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Synthesis of tantalum fluoride complexes supported by bis(trimethylsilyl)benzamidinate ligands. X-ray structures of $[PhC(NSiMe_3)_2]_2TaF_3$ and $[PhC(NSiMe_3)_2]_2TaFPh_2$

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Dedicated to Professor Martin Bennett on the occasion of his retirement.

Abstract

The reaction of $[PhC(NSiMe_3)_2]Li(TMEDA)$ with TaF_5 yields complex **1**, $[PhC(NSiMe_3)_2]_2TaF_3$, in 40% isolated yield. The solid-state structure of **1** shows a pentagonal, bipyramidal coordination geometry. Variable temperature ^{19}F-NMR experiments reveal one singlet at an ambient temperature; decoalescence to two singlets (1:2 integration) is observed at $-20°C$. Complex **1** reacts with Me_2Mg to produce $[PhC(NSiMe_3)_2]_2TaMe_3$ (**2**). The reaction of **1** with Ph_2Mg yields $[PhC(NSiMe_3)_2]_2TaF_2Ph$ (**3**) and $[PhC(NSiMe_3)_2]_2TaFPh_2$ (**4**). Characterization of **4** by X-ray crystallography shows a ligand arrangement similar to that of **1**.

Keywords: Tantalum; Amidinate complexes; Metal fluoride complexes

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1. Introduction

Transition metal fluoride complexes catalyze a wide variety of transformations, including olefin polymerization [1], reduction of perfluorocarbons [2] and hydrosilylation of amines [3]. In addition, transition metal fluoride compounds have been studied for their potential role in C–F bond activation reactions [4]. The ability of fluoride ligands to act as strong π-donors toward metals sets their reactivity apart from that of other halide derivatives [5,6]. In contrast to their chloride or bromide counterparts, transition metal fluorides are often not suitable synthons for the introduction of organometallic ligands. Consequently, the properties of many potential fluoride derivatives remain unexplored. The synthesis of fluoride complexes with cyclopentadienyl ligands is most often achieved through the metathesis of the bromide or chloride ligands of the organometallic complex with an alkali metal (CsF, NaF) [3,7] or main group (AsF_3, Me_3SnF) [8,9] fluoride transfer agent. Clearly, these routes add the complication of an additional step to first introduce the ancillary ligand. These reactions also often proceed in low yield and may produce solvated complexes.

A limited number of organotantalum fluoride complexes have been reported. Most are half-sandwich complexes [10,11] which, along with a few alkyl derivatives [9,12], have been prepared by halide metathesis routes. The synthesis of the monomeric metallocene complex, $Cp^*_2TaF_3$ ($Cp^*=\eta^5-C_5Me_5$) by reaction of pyridinium·HF_x with $Cp^*_2TaH_3$ was recently reported [13]. To the best of our knowledge, there have been no reports of organometallic derivatives prepared directly from TaF_5.

Nitrogen-based ancillary ligands have received attention for their ability to support metal centers in a range of catalytic reactions [14–16]. We have studied use of the bis(trimethylsilyl)benzamidinate ligand in early transition metal complexes [17–19]. This ligand imparts considerable steric shielding (similar to Cp* [20]) and

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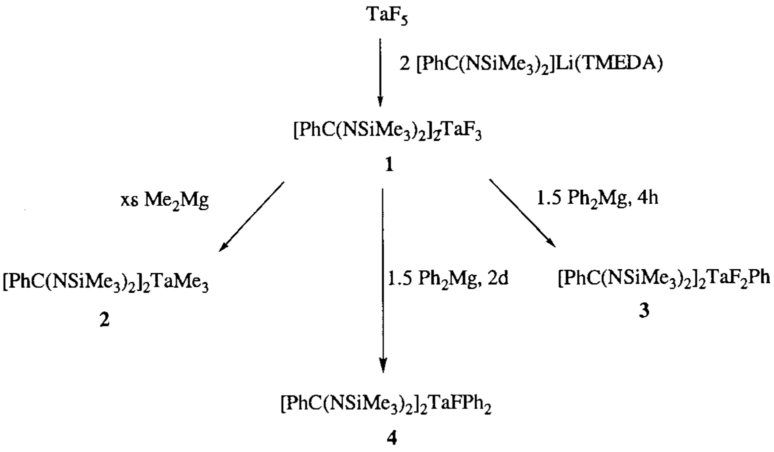

Scheme 1. Synthesis of alkyl and aryl derivatives from **1**.

excellent solubility properties to its metal complexes. Additionally, the amidinate is a four-electron donor [20], which should provide a more electrophilic metal center than in analogous metallocene complexes. Herein we report the synthesis of $[PhC(NSiMe_3)_2]_2TaF_3$ directly from tantalum pentafluoride, as well as substitution of the remaining Ta–F bonds with common reagents to yield alkyl and aryl derivatives.

2. Results and discussion

2.1. Synthesis and characterization of $[PhC(NSiMe_3)_2]_2TaF_3$ *(**1**)*

Complex **1** was prepared by reaction of TaF_5 with two equivalents of $Li[PhC(NSiMe_3)_2](TMEDA)$ in toluene at room temperature (Scheme 1). The product is very soluble in hydrocarbon solvents, but pale yellow crystals may be isolated from hexanes in 40% yield. An X-ray diffraction study was undertaken; an ORTEP diagram of **1** is shown in Fig. 1. Selected bond lengths and angles are shown in Table 1.

Inspection of the structural parameters suggests that of the three common idealized geometries for seven-coordinate molecules (capped octahedron, pentagonal bipyramid, capped trigonal prism) [21,22], the environment of the complex is best described as a distorted pentagonal bipyramid. The X-ray structures of other $(amidinate)_2TaX_3$ (X=Me, Cl) complexes also show a distorted pentagonal bipyramidal geometry [19,23,24]. Three of the amidinate nitrogens (N1, N3, N4) and two of the fluorides (F1, F2) of **1** lie in the pseudo pentagonal plane and the remaining nitrogen and fluoride atoms (N2 and F3) occupy the axial positions. The mean distance of equatorial atoms from the least-squares plane is 0.38 Å. The three fluorides bound to the tantalum in **1** are arranged in an arc; the F–Ta–F angle between the two outer fluorides, F1 and F2 is 142°, and the inner fluoride, F3, is separated by 75–83° from the outer fluorides. This arc geometry is observed in the related compound, $[PhC(NSiMe_3)_2]_2TaMe_3$ [19].

The steric bulk of the nitrogen substituents affects the amount of perturbation from an idealized pentagonal bipyramidal geometry, as well as the geometrical arrangement of the amidinate ligands. If the nitrogen substituents are small (e.g. ^{i}Pr, Cy), all four nitrogen atoms may be equatorial, making it possible for the three remaining substituents to arrange in a T-formation [25,26]. If the steric bulk of the nitrogen substituents (e.g. $SiMe_3$) or the other tantalum substituents are large, then one nitrogen must be located in the axial

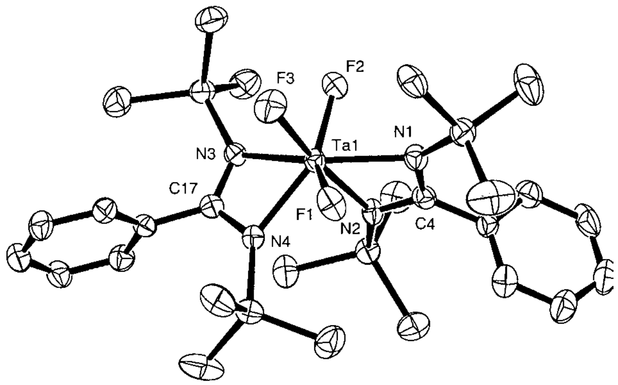

Fig. 1. ORTEP diagram of **1** drawn with 50% probability thermal ellipsoids. Hydrogen atoms omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **1**

Ta–F1	1.924(2)	F1–Ta–N4	77.9(1)
Ta–F2	1.926(2)	F2–Ta–N1	78.4(1)
Ta–F3	1.893(2)	N1–Ta–F1	75.8(1)
Ta–N1	2.181(3)	F2–Ta–N3	79.4(1)
Ta–N2	2.213(3)	N4–Ta–N3	61.3(1)
Ta–N3	2.192(3)	N1–Ta–N2	61.0(1)
Ta–N4	2.124(3)	F3–Ta–N2	171.8(1)

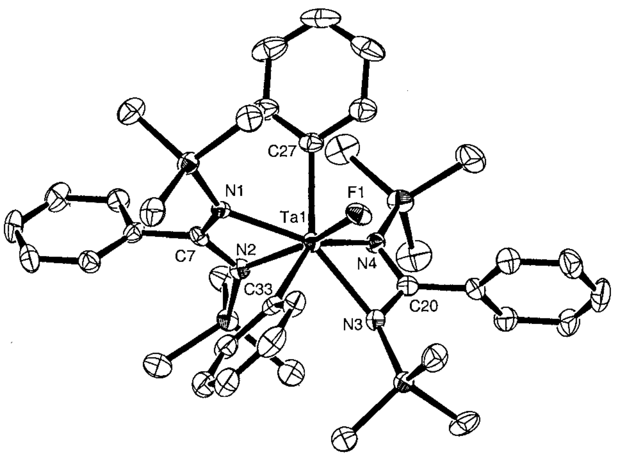

Fig. 2. ORTEP diagram of **4** drawn with 50% probability thermal ellipsoids. Hydrogen atoms omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for **4**

Ta–F1	1.886(3)	N4–Ta–C27	80.0(1)
Ta–C27	2.281(5)	N1–Ta–C27	74.4(1)
Ta–C33	2.270(5)	N1–Ta–C33	72.5(1)
Ta–N1	2.212(3)	C33–Ta–N3	79.8(1)
Ta–N2	2.140(4)	N4–Ta–N3	61.6(1)
Ta–N3	2.232(4)	N1–Ta–N2	61.8(1)
Ta–N4	2.164(4)	F1–Ta–N2	165.3(1)

position, leaving the equatorial plane significantly distorted [19,23] and resulting in the arc formation described above. The steric bulk from the pair of bis(trimethylsilyl)benzamidinate ligands also inhibits the formation of a dimeric structure. The monopentamethylcyclopentadienyl complex, Cp*TaF_4, is dimeric in the solid state while the mixed ligand complex, Cp*[(*p*-MeO)PhC$(NSiMe_3)_2$]TaF_3 [27] and [PhC$(NSiMe_3)_2$]$_2TaF_3$ are both monomeric. This is consistent with steric similarity of [PhC$(NSiMe_3)_2$] to Cp*.

Identical C–N bond lengths indicate delocalization within the NCN amidinate core. The $Ta–F_{ax}$ and $Ta–F_{eq}$ bond lengths are 1.893(2) and 1.925(2) Å (average), respectively. The Ta–F bond lengths of **1** are longer than the terminal Ta–F bonds in $[TaF_5]_4$ (1.77 Å) [28]. The elongation is also observed in {$[Cp^*TaF_4]_2$}{AsF_3} (1.90 Å average Ta–F bond length) [10].

Variable temperature ^{19}F-NMR spectroscopic studies on **1** suggest fluxional behavior of the fluoride ligands on the NMR timescale. At 25°C, a single resonance (sharp singlet) is observed which upon cooling to − 50°C decoalesces into two resonances (singlets, ratio 2:1). No F–F coupling was observed, probably due to line broadening from the quadrupolar ^{181}Ta nucleus ($I = 7/2$) [29]. As observed in other reported group III–V complexes with two bis(trimethylsilyl)benzamidinate ligands [17,19,20,30], a single trimethylsilyl peak is observed in the ^{1}H-NMR spectrum at room temperature. Decoalescence of this peak was not observed upon cooling to − 138°C. A variety of pentagonal bipyramidal and capped trigonal prismatic configurations are plausible solution structures of **1**. Each of these, yields two distinct fluoride environments and allows for equilibration of all four $SiMe_3$ groups either by symmetry alone or a combination of symmetry and rotation about the twofold axis within the benzamidinate ligand ('ring flipping'). The facile configurational interconversion is precedented in seven coordinate complexes [22,31,32]; additionally, ring flipping has been observed to occur in amidinate complexes [33–35].

The trifluoride (**1**) is stable in solution at room temperature for several days, as monitored by ^{1}H- and ^{19}F-NMR spectroscopy in C_6D_6, but it decomposes to a mixture of unidentified products at temperatures above 75°C. In solution, **1** does not react with dry O_2; as a solid or in solution it decomposes slowly in air.

2.2. Synthesis and characterization of aryl and alkyl derivatives

To explore the lability of the fluoride ligands, we examined the reaction of **1** with alkylating agents. Complex **1** reacts with an excess of Me_2Mg to form the known trimethyl compound, [PhC$(NSiMe_3)_2$]$_2TaMe_3$ (**2**) [19]. Complex **1** also undergoes salt metathesis reactions with diphenylmagnesium to form tantalum aryl derivatives (Scheme 1). The reaction of **1** with 1.5 equivalents of Ph_2Mg in diethyl ether or THF for several days yields a mixture of [PhC$(NSiMe_3)_2$]$_2$-TaF_2Ph (**3**) and [PhC$(NSiMe_3)_2$]$_2TaFPh_2$ (**4**). Monitoring the reaction by ^{1}H-NMR spectroscopy reveals that **3** forms quantitatively after 4 h, while introduction of the second phenyl group is substantially slower. Formation of **4** is still incomplete after 2 d, when decomposition is observed in the ^{1}H-NMR spectrum. Colorless crystals of **3** can be isolated, however, from hexanes in 40% yield when the reaction of **1** with 1.5 equivalents Ph_2Mg in diethyl ether is stopped after 4 h.

The reaction of **1** with 1.5 equivalents Ph_2Mg in diethyl ether for 2 d affords pale purple bis(aryl) complex **4** in 20% yield after crystallization from hexanes. An ORTEP diagram of **4** is shown in Fig. 2 and selected bond lengths and angles are shown in Table 2. Several geometric features of **4** are similar to those revealed in the X-ray structure of **1** (Table 3). The ligands are coordinated to the tantalum atom in a distorted pentagonal bipyramidal configuration in which the two phenyl groups (C27 and C33), both occupy equatorial positions, along with three of the amidinate nitrogen atoms (N1, N3, N4). The mean deviation of the equatorial atoms from the plane is 0.30 Å. The two ipso phenyl carbons (C27 and C33) and the fluoride are arranged in an arc, as the F ligands are in **1**. For the carbon atoms

C27 and C33, which are in the outer positions, the C–Ta–C angle is 139.4°. The fluoride lies in the inside position and is separated 82–83° from C27 and C33. Ta–F bond length of 1.886(3) Å is comparable to the Ta–F_{ax} bond length in **1.** The two Ta–C bond lengths for the two phenyl groups are essentially equivalent, at 2.281(5) and 2.270(5) Å. The room temperature ^{1}H-NMR spectrum shows only one set of resonances for the metal-bound phenyl groups, suggesting an averaged symmetrical configuration of the phenyl groups in solution.

Table 3
Crystallographic data and refinement details for **1** and **4** [a]

	Compound **1**	Compound **4**
Empirical formula	$C_{26}H_{46}N_4F_3Si_4Ta$	$C_{38}H_{56}N_4Si_4Ta$
Formula weight	764.96	881.18
Temperature (°C)	−101	−93
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (#14)	$C2/c$ (#15)
a (Å)	16.9883(2)	22.2291(13)
b (Å)	11.0893(2)	12.5074(7)
c (Å)	18.3154(1)	30.4723(18)
B(°)	94.306(1)	102.952(1)
V (Å^3)	3440.67(6)	8257(1)
Z	4	8
D_{calc} (g cm^{-3})	1.477	1.418
Diffractometer	Siemens SMART	Siemens SMART
Radiation	Mo–K_α	Mo–K_α
Monochromator	Graphite	Graphite
Detector	CCD area detector	CCD area detector
Scan type (°)	ω, 0.3	ω, 0.3
Frame collection time (s)	10	20
Reflections measured	Hemisphere	Hemisphere
2θ range (°)	3–46.5	3–46.5
μ (mm^{-1})	33.67	2.81
T_{min}, T_{max}	0.334, 0.567	0.658, 0.863
Crystal dimensions (mm)	0.40 × 0.31 × 0.10	0.13 × 0.11 × 0.07
Reflections measured	14 173	17 288
Unique reflections	5208	6222
Observations ($I > 3\sigma$)	4102	4666
Variables	343	433
Data/parameter	11.96	10.78
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_{int} (%)	2.5	2.74
R (%)	2.1	2.38
R_w (%)	2.7	3.01
Goodness-of-fit	2.7	1.192
Largest difference peak and hole (e Å^{-3})	0.54 and −0.71	1.71 and −0.80
Hydrogen atoms	Idealized positions	Idealized positions

[a] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $Rw = \{[\Sigma_w(|F_o| - |F_c|)^2]/\Sigma_w|F_o^2|\}^{1/2}$, Goodness-of-fit $= \{[\Sigma_w(|F_o| - |F_c|)^2]/(n_o - n_v)\}^{1/2}$.

3. Conclusion

In this report, we have shown that the nitrogen-based bis(trimethylsilyl)benzamidinate ligand is an excellent reagent for synthesizing derivatives directly from tantalum pentafluoride. This ligand provides easy access to complexes which are analogous to those used in a wide variety of useful reactions. Both the fluoride and amidinate ligands of **1** exhibit dynamic behavior on the NMR timescale. The metal–fluoride bonds of **1** are labile, as demonstrated by their straightforward displacement in the conversion of **1** to alkyl and aryl complexes. No tendency for dimerization of the products was observed, which we attribute to the steric bulk of the bis(trimethylsilyl)benzamidinate ligand. Future studies will determine how the reactivity of these amidinate tantalum fluoride complexes compares with the reactivity of other tantalum fluoride derivatives.

4. Experimental

4.1. General considerations

Standard Schlenk-line and glove box techniques were used throughout [36]. Hexanes and tetrahydrofuran (THF) were distilled from Na–benzophenone under nitrogen. Toluene was distilled from Na under nitrogen. C_6D_6 was vacuum transferred from Na–benzophenone. Ph_2Mg was prepared according to the literature procedure [37]. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra were recorded at ambient temperatures, unless otherwise noted. Chemical shifts (δ) are given relative to the residual proton in the deuterated solvent at 7.15 for C_6D_6. ^{19}F chemical shifts are given relative to an external $CFCl_3$ standard in the given solvent at 0.00 ppm. IR samples were prepared as mineral oil mulls and taken between KBr plates. Elemental analysis data were obtained by the microanalysis Facility of the College of Chemistry, University of California, Berkeley, CA. Single crystal X-ray determinations were performed at the College of Chemistry X-ray diffraction facility, University of California, Berkeley, CA.

4.2. $[PhC(NSiMe_3)_2]_2TaF_3$

Toluene (125 ml) was added to a 500-ml round-bottomed flask loaded with TaF_5 (2.50 g, 9.05 mmol), forming a slurry. A solution of Li[PhC(NSiMe$_3$)$_2$]-(TMEDA) (7.00 g, 18.1 mmol) in toluene (100 ml) was added dropwise to yield a yellow solution. After stirring the mixture at room temperature overnight, the volatile materials were removed under reduced pressure, affording a pale yellow solid. One extraction with hexanes (225 ml) followed by filtration through a Celite pad on a fritted disk gave a clear yellow solution. Concentration of the solution to 80 ml followed by cooling to −30°C afforded pale yellow crystals. Repeating this procedure gave a second crop, total 2.77 g, 40% yield. ^{1}H-NMR (C_6D_6, 400 MHz): δ 7.25 (d, 4H, $J=8$ Hz, *o*-Ar), 6.95–6.89 (m, 6H, *m*, *p*-Ar), 0.23 (s, 36H, Si*Me*$_3$). ^{13}C{^{1}H}-NMR (C_6D_6, 75.5 MHz): δ 184.6 (N*C*N), 139.3 (Ar), 129.9 (Ar), 128.1 (Ar), 127.0 (Ar), 2.0 (Si*Me*$_3$). ^{19}F-NMR (C_6D_6, 376.5 MHz): δ 67.5. IR (cm^{-1}): 1459 (s, br), 1446 (s, br), 1423 (s), 1407 (s), 1247 (s), 1083 (w), 1000 (s), 918 (w), 848 (s, br), 833 (s), 786 (s), 765 (s), 721 (s), 703 (s), 694 (m), 599 (m), 549 (s), 516 (m). Anal. Calc. for $C_{26}H_{46}N_4F_3Si_4Ta$: C 40.82, H 6.06, N 7.32. Found: C 40.83, H 6.09, N 7.33.

4.3. [PhC(NSiMe$_3$)$_2$]$_2$TaF$_2$Ph

THF (60 ml) was added to a 100-ml round-bottomed flask loaded with $[PhC(NSiMe_3)_2]_2TaF_3$ (0.465 g, 0.608 mmol) and Ph_2Mg (0.108 g, 0.608 mmol) forming a clear yellow solution. After the reaction mixture was stirred at room temperature for 4 h, the volatile materials were removed under reduced pressure to afford a red–brown solid. One extraction with hexanes (50 ml) followed by filtration through a Celite pad on a fritted disk gave a clear red solution. Concentration of the filtrate in vacuo to 4 ml followed by cooling to −30°C afforded colorless crystals (0.200 g, 40% yield). ^{1}H-NMR (C_6D_6, 400 MHz): δ 8.83 (d, 2H, $J=7$ Hz, *o*-Ar), 7.49 (t, 2H, $J=7$ Hz, *m*-Ar), 7.33–7.26 (m, 5H, Ar), 6.97–6.93 (m, 6H, Ar), 0.11 (s, 36H, Si*Me*$_3$). ^{13}C{^{1}H}-NMR (C_6D_6, 75.5 MHz): δ 182.8 (N*C*N), 140.7 (Ar), 139.2 (Ar), 139.1 (Ar), 130.2 (Ar), 128.5 (Ar), 127.4 (Ar), 2.6 (Si*Me*$_3$). The remaining carbon resonances for the phenyl group were not located. ^{19}F-NMR (C_6D_6, 376.5 MHz): δ 108.5 (s, br). IR (cm^{-1}): 1601(w), 1452 (s, br), 1434 (s, br), 1413 (s, br), 1402 (s, br), 1395 (s, br), 1275 (s), 1064 (w), 1008 (m), 979 (s), 925 (w), 840 (s, br), 796 (s), 771 (s), 757 (s), 746 (s), 700 (s), 553 (s), 512 (m). Anal. Calc. for $C_{32}H_{51}N_4F_2Si_4Ta$: C 46.70, H 6.25, N 6.81. Found: C 46.89, H 6.27, N 6.86.

4.4. [PhC(NSiMe$_3$)$_2$]$_2$TaFPh$_2$

Et_2O (60 ml) was added to a 100-ml round-bottomed flask loaded with $[PhC(NSiMe_3)_2]_2TaF_3$ (0.251 g, 0.328 mmol) and Ph_2Mg (0.097 g, 0.54 mmol) forming a clear orange solution. After the reaction mixture was stirred at room temperature for 2 days, the volatile materials were removed under reduced pressure to afford a red–brown solid. One extraction with hexanes (50 ml) followed by filtration through a Celite pad on a fritted disk gave a clear red solution. Concentration of the filtrate in vacuo to 4 ml followed by cooling to −30°C afforded colorless crystals (0.060 g, 20% yield). ^{1}H-NMR (C_6D_6, 400 MHz): δ 8.56 (d, 4H, $J=7$ Hz, *o*-Ar), 7.45 (t, 4H, $J=7$ Hz, *m*-Ar), 7.35–7.25 (m, 6H, Ar), 6.97–6.93 (m, 6H, Ar), −0.07 (s, 36H, Si*Me*$_3$). ^{13}C{^{1}H}-NMR (C_6D_6, 75.5 MHz): δ 179.1 (N*C*N), 140.3 (Ar), 140.2 (Ar), 140.1 (Ar), 130.1 (Ar), 128.5 (Ar), 126.0 (Ar), 3.5 (Si*Me*$_3$). The remaining carbon resonances for the phenyl groups were not located. ^{19}F-NMR (C_6D_6, 376.5 MHz): δ 131.1 (s, br). IR (cm^{-1}): 1601 (w), 1525 (s), 1484 (s), 1463 (s, br), 1444 (s, br), 1429 (s, br), 1400 (s, br), 1375 (s, br), 1249 (s), 1056 (w), 1008 (m), 987 (s), 925 (w), 842 (w), 835 (s, br), 784 (s), 773 (s), 756 (s), 736 (s), 711 (s), 702 (s), 580 (s), 553 (s), 509 (m). Anal. Calc. for $C_{38}H_{56}N_4FSi_4Ta$: C 51.80 H 6.41, N 6.36. Found: C 51.76, H 6.38, N 6.45.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 141165 for **1** and CCDC no. 141166 for **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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