Trimethylsilyl Imide Complexes of Tantalum: Can The Silyl Group Be Eliminated?

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Abstract

We report the synthesis and structure of a series of tantalum(V) complexes having the trimethylsilylimide moiety and using as ancillary support the pincer ligand PNP ($\text{PNP}^- = \text{N}[2\text{-P}^i\text{Pr}_2\text{-4-methylphenyl}]_2$). Via transmetallation of $\text{Li}(\text{PNP})$ with $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}(\text{SiMe}_3)$ ($\text{py} = \text{pyridine}$), the precursor complex $(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)\text{Cl}_2$ (**1**) could be prepared in 94% isolated yield. Attempts to promote FSiMe_3 elimination when **1** was treated with FSnMe_3 resulted in mixtures from which the salt-like product $[\{(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)\}_2(\mu_2\text{-F})_3][\text{Me}_3\text{ClSn}(\mu_2\text{-X})\text{SnClMe}_3]$ (**2**) ($\text{X}^- = \text{F}$ or Cl) was structurally identified. However, conducting the reaction with NaOAr ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) resulted in clean formation to $(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)(\text{OAr})\text{Cl}$ (**3**) in 79% isolated yield, and when **3** was mixed with FSnMe_3 , the fluoride-imide complex $(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)(\text{OAr})\text{F}$ (**4**) and ClSnMe_3 were formed cleanly. Attempts to promote FSiMe_3 elimination in **4** thermally and photochemically did not yield the desired nitride $(\text{PNP})\text{Ta}=\text{N}(\text{OAr})$. Complexes **1-4** were characterized by single-crystal X-ray diffraction studies and in the case of complexes **1**, **3** and **4** a variety of multinuclear NMR studies are presented and discussed.

Introduction

The ubiquitous metal nitride group can allow for the formation of unique materials with many different technological applications relating to the metallic conductivity and refractory properties that can result in their use as diffusion barriers in microelectronic devices.¹⁻² Likewise, transition metals supported with the nitride group have been also used in important transformations such as alkane dehydrogenation.³ As an alternative to kinetically stable materials prepared by chemical vapor deposition (CVD),² we are interested in developing new and mild synthetic routes using molecular precursors to monomeric and thus molecular forms of transition metal nitrides. In particular, mononuclear forms of tantalum nitrides have not been reported, which is rather disappointing since nitride forms of Ta (Ta_3N_5 or TaN) constitute important materials with interesting electronic and physical properties, in particular for their use as diffusion barriers in integrated circuits.²

We recently reported the synthesis of a mononuclear niobium methylidyne $(\text{PNP})\text{Nb}\equiv\text{CH}(\text{OAr})$ ($\text{PNP}^- = \text{N}[2\text{-P}^i\text{Pr}_2\text{-4-methylphenyl}]_2$, $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$), which served as a precursor to the molecular nitride $(\text{PNP})\text{Nb}\equiv\text{N}(\text{OAr})$ via a nitrile for alkylidyne cross metathesis reaction.⁴ By analogy, one would expect that tantalum should also form stable nitrides with such choice of supporting ligands. Unfortunately, Ta(IV) precursors such as TaCl_4 (ill-defined)⁵ or $\text{TaCl}_4(\text{tmeda})$ ⁶ can be quite limited reactive-wise when compared to the niobium counterparts. For this reason, we focused our attention on the silylimide precursor $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}(\text{SiMe}_3)$ originally reported by Doherty and co-workers,⁷ since this species should provide access to a more coordinatively accessible tantalum center given the lability of the two py ligands. Herein we report our attempt to generate a mononuclear form of tantalum nitride via FSiMe_3 elimination. We report a synthetic approach to the trimethylsilyl imide precursors and provide structural and spectroscopic data for a series of tantalum complexes.

Experimental Details

General Considerations

All operations were performed in an M. Braun glove box under a nitrogen atmosphere unless otherwise stated or using standard Schlenk techniques under an argon atmosphere unless otherwise stated. Anhydrous pentane, hexane and toluene were purchased from Fisher Scientific or Aldrich. All anhydrous solvents were purified and dried by passage through two columns of activated alumina and Q-5 drying agent in a Grubbs-type solvent system. Stabilizer-free Et_2O was purchased from Fisher Scientific and dried by passage through two columns of activated alumina. Anhydrous pyridine was purchased from Aldrich and dried by passage through two columns of activated alumina. All bulk solvents were kept over sodium and 4 Å molecular sieves. A benzene- d_6 (C_6D_6 , Cambridge Isotope Laboratories) was dried and degassed over a potassium mirror prior to use. Celite and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}(\text{SiMe}_3)$ ($\text{py} = \text{pyridine}$),⁷ $\text{Li}(\text{PNP})$,⁸ FSnMe_3 ⁹ and NaOAr ¹⁰ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) were prepared according to the reported procedures. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AV-II 500 MHz, AVIII 400 MHz or DMX 300 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are referenced to the internal residual proton or carbon resonances of C_6D_6 (7.16 ppm or 128.06 ppm). ^{19}F and ^{31}P NMR chemical shifts are reported with respect to external $\text{CF}_3\text{CO}_2\text{H}$ (−78.5 ppm) and H_3PO_4 (0.0 ppm). Elemental analyses were performed at a FLASH EA 1112 Series CHN analyzer (Thermo Finnigan).

Synthesis of $(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)\text{Cl}_2$ (**1**)

To a pale yellow solution of $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}(\text{SiMe}_3)$ (500 mg, 939 μmol) in toluene (15 mL) was added $\text{Li}(\text{PNP})$ (409 mg, 939 μmol) as a solid at room temperature and additional toluene (10 mL) was used to add the remainder of $\text{Li}(\text{PNP})$, resulting in a color

change to reddish brown. After stirring for 18 h at 70 °C, the reaction mixture changed color to purple. The volatiles were removed under vacuum. The purple residue was extracted into toluene (10 mL) and the solution filtered through a medium porosity glass frit containing Celite. The Celite was washed with toluene (5 mL). The purple filtrate was evaporated to dryness and the residue was triturated twice with pentane (3 mL) to yield **1** as purple powder (681 mg, 887 μ mol, 94% yield). Purple crystals suitable for X-ray analysis were grown from a concentrated pentane solution at –35 °C.

^1H NMR (400 MHz, benzene- d_6 , 300 K): δ 7.10 (br, 2H, Ar-CH), 6.90-6.85 (br, overlapped 4H, Ar-CH), 2.59-2.50 (br, 2H, PCH(CH $_3$) $_2$), 2.11 (s, 3H, ArCH $_3$), 2.09 (s, 3H, ArCH $_3$), 1.67-1.55 (overlapped m, 6H, PCH(CH $_3$) $_2$), 1.37-1.14 (overlapped m, 36H, PCH(CH $_3$) $_2$), 0.77 (br m, 3H, PCH(CH $_3$) $_2$), 0.05 (s, 9H, Si(CH $_3$) $_3$). ^{13}C NMR (126 MHz, benzene- d_6 , 300 K): δ 159.46 (br, PNP-Ar), 158.91 (br, PNP-Ar), 134.01 (PNP-Ar), 133.26 (PNP-Ar), 132.46 (PNP-Ar), 132.17 (d, J_{CP} = 13 Hz, PNP-Ar), 130.63 (PNP-Ar), 130.25 (PNP-Ar), 129.34 (PNP-Ar), 128.95 (PNP-Ar), 128.57 (PNP-Ar), 119.30 (d, J_{CP} = 7.3 Hz, PNP-Ar), 119.14 (d, J_{CP} = 5.5 Hz, PNP-Ar), 26.23 (d, J_{CP} = 12 Hz, PCH(CH $_3$) $_2$), 25.35 (d, J_{CP} = 16 Hz, PCH(CH $_3$) $_2$), 24.68 (br d, J_{CP} = 5.5 Hz, PCH(CH $_3$) $_2$), 23.56 (d, J_{CP} = 15 Hz, PCH(CH $_3$) $_2$), 20.89 (ArCH $_3$), 20.82 (ArCH $_3$), 20.49 (d, J_{CP} = 15 Hz, PCH(CH $_3$) $_2$), 19.89 (br, PCH(CH $_3$) $_2$), 19.54 (d, J_{CP} = 13 Hz, PCH(CH $_3$) $_2$), 19.32 (d, J_{CP} = 9.2 Hz, PCH(CH $_3$) $_2$), 18.74 (br, PCH(CH $_3$) $_2$), 18.37 (br, PCH(CH $_3$) $_2$), 16.38 (br, PCH(CH $_3$) $_2$), 15.57 (br, PCH(CH $_3$) $_2$), 2.62 (Si(CH $_3$) $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, benzene- d_6 , 300 K) δ 46.98 (d, J_{PP} = 140 Hz, PNP), 42.88 (d, J_{PP} = 140 Hz, PNP). Anal. Calcd. for C $_{29}$ H $_{49}$ N $_2$ Cl $_2$ P $_2$ SiTa: C, 45.38; H, 6.43; N, 3.65. Found: C, 45.91; H, 7.16; N, 3.27. Multiple attempts to obtain satisfactorily elemental analysis failed.

Treatment of (PNP)Ta=N{SiMe $_3$ }Cl $_2$ (1**) with excess FSnMe $_3$.**

To a purple solution of **1** (200 mg, 261 μ mol) in toluene (10 mL) was added a suspension of FSnMe $_3$ (101 mg, 552 μ mol) in toluene (1 mL). After stirring for 8 h, the white solid of FSnMe $_3$ was consumed completely and the reaction mixture changed in color from red to brown. The solution filtered through a pipet containing glass wool. The volatiles were removed under vacuum, and the brown residue was triturated twice with pentane (2 mL x 2) to give brown powder (89.1 mg). ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra showed a mixture of complex **2** and some unidentified products. Yellow crystals suitable of complex **2** for X-ray analysis were grown from a concentrated pentane solution at –35 °C.

Synthesis of (PNP)Ta=N{SiMe $_3$ }(OAr)Cl (3**)**

To a purple solution of **1** (100 mg, 130 μ mol) in Et $_2$ O (10 mL) was added NaOAr (26.1 mg, 130 μ mol) as a solid at room temperature and additional Et $_2$ O (1 mL) was used to add the remainder of NaOAr. After stirring for 3 h, the reaction mixture changed in color to red. The volatiles were removed under vacuum, and the red residue was extracted into hexane (3 mL) and the solution filtered through a medium porosity glass frit containing Celite. The Celite was washed twice with hexane (3 mL). The red filtrate was evaporated to dryness and the residue was dissolved in pentane (2 mL). The red pentane solution was stored at –35 °C overnight to give **3** as red crystals (93.5 mg, 103 μ mol, 79% yield). Red crystals suitable for X-ray analysis were grown from a concentrated pentane solution at –35 °C.

^1H NMR (400 MHz, benzene- d_6 , 300 K): δ 7.26 (d, J_{HH} = 6.8 Hz, 2H, Ar-CH), 7.12 (br, 2H, Ar-CH), 7.03 (d, J_{HH} = 7.2 Hz, 1H, Ar-CH), 7.01 (d, J_{HH} = 7.2 Hz, 1H, Ar-CH), 6.91 (br virtual t, overlapped 3H, Ar-CH), 4.66 (br, 2H, OArCH(CH $_3$) $_2$), 2.57 (br, 2H, PCH(CH $_3$) $_2$), 2.15 (s, 3H, ArCH $_3$), 2.14 (s, 3H, ArCH $_3$), 2.15-2.13 (overlapped, 2H, PCH(CH $_3$) $_2$), 1.40, 1.24, 1.03 (br, overlapped 36H, PCH(CH $_3$) $_2$ and OArCH(CH $_3$) $_2$), 0.00 (s, 9H, Si(CH $_3$) $_3$). ^{13}C NMR (126 MHz, benzene- d_6 , 300 K): δ 160.92 (br, PNP-Ar), 160.69 (br, PNP-Ar), 158.30 (OAr), 140.16 (OAr), 132.60 (d, J_{CP} = 17 Hz, PNP-Ar), 131.46 (ArO), 129.97 (OAr), 123.82 (br, PNP-Ar), 122.42 (ArO), 26.65 (br, OArCH(CH $_3$) $_2$), 26.18 (OArCH(CH $_3$) $_2$), 23.61 (br, PCH(CH $_3$) $_2$), 20.86 (ArCH $_3$), 19.41 (br, PCH(CH $_3$) $_2$), 3.54 (Si(CH $_3$) $_3$). Fluxional behavior in solution prevented us from measuring reliable ^{13}C NMR spectral signals in the PNP ligand's aromatic rings. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, benzene- d_6 , 300 K) δ 50.33 (d, J_{PP} = 129 Hz, PNP), 38.93 (br d, $\Delta\nu_{1/2}$ = 255 Hz, PNP). Anal. Calcd. for C $_{41}$ H $_{66}$ N $_2$ OClP $_2$ SiTa: C, 54.15; H, 7.32; N, 3.08. Found: C, 53.80; H, 7.42; N, 2.84.

Synthesis of (PNP)Ta=N{SiMe $_3$ }(OAr)F (4**)**

To a red solution of **3** (230 mg, 253 μ mol) in toluene (10 mL) was added a suspension of FSnMe $_3$ (50.1 mg, 274 μ mol) in toluene (2 mL). After stirring for 3 h, the white solid of FSnMe $_3$ was consumed completely and the reaction mixture changed in color from red to yellowish brown. The solution filtered through a pipet containing glass wool. The volatiles were removed under vacuum, and the brown residue was triturated twice with pentane (2 mL x 2) to yield **4** as pale brown powder (169 mg, 189 μ mol, 75% yield). Pale brown crystals suitable for X-ray analysis were grown from a concentrated pentane solution at –35 °C.

^1H NMR (300 MHz, benzene- d_6 , 300 K): δ 7.22 (d, J_{HH} = 7.8 Hz, 2H, Ar-CH), 6.69 (virtual t, overlapped 3H, Ar-CH), 6.88 (virtual t, overlapped 4H, Ar-CH), 3.95 (br, 2H, OArCH(CH $_3$) $_2$), 2.89 (br, 4H, PCH(CH $_3$) $_2$), 2.12 (s, 6H, ArCH $_3$), 1.36 (d, J_{HH} = 5.4 Hz, 6H, ArCH(CH $_3$) $_2$), 1.23 (dd, J_{HH} = 8.1 Hz, J_{HP} = 15.3 Hz, PCH(CH $_3$) $_2$), 1.11 (br, 6H, PCH(CH $_3$) $_2$), 0.23 (s, 9H, Si(CH $_3$) $_3$). ^{13}C NMR (126 MHz, benzene- d_6 , 300 K, selected data): δ 157.76 (br, OAr), 138.73 (OAr), 132.54 (br, PNP-Ar), 129.27 (OAr), 128.57 (PNP-Ar), 123.48 (OAr), 121.23 (PNP-Ar), 26.00 (OArCH(CH $_3$) $_2$), 25.14 (br, OArCH(CH $_3$) $_2$), 23.74 (br, PCH(CH $_3$) $_2$), 20.75 (ArCH $_3$), 19.16 (br, PCH(CH $_3$) $_2$), 4.39 (Si(CH $_3$) $_3$). Fluxional behavior in solution prevented us from measuring ^{13}C signals in the PNP ligand's aromatic rings. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, benzene- d_6 , 300 K) δ 46.27 (br, $\Delta\nu_{1/2}$ = 264 Hz, PNP), 33.29 (br, $\Delta\nu_{1/2}$ = 190 Hz, PNP). $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, benzene- d_6 , 300 K) δ 41.88 (br, $\Delta\nu_{1/2}$ = 89 Hz, Ta-F). Anal. Calcd. for C $_{41}$ H $_{66}$ N $_2$ FOP $_2$ SiTa: C, 55.15; H, 7.45; N, 3.14. Found: C, 55.26; H, 6.99; N, 3.15.

X-ray Crystallographic Studies

Crystallographic data for are summarized Table S1-S4. Suitable crystals for X-ray analