^-$-(toluene)*

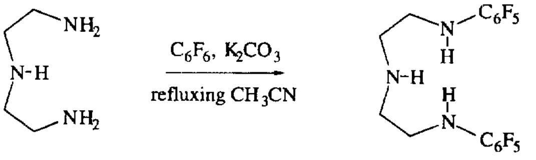
A toluene solution (4 ml) of $B(C_6F_5)_3$ (154 mg, 0.301 mmol) was added to a toluene solution (2 ml, −35°C) of $[(C_6F_5NCH_2CH_2)_2NH]TaMe_3$ (198 mg, 0.301 mmol). The reaction mixture was warmed slowly to room temperature and a pale-yellow precipitate formed in 20 min. The supernatant was decanted away and the solid was dried in vacuo to afford > 95% pure product, according to ^1H and ^{19}F NMR spectra; yield 335 mg (95%). X-ray quality crystals were obtained from dichloromethane at −35°C. ^1H NMR (CD_2Cl_2): δ 4.72 (td, 2, CH_2), 4.19 (dd, 2, CH_2), 4.01 (dt, 2, CH_2), 3.49 (m, 2, CH_2), 1.38 (s, 3, Me), 1.27 (s, 3, Me), 0.47 (s, 3, Me); the NH resonance was observed as a shoulder on the resonance at 4.72 ppm. ^{19}F NMR (CD_2Cl_2): δ −134.72 (d, 6), −143.38 (d, 4), −151.20 (t, 2), −160.06 (t, 4), −166.27 (t, 3), −169.04 (t, 6). *Anal.* Calc. for $C_{44}H_{26}N_3F_{25}BTa$: C, 41.83; H, 2.07; N, 3.33. Found: C, 41.51; H, 1.84; N, 3.18%.

2.2.10. *Observation of {[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NH]TaMe$_2$}$^+$-{B(C$_6$F$_5$)$_4$}$^-$*

To a CD_2Cl_2 solution (0.3 ml, −35°C) of $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$ (20 mg, 0.0303 mmol) was added a CD_2Cl_2 solution (0.4 ml, 22°C) of $[PhMe_2NH][B(C_6F_5)_4]$ (24 mg, 0.0300 mmol). ^1H and ^{19}F NMR spectra of the product were analogous to those of $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+\{MeB(C_6F_5)_3\}^-$ except that free Me_2NPh was present. ^1H NMR (CD_2Cl_2): δ 4.65 (td, 2, CH_2), 4.50 (s, br, 1, NH), 4.17 (dd, 2, CH_2), 3.90 (dt, 2, CH_2), 3.44 (m, 2, CH_2), 1.30 (s, br, 6, Ta*Me*). ^{19}F NMR (CD_2Cl_2): δ −134.51 (s, br, 8), −143.63 (d, 4), −151.60 (t, 2), −160.32 (t, 4), −164.81 (t, 4), −168.80 (t, 8). Resonances for Me_2NPh were observed at 7.29 (t, 2, Ph), 6.85–6.81 (m, 3, Ph), and 2.99 (s, 6, N*Me*).

3. Results

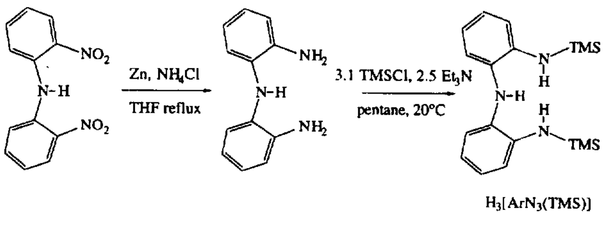
The reaction between $(H_2NCH_2CH_2)_2NH$ and hexafluorobenzene yields the pentafluorophenyl-substituted triamine shown in Eq. (2). This ligand is analogous to $(Me_3SiNHCH_2CH_2)_2NH$ ($H_3[N_3(TMS)]$) [7], although it will not have the potential disadvantage that any trimethylsilyl-substituted amido ligand has, namely loss of the trimethylsilyl group in a synthesis to give trimethylsilylchloride and intractable metal-containing products or relatively facile C–H activation within a TMS methyl group. Acetonitrile as a solvent is more convenient than dimethyl sulfoxide, the preferred solvent for the synthesis of $N(CH_2CH_2NHC_6F_5)_3$ [9].



(2)

$H_3[N_3(C_6F_5)]$

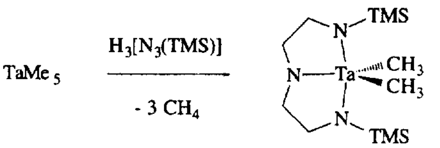
A triamido ligand whose backbone is potentially more robust than ligands based on diethylenetriamine can be prepared by reducing 2,2′-dinitrodiphenylamine [10] with zinc dust and NH_4Cl in THF. Addition of trimethylchlorosilane to $(o\text{-}C_6H_4NH_2)_2NH$ in the presence of triethylamine yields $H_3[ArN_3(TMS)]$ (Eq. (3)). So far we have not been able to prepare the C_6F_5-substituted version of $H_3[ArN_3(TMS)]$.



(3)

$H_3[ArN_3(TMS)]$

The most convenient entry into tantalum alkyl chemistry that we have found so far employs $TaMe_5$ [8,11]. $TaMe_5$ can be prepared on a large scale in ether from $TaMe_3Cl_2$ [12,13] and methyllithium. It has rarely been employed as a starting material to make tantalum methyl complexes, perhaps in part because it begins to decompose in diethyl ether above ~0°. Therefore reactions that involve $TaMe_5$ must compete effectively with its decomposition. Addition of $H_3[N_3(TMS)]$ or $H_3[ArN_3(TMS)]$ to a solution of $TaMe_5$ at −35°C followed by slowly warming the solution to room temperature over a period of 1–10 h produced yellow crystalline $[N_3(TMS)]TaMe_2$ (Eq. (4)) or red crystalline $[ArN_3(TMS)]TaMe_2$,

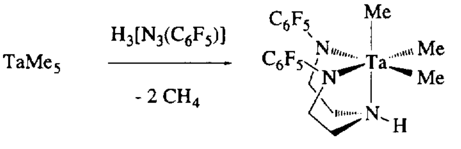


(4)

$[N_3(TMS)]TaMe_2$

respectively. It seems likely that a diamine adduct of $TaMe_5$ analogous to $(dmpe)TaMe_5$ [11] forms first and stabilizes $TaMe_5$ toward intermolecular loss of methane. $H_3[ArN_3(TMS)]$ is less basic, more sterically demanding, and less flexible than $H_3[N_3(TMS)]$ and therefore more time is required (at a temperature where $TaMe_5$ does not decompose) in order for the yield of $[ArN_3(TMS)]TaMe_2$ to be high. The spectra of both $[N_3(TMS)]TaMe_2$ or $[ArN_3(TMS)]TaMe_2$ are characteristic of a molecule that has C_{2v} symmetry. The methyl resonances are found between 0 and 1 ppm. For reasons that are not clear we have not yet been able to obtain satisfactory elemental analyses for any complexes containing a TMS-substituted ligand.

Addition of $(C_6F_5NHCH_2CH_2)_2NH$ ($H_3[N_3(C_6F_5)]$) to $TaMe_5$ yields first an isolable trimethyl complex in which a proton remains on the central nitrogen atom (Eq. (5)).

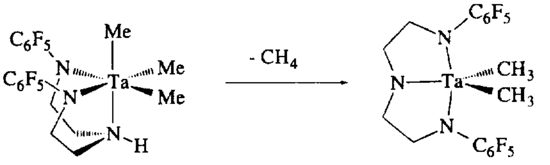


(5)

$[HN_3(C_6F_5)]TaMe_3$

Proton NMR spectra at room temperature reveal that the methyl groups are all equivalent (0.96 ppm) and the NH resonance is observed as a broad singlet at 2.43 ppm. Below −80°C in toluene-d_8 the methyl resonance divides into two broad resonances in a ratio of 2:1. Therefore we propose that $[HN_3(C_6F_5)]TaMe_3$ has the *fac* form shown in Eq. (5), rather than the *mer* form, in which three methyl resonances would be expected, although the data are not definitive. The mechanism of methyl group equilibration in the *fac* form could consist either of dissociation of the NH donor to give a fluxional five-coordinate species, or a 'turn-stile' rotation of the three methyl groups with respect to the three nitrogen atoms. More exotic mechanisms that involve reversible migration of a methyl group to an amido nitrogen or to the amine donor cannot be discounted, but seem considerably less likely to take place at a rate of the order of the NMR time scale.

$[HN_3(C_6F_5)]TaMe_3$ is relatively unstable, even in the solid state. It evolves one equivalent of methane to give $[N_3(C_6F_5)]TaMe_2$ (Eq. (6)). The proton and carbon NMR spectra of $[N_3(C_6F_5)]TaMe_2$ are somewhat unusual. They both are characteristic of a molecule that has C_{2v} symmetry, but the methyl resonance in each is a quintet (0.63 ppm in the ^1H NMR spectrum with $J = 3.6$ Hz; 63.49 ppm in the ^{13}C NMR spectrum with $J = 5.0$ Hz). The proton-coupled, fluorine-decoupled carbon spectrum showed no coupling beyond that attributable to CH coupling. Therefore we propose that the quintet arises from coupling to four fluorines, presumably the four *ortho* fluorines in the C_6F_5 rings. The C–F and H–F couplings are much larger than those found in $[(C_6F_5NCH_2CH_2)_3N]TiMe$ (~1.5 Hz) [14]. Therefore we suspected that one *ortho* fluorine from each ring may be interacting with the metal to a significant degree.



(6)

$[HN_3(C_6F_5)]TaMe_3$ $[N_3(C_6F_5)]TaMe_2$

An X-ray study of $[ArN_3(TMS)]TaMe_2$ showed it to have an approximate TBP structure (Fig. 1; Tables 1 and 2) analogous to that found for $[(Et_3SiNCH_2CH_2)_2N]Ta(CH_2CH_3)[N(CH{=}CH_2)(SiEt_3)]$ [2]. The $ArN_3(TMS)$ ring system is slightly twisted out of planarity, most likely as a consequence of steric interaction between the protons *ortho* to the central nitrogen atom. The Ta–methyl bond lengths are not unusual, although the C(1)–Ta–C(2) angle is 130.6(2)°, much larger than the analogous N_{eq}–Ta–C_{eq} angle in $[(Et_3SiNCH_2CH_2)_2N]Ta(CH_2CH_3)[N(CH{=}CH_2)(SiEt_3)]$ (109°). The Ta–N_{ax} bond lengths are somewhat shorter than the Ta–N_{eq} bond length, and both are shorter than would be

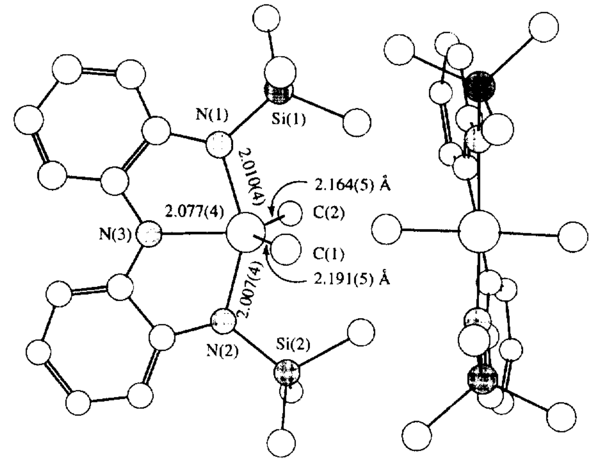


Fig. 1. Two views of the structure of $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2N]TaMe_2$; Ta–N(1)–Si(1) = 117.2(2)°, Ta–N(2)–Si(2) = 115.8(2)°. (See Table 2 for a comparison of bond lengths and angles in several structures.)

Table 1
Summary of crystallographic data, collection parameters and refinement parameters [a]

	$[ArN_3(TMS)]TaMe_2$	$[N_3(C_6F_5)]TaMe_2$	$[N_3(TMS)(AlMe_3)]TaMe_2$	$\{[HN_3(C_6F_5)]TaMe_2\}^+$ [b]
Empirical formula	$C_{20}H_{32}N_3Si_2Ta$	$C_{18}H_{14}F_{10}N_3Ta$	$C_{15}H_{41}AlN_3Si_2Ta$	$C_{44}H_{25}BF_{25}N_3Ta$
Formula weight	551.62	643.27	527.62	1262.43
Color, habit	red blocks	yellow cubes	pale yellow prisms	colorless prisms
Dimensions (mm)	0.33×0.26×0.10	0.33×0.32×0.28	0.32×0.15×0.10	0.21×0.18×0.30
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
a (Å)	11.658(3)	10.7030(1)	15.9297(4)	24.1706(5)
b (Å)	15.999(4)	14.8359(1)	22.7540(4)	15.1650(2)
c (Å)	12.505(2)	12.9842(1)	7.4416(2)	24.4337(5)
β (°)	105.54(2)	111.402(1)	90	90
V (Å^3)	2247.1(9)	1919.57(3)	2697.31(11)	8956.1(3)
Space group	$P2_1/c$	$P2_1/n$	$Cmc2_1$	$Pbca$
Z	4	4	4	8
ρ(calc.) (Mg m^{-3})	1.630	2.226	1.299	1.873
Collection temperature (K)	148(2)	183(2)	183(2)	183(2)
F(000)	1096	1224	1064	4904
μ(Mo Kα) (mm^{-1})	5.007	5.832	4.198	2.597
Total unique reflections	3207	2716	1788	4182
Observations	3207 [c]	2716 [c]	1788 [c]	4182 [c]
No. variable parameters	236	290	106	227
R	0.0314	0.0306	0.0692	0.084
R_w	0.0873	0.0775	0.1948	0.162
Goodness of fit indicator	1.063	1.126	1.144	1.462

[a] All experiments were carried out with a Siemens SMART/CCD system employing ω scans.

[b] A toluene solvate of the $[B(C_6F_5)_3(CH_3)]^-$ salt.

[c] Refinement was based upon F^2 and all unique data were used.

Table 2
A comparison of core bond lengths (Å) and angles (°)

	M–N$_{eq}$	M–N$_{ax}$	N$_{ax}$–M–N$_{ax}$	Ta–C	C–M–C
$[(Me_3SiN\text{-}o\text{-}C_6H_4)_2N]TaMe_2$	2.077(4)	2.010(4) 2.007(4)	149.8(2)	2.191(5) 2.164(5)	130.6(2)
$[(C_6F_5NCH_2CH_2)_2N]TaMe_2$	1.967(4)	2.087(4) 2.078(5)	152.0(2)	2.191(6) 2.199(6)	142.9(2)
$[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$	2.22(2)	1.985(9)	148.9(6)	2.14(3) 2.20(3)	106.6(12)
$\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$	2.280(15)	1.981(12) 1.965(13)	142.6(5)	2.09(2) 2.11(2)	102.0(6)
$[2,6\text{-}(CH_2NAr)_2C_5H_3N]ZrMe_2$ [a]	2.325(4)	2.101(4) 2.104(5)	139.6(2)	2.243(6) 2.248(7)	102.4(3)

[a] Ar = $2,6\text{-}Et_2C_6H_3$, Ref. [4].

expected on the basis of σ bonding alone (~2.2 Å). The N$_{ax}$–Ta–N$_{ax}$ angle is 149.8(2)°, which is typical for all four species discussed here, the structural data for which are gathered in Table 2 for purposes of comparison. Fractional atomic coordinates are given in Table 3.

An X-ray study of $[N_3(C_6F_5)]TaMe_2$ revealed a molecule that has an approximate TBP structure for the TaN_3C_2 core similar to that found for $[ArN_3(TMS)]TaMe_2$, but one in which two *ortho* fluorine atoms are within a weakly bonding distance of the metal (Fig. 2; Tables 1 and 2). An interaction of this general type was also found in $[(C_6F_5NCH_2CH_2)_3N]V$ [15], although the V···F distance is much longer (2.652 Å) than the Ta···F distance in $[N_3(C_6F_5)]TaMe_2$ (~2.4 Å), a difference that is even greater when one considers the smaller size of V(III) relative to Ta(V). The Ta···F interaction is much longer than a typical Ta–F covalent bond, e.g. ~1.90 Å in $[Ta_2F_{10}O]^{2-}$ [16] or $[Ta(\eta^5\text{-}C_5Me_5)F_4]_2$ [17]. However, since the C_6F_5 ring is freely rotating on the ^{19}F NMR time scale, even at −80°C, the strength of the Ta···F interaction cannot be more than ~10 kcal mol^{-1} at most. This interaction must be the origin of the relatively large two bond (CF) or three bond (HF) couplings, which are averages of coupling to a fluorine that is 'bound' to tantalum and one that is 'unbound'. As a consequence of the interaction between Ta and F(11) and F(21) the entire ligand system forms an approximately planar pentagonal arrangement around the metal, the internal angles (starting with F–Ta–F and proceeding clockwise in Fig. 2) being 65, 72,

Table 3

Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters of the non-hydrogen atoms for $[ArN_3(TMS)]TaMe_2$, $[N_3(C_6F_5)]TaMe_2$, $[N_3(TMS)(AlMe_3)]TaMe_2$ and $[(C_6F_5NCH_2CH_2)_2NH)]TaMe_2\}^+$-$\{B(C_6F_5)_3(CH_3)\}^-$(toluene)

	x	y	z	U_{eq}
$[ArN_3(TMS)]TaMe_2$				
Ta1	5221(1)	1707(1)	668(1)	21(1)
Si1	2381(1)	1750(1)	−472(1)	28(1)
Si2	7890(1)	2208(1)	699(1)	30(1)
N1	3552(3)	1371(2)	643(3)	25(1)
N2	6976(4)	1678(2)	1406(4)	22(1)
N3	5411(3)	948(2)	2052(3)	21(1)
C1B	4371(4)	729(3)	2369(4)	23(1)
C1A	3330(4)	946(3)	1544(4)	26(1)
C1C	4281(5)	384(3)	3369(4)	28(1)
C1D	3166(5)	218(3)	3518(5)	35(1)
C1F	2213(4)	757(3)	1714(5)	32(1)
C1E	2148(5)	379(3)	2685(5)	36(1)
C1	4918(5)	3035(3)	919(5)	33(1)
C2F	8649(4)	993(3)	2826(4)	29(1)
C2B	6563(4)	683(3)	2621(4)	21(1)
C2A	7450(4)	1128(3)	2288(4)	22(1)
C2E	8974(4)	389(3)	3646(4)	30(1)
C2D	8106(5)	−99(3)	3900(4)	31(1)
C2	5344(5)	1039(3)	−802(4)	33(1)
C3C	6901(4)	38(3)	3388(4)	25(1)
C11	2999(6)	2229(4)	−1561(5)	45(1)
C12	1402(5)	864(3)	−1144(5)	38(1)
C13	1554(5)	2586(3)	66(5)	41(1)
C21	8730(5)	1434(4)	96(5)	41(1)
C22	8888(6)	2968(4)	1634(6)	55(2)
C23	6927(6)	2828(4)	−470(5)	51(2)
$[(C_6F_5NCH_2CH_2)_2N]TaMe_2$				
Ta1	1338(1)	2096(1)	1138(1)	27(1)
F11	904(4)	3158(2)	2415(3)	40(1)
F12	387(4)	4117(2)	3980(3)	46(1)
F13	23(4)	3256(3)	5716(3)	49(1)
F14	157(4)	1417(3)	5806(3)	57(1)
F15	646(4)	464(3)	4302(3)	54(1)
F21	1174(4)	3659(2)	591(3)	39(1)
F22	1310(4)	5355(2)	−97(3)	51(1)
F23	2009(4)	5654(3)	−1908(3)	60(1)
F24	2517(4)	4205(3)	−2988(3)	59(1)
F25	2362(4)	2538(3)	−2353(3)	49(1)
N1	1169(5)	1360(3)	2450(4)	32(1)
N2	1681(5)	2189(3)	−334(4)	33(1)
N3	1618(5)	839(3)	790(4)	34(1)
C1	1217(8)	381(4)	2422(5)	47(2)
C2	1842(8)	118(5)	1597(6)	54(2)
C3	1736(7)	1350(4)	−932(5)	39(1)
C4	2095(7)	605(4)	−105(5)	42(2)
C5	3274(6)	2683(5)	2153(5)	40(1)
C6	−830(6)	2374(5)	439(5)	44(2)
C11	722(6)	2711(4)	3286(5)	32(1)
C12	467(6)	3215(4)	4065(5)	33(1)
C13	285(6)	2786(4)	4939(5)	35(1)
C14	365(6)	1864(5)	4978(5)	38(1)
C15	630(6)	1370(4)	4179(5)	35(1)
C16	853(5)	1777(4)	3283(5)	32(1)
C21	1508(6)	3791(4)	−329(4)	33(1)
C22	1557(6)	4659(4)	−657(5)	37(1)
C23	1890(6)	4812(4)	−1576(5)	42(2)
C24	2150(6)	4072(5)	−2109(5)	43(2)
C25	2080(6)	3201(5)	−1759(5)	36(1)
C26	1759(6)	3021(4)	−822(5)	29(1)
$[(Me_3SiNCH_2CH_2)_2NAlMe_3)]TaMe_2$				
Ta	0	−1413(1)	−3898	28(1)
Si1	−2052(3)	−1143(2)	−3561(7)	35(1)
Al1	0	−2522(3)	−7151(10)	38(2)
N1	−1201(6)	−1643(5)	−3773(29)	31(3)
N2	0	−2370(8)	−4446(25)	30(4)
C1	−1495(9)	−2255(6)	−3781(45)	41(4)
C2	−763(9)	−2657(6)	−3568(30)	39(5)
C3	−1027(9)	−2164(8)	−8249(24)	47(5)
C4	0	−3390(12)	−7404(55)	64(9)
C5	0	−923(13)	−1345(39)	32(6)
C6	0	−771(14)	−6002(45)	54(9)
C11	−2480(14)	−1214(13)	−1247(35)	59(6)
C12	−2840(18)	−1318(12)	−5337(44)	71(8)
C13	−1752(11)	−358(8)	−3920(52)	60(5)
$[(C_6F_5NCH_2CH_2)_2NH)]TaMe_2\}^+\{B(C_6F_5)_3(CH_3)\}^-$(toluene)				
Ta1	1557.2(3)	2732.3(5)	3741.5(3)	418(3)
F12	616(6)	4275(8)	4518(5)	79(4)
F13	−473(6)	4223(11)	4727(5)	118(6)
F14	−971(5)	2656(13)	4959(5)	128(6)
F15	−364(6)	1140(10)	4961(5)	109(5)
F16	720(5)	1220(8)	4741(5)	79(4)
F22	2097(4)	1260(7)	2600(5)	66(3)
F23	2087(4)	1401(8)	1504(5)	81(4)
F24	2218(4)	3033(8)	1035(4)	72(3)
F25	2337(4)	4461(9)	1668(4)	72(3)
F26	2335(4)	4318(7)	2767(4)	59(3)
F32	150(5)	2283(8)	7655(4)	79(4)
F33	−385(7)	1993(10)	8591(5)	119(5)
F34	−1355(6)	2810(9)	8819(5)	104(4)
F35	−1799(5)	3905(9)	8039(5)	88(4)
F36	−1322(4)	4111(8)	7084(5)	74(3)
F43	892(5)	5663(8)	7690(5)	94(4)
F44	1530(5)	5915(8)	6799(6)	98(4)
F45	89(4)	4470(7)	7693(4)	70(3)
F45	1379(5)	4885(8)	5895(5)	87(4)
F46	599(4)	3653(8)	5889(4)	69(3)
F52	919(4)	2451(5)	6780(5)	64(3)
F53	1171(5)	790(8)	6526(6)	106(5)
F54	398(5)	−329(8)	6138(5)	76(3)
F55	−658(5)	247(7)	6023(5)	80(4)
F56	−938(4)	1869(7)	6304(4)	66(3)
N1	1289(5)	2757(10)	4501(5)	44(4)
N2	2242(5)	2704(10)	3296(5)	44(4)
N3	2297(6)	2823(19)	4318(7)	126(10)
C1	1602(8)	2823(15)	5023(8)	70(6)
C2	2181(8)	2689(13)	4869(7)	54(5)
C3	2816(8)	2706(18)	3488(8)	85(8)
C4	2816(7)	2663(12)	4087(7)	50(5)
C5	1140(7)	3789(11)	3362(7)	46(5)
C6	1134(7)	1638(12)	3429(8)	59(6)
C7	−615(7)	3707(12)	6229(7)	54(5)
C11	693(7)	2724(14)	4599(6)	43(5)
C12	388(8)	3484(18)	4611(7)	59(6)
C13	−170(12)	3476(22)	4709(8)	79(8)
C14	−428(10)	2747(27)	4850(9)	84(8)
C15	−153(10)	1942(16)	4852(7)	56(6)

(continued)

Table 3 (*continued*)

	x	y	z	U_{eq}
C16	427(9)	1958(12)	4733(7)	50(5)
C21	2201(6)	2813(13)	2729(8)	43(5)
C22	2144(6)	2080(12)	2383(10)	52(6)
C23	2144(7)	2144(21)	1816(10)	70(7)
C24	2224(8)	2918(25)	1592(8)	80(10)
C25	2275(7)	3675(16)	1917(11)	62(6)
C26	2260(7)	3589(13)	2474(8)	41(5)
C31	−569(7)	3155(12)	7309(6)	41(5)
C32	−354(8)	2625(13)	7725(8)	50(5)
C33	−613(9)	2516(11)	8211(8)	49(5)
C34	−1111(9)	2935(12)	8327(9)	56(6)
C35	−1327(8)	3444(13)	7928(8)	51(5)
C36	−1068(7)	3549(12)	7439(8)	47(5)
C41	291(7)	3990(12)	6795(7)	44(5)
C43	814(8)	5166(13)	7252(10)	60(6)
C44	1124(8)	5276(12)	6797(11)	62(6)
C45	1057(8)	4766(15)	6350(9)	59(6)
C45	403(7)	4527(12)	7234(8)	46(5)
C46	640(7)	4140(12)	6362(7)	43(5)
C51	−22(6)	2305(11)	6527(7)	36(4)
C52	510(7)	1926(11)	6579(7)	42(5)
C53	645(8)	1057(14)	6456(9)	62(6)
C54	264(8)	515(13)	6245(8)	52(5)
C55	−272(8)	799(13)	6203(8)	52(5)
C56	−390(7)	1652(14)	6341(7)	47(5)
B	−234(8)	3284(14)	6721(9)	46(6)
C1S	2104(8)	00(12)	4925(9)	55(5)
C2S	1971(8)	04(15)	4400(10)	67(6)
C3S	2333(14)	148(16)	3995(10)	85(8)
C4S	2875(15)	322(13)	4130(14)	93(11)
C5S	3020(9)	308(14)	4666(16)	87(9)
C6S	2639(11)	160(13)	5059(10)	71(6)
C7S	1691(9)	−177(16)	5366(10)	100(8)

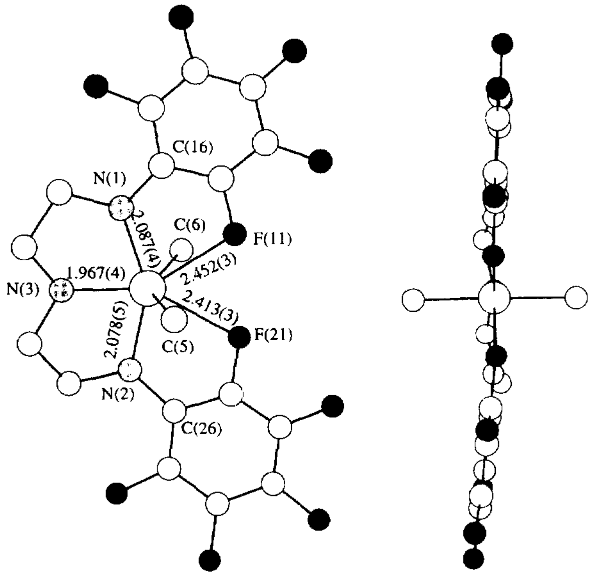
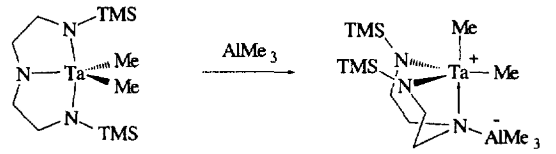


Fig. 2. Two views of the structure of $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$; Ta–N(1)–C(16) = 121.3(4)°, Ta–N(2)–C(26) = 122.3(4)°.

76, 76 and 72°, for a total of ~360°. The C(5)–Ta–C(6) angle therefore is forced 'open' to 142.9(2)°. The Ta–C bond lengths, however, are virtually the same as in $[ArN_3(TMS)]TaMe_2$, as is the N_{ax}–Ta–N_{ax} angle (Table 2). The Ta–N_{ax} distances are longer and the Ta–N_{eq} distance is ~0.1 Å shorter than the analogous distances in $[ArN_3(TMS)]TaMe_2$ (Table 2).

Addition of $AlMe_3$ to $[N_3(TMS)]TaMe_2$ led to formation of a zwitterionic species in which the aluminum has added to the central nitrogen. We proposed that the resulting species had the pseudo-trigonal bipyramidal structure shown in Eq. (7) on the basis of the fact that two inequivalent tantalum methyl groups clearly are still present and have ^1H chemical shifts that are similar (0.85 and 0.55 ppm). Proton NMR spectra of $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ in the presence of $[N_3(TMS)]TaMe_2$ show that the Ta–Me groups in $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ equilibrate, most likely by intermolecular exchange of trimethylaluminum between $[N_3(TMS)]TaMe_2$ and $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$. An X-ray study of $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ (Fig. 3) showed that it is only a slightly perturbed version of what we would expect the structure of $[N_3(TMS)]TaMe_2$ to be on the basis of the structures of $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ [2] and $[ArN_3(TMS)]TaMe_2$. The Al–N_{eq} bond length (2.04(2) Å) is approximately what is found for an $AlMe_3$–N(amine) bond (e.g. 2.028(3) Å in $(AlMe_3)_2[14]aneN_4$ [18]), and the nitrogen is virtually tetrahedral. (All angles at N_{eq} are 110.5° except C–N_{eq}–C, which is 105.5°.) The dramatically lengthened Ta–N_{eq} bond length (2.22(2) Å) is what would be expected if N(2) is now behaving essentially as a pure σ donor to Ta. The N_{ax}–Ta–N_{ax} angle has changed little from what it was in the first two complexes (Table 2),



(7)

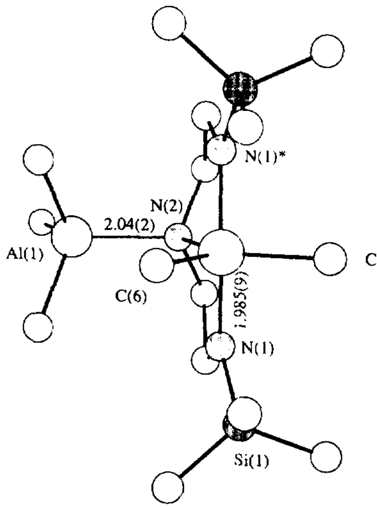
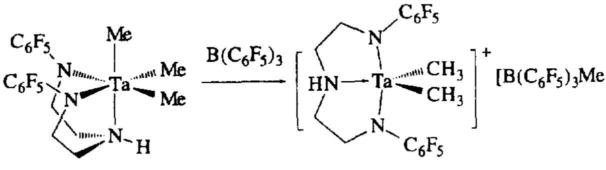


Fig. 3. Structure of $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$; Ta–N(2)–Si(1) = 124.7(6) Å, N(2)–Ta–C(6) = 122.4(10)°; N(2)–Ta–C(5) = 131.0(9)°.

but the Ta–N_{ax} distances are significantly shorter. The Ta–C bonds are also essentially unchanged, but the C(5)–Ta–C(6) angle (106.6(12) Å) is more like the N_{eq}–Ta–C_{eq} angle found in $[(Et_3SiNCH_2CH_2)_2N]Ta(CH_2CH_3)[N(CH{=}CH_2)(SiEt_3)]$ (109°) [2]. The Ta–N(1)–Si(1) angle (124.7(6)°) is similar to the analogous Ta–N–C angles of 121.3(4) and 122.3(4)° in $[N_3(C_6F_5)]TaMe_2$, but slightly larger than the Ta–N–Si angles of 115.8(2) and 117.2(2)° found in $[ArN_3(TMS)]TaMe_2$. We propose that the smaller C–Ta–C angle in $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ leads to greater steric repulsion between the TMS groups and the equatorial methyl groups and to the Ta–N–Si angles of ~125°. We also propose that the smaller C–Ta–C angle is an electronic consequence of the loss of π bonding between N(2) and Ta (see Section 4).

Cationic species can be obtained by adding a proton to N_{eq} in $[N_3(C_6F_5)]TaMe_2$. For example, the NMR spectrum of a mixture of $[N_3(C_6F_5)]TaMe_2$ and $[PhMe_2NH][B(C_6F_5)_4]$ in CD_2Cl_2 at −35°C suggests that $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+\{B(C_6F_5)_4\}^-$ and free Me_2NPh are formed; the NH resonance is found at 4.50 ppm as a broad singlet. Cationic species also can be prepared by removing a methyl ligand from $[HN_3(C_6F_5)]TaMe_3$ with $B(C_6F_5)_3$ [19,20] (Eq. (8)). An X-ray structure of $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+\{MeB(C_6F_5)_3\}^-$ (a toluene solvate; Fig. 4) shows that the anion and the toluene are separated from the cation, with no contacts less than 3 Å. The molecule of toluene is found near the cation, but not close enough to be bonded to it. The cation has a core structure that is closely analogous to that of $[N_2(TMS)NAlMe_3]TaMe_2$ (Table 2) except that N_{eq} is only modestly distorted from planarity with C–N_{eq}–C = 123.1° and Ta–N_{eq}–C angles of 116.4 and 115.6° (sum = 355.1°). For comparison, the analogous angles in $[(Et_3SiNCH_2CH_2)_2N]Ta(CH_2CH_3)[N(CH{=}CH_2)(SiEt_3)]$ are 110.2, 120.9 and 122.8° (sum = 353.9°), while the analogous sum of angles in $[N_2(TMS)NAlMe_3]TaMe_2$ is 326.5°. The C–Ta–C angle is now only 102.0(6)°, close to that found in $[N_2(TMS)NAlMe_3]TaMe_2$. We propose that the *ortho* fluorines on the C_6F_5 rings have no room to interact with the metal, as they do in $[N_2(C_6F_5)]TaMe_2$, and the rings consequently are turned so they are approximately perpendicular to the TaN_3 'pseudo-plane'. A more spherically symmetric (versus almost planar) cation also may lead to more efficient packing in the crystal.



(8)

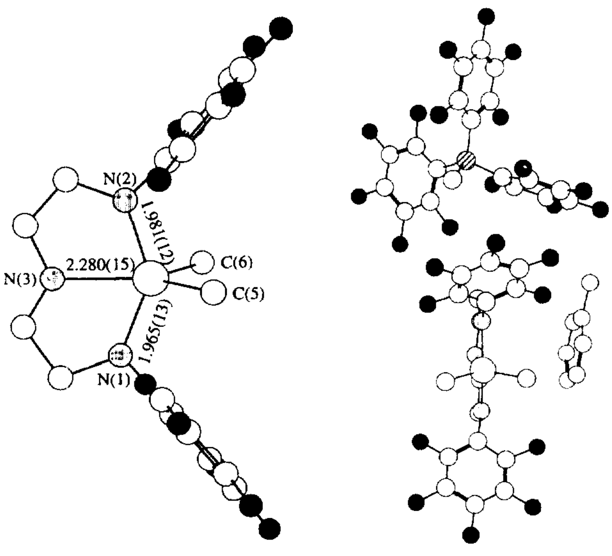
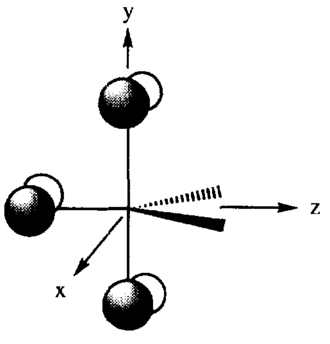


Fig. 4. Structure of $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+\{B(C_6F_5)_3(CH_3)\}^-$(toluene); Ta–N(2)–$C_{ipso}$ = 118.7(10)°, Ta–N(1)–C_{ipso} = 118.6(10)°.

It is interesting to contrast the reactions of $[N_3(TMS)]TaMe_2$ with $AlMe_3$ and $[N_3(C_6F_5)]TaMe_2$ with a proton source with analogous reactions involving $[ArN_3(TMS)]TaMe_2$. For example, $[ArN_3(TMS)]TaMe_2$ does not react with $[HMe_2NPh][B(C_6F_5)_4]$. Presumably the basicity of the central amido nitrogen in the $[ArN_3(TMS)]^{3-}$ ligand is simply too low compared to what it is in the $[N_3(TMS)]^{3-}$ ligand as a consequence of conjugation of the lone pair on that nitrogen with the two phenyl systems. Protonation of the amido nitrogen in the distantly related $[(Ph_2PCH_2SiMe_2)_2N]^-$ ligand bound to iridium has been observed in a variety of circumstances, especially those that involve dihydrogen [21–23].

4. Discussion

The π bonding in TBP complexes of the type discussed here can be evaluated qualitatively using the coordinate system shown below. (The three p orbitals parallel to the *x* axis that are shown below correspond to the three p orbitals on the nitrogen atoms.) The d_{yz} orbital (B_2 symmetry in C_{2v}) cannot be involved in bonding of any type in the trigonal bipyramidal species shown. The two d orbitals that are likely to be most important for π bonding are the d_{xy} (A_2 symmetry in C_{2v}, overlapping with the unsymmetric combination of the p orbitals on the axial nitrogens) and d_{xz} (B_1 symmetry in C_{2v}, overlapping with the p orbital on the equatorial nitrogen). The X-ray structural data suggest that in $[ArN_3(TMS)]TaMe_2$ and $[(C_6F_5NCH_2CH_2)_2N]$-



$TaMe_2$ there is a considerable degree of π bonding between Ta and both axial and equatorial nitrogens. A representation of the equatorial σ bonds transforms as $2A_1$ (p_z, $d_{x^2-y^2}$ or d_{z^2}) + B_1 (p_x or d_{xz}). Therefore, in the presence of d_{xz} π bonding to N_{eq}, only p_x is available to form two σ hybrids to the two methyl groups in the equatorial positions and the C–Ta–C angle is relatively large. In the absence of significant π bonding between the metal and N_{eq}, as in $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ and $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$, d_{xz} also may be used to form the bonds to the methyl groups, and the C–Ta–C angle can be much smaller. It should be noted, however, that the Ta–N_{eq} bond length in $[(Et_3SiNCH_2CH_2)_2N]Ta(CH_2CH_3)[N(CH{=}CH_2)(SiEt_3)]$ (1.966(8) Å) suggests that π bonding (using the d_{xz} orbital) is significant, yet the N_{eq}–Ta–C_{eq} angle in $[(Et_3SiNCH_2CH_2)_2N]Ta(CH_2CH_3)[N(CH{=}CH_2)(SiEt_3)]$ (109°) is closer to the 'small' C–Ta–C angle found in $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ and $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$.

The structures of $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ and $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$ are remarkably similar to the structure of $[2,6\text{-}(ArNCH_2)_2C_5H_3N]ZrMe_2$ (Ar = 2,6-$Et_2C_6H_3$) [4]. Several structural parameters for this species are listed for comparison in Table 2. The Zr–N_{ax}, Zr–N_{eq} and Zr–C distances are all approximately 0.1 Å longer than the corresponding distances in the two tantalum complexes, presumably as a consequence of the larger size of Zr^{4+} compared to Ta^{5+}. However, the N_{ax}–M–N_{ax} and C–M–C angle in both the zirconium and tantalum complexes are closely similar, consistent with relatively poor π bonding between the pyridyl nitrogen and the zirconium center. It was concluded on the basis of extended Hückel MO studies that $[2,6\text{-}(ArNCH_2)_2C_5H_3N]^{2-}$ is an eight electron ligand (with little π bonding between the metal and the pyridyl nitrogen), and that the frontier orbitals in the $[2,6\text{-}(ArNCH_2)_2C_5H_3N]Zr$ fragment consist of two a_1 orbitals and one b_2 orbital, although their energies are significantly different from the a_1 and b_2 orbital energies in the analogous $(\eta^5\text{-}C_5H_5)_2Zr$ fragment. Therefore it is perhaps not circumstantial that the C–M–C angles in $[2,6\text{-}(ArNCH_2)_2C_5H_3N]Zr$, $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$ and $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$ are all similar and not much different than in a typical zirconocene dialkyl complex.

The $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$ complex is especially interesting in view of the rarity of cationic tantalum(V) complexes [24]. $[Cp_2TaMe_2]^+BF_4^-$ and related species were prepared by treating trimethyl complexes with $[CPh_3]^+BF_4^-$ in dichloromethane [25,26]. $[Ta(\eta^5\text{-}C_5H_4Me)_2Me_2]^+BF_4^-$ and $[Ta(\eta^5\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)Me_2]^+BF_4^-$ were prepared by similar methods. $[Ta(\eta^5\text{-}C_5H_4Me)_2(Me)(Br)]^+$ salts were also prepared, although they were not thoroughly characterized. Niobium and tantalum complexes of the type $[MCp_2(CH_2SiMe_3)_2]^+$ have been prepared by oxidation of the $MCp_2(CH_2SiMe_3)_2$ complexes with AgX ($X^- = BF_4^-$ or SbF_6^-) [27]. Two biscyclopentadienyl complexes have been structurally characterized, $[Ta(\eta^5\text{-}C_5Me_5)_2(Me)(OH)][B(OH)(C_6F_5)_3]$ [28] and $[Ta(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Me_2][CF_3SO_3]$ [29]. In each case a pseudotetrahedral cation is observed. In the latter compound the triflate ion is interacting weakly with the cation through contacts that vary between 3.3 and 3.5 Å. The Cp–Ta–Cp* angle is typical (136°), as are the Me–Ta–Me angle (96°) and Ta–Me distances (2.168(12) and 2.174(12) Å). These values should be compared with the N_{ax}–Ta–N_{ax} angle (143°), Me–Ta–Me angle (102°) and Ta–Me distances (2.09(2) and 2.11(2) Å) in $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$. We could find no other examples of Ta(V) alkyl cations in the literature in which the tantalum is the cationic center. (In a complex such as $[Cp^*(i\text{-}Pr_2HNBC_4H_4)TaMe_2]^+$ the positive charge is localized on the nitrogen center [30].) Relatively weakly coordinating anions such as $[B(C_6F_5)_3(CH_3)]^-$ [19,20] and $[B(C_6F_5)_4]^-$ [31,32] are most likely to be compatible with cationic tantalum centers, unless the coordination sphere is extremely crowded, as in 16 electron biscyclopentadienyl complexes such as $[Ta(\eta^5\text{-}C_5H_4Me)_2Me_2]^+BF_4^-$. Even in $[(Me_3SiNCH_2CH_2)_3N]Ta(Me)(triflate)$ [33] the triflate ion binds to the metal (Ta–O = 2.243 Å) at the expense of amine nitrogen donor binding (Ta–N = 2.536 Å).

The results reported here suggest that planar triamido ligands are able to stabilize five-coordinate TBP complexes, but also that TBP complexes that contain a diamido amine ligand (with an electrophile bound to the central nitrogen) are also favorable species. Two TBP complexes that contain C_6F_5-substituted diamido amine ligands have been reported (one containing Re [34] and one containing V [15]), other TMS-substituted diamidoamine ligands and complexes thereof are known [7,35–38], and Ti and Zr complexes that contain the $[(t\text{-}BuN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ligand have been reported recently [39]. It should prove interesting to explore the chemistry of $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+$ and similar cationic species vis-a-vis related metallocene species, and to attempt to prepare other types of $\{[(C_6F_5NCH_2CH_2)_2E]TaMe_2\}^+$ complexes in which E (the donor) is not NH. Since $[TaCp_2Me_2]^+$ relatively easily loses a proton to give $TaCp_2(CH_2)Me$, it also will be interesting to determine whether the 'acidity' of α protons in tantalum(V) cations outside the biscyclopentadienyl class is also significant, and if so, whether such alkylidene complexes can be observed or isolated. If such cationic species do not lose an alkyl α proton relatively easily, then they perhaps could be viable intermediates in Ziegler–Natta-like olefin polymerization reactions.

5. Supplementary material

An ORTEP drawing, crystal data and structural refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and observed and calculated structure factors for $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2N]TaMe_2$, $[(C_6F_5NCH_2CH_2)_2N]TaMe_2$, $[(Me_3SiNCH_2CH_2)_2NAlMe_3]TaMe_2$, and $\{[(C_6F_5NCH_2CH_2)_2NH]TaMe_2\}^+\{B(C_6F_5)_3Me\}^-$-(toluene) (60 pages) are available from the authors on request.

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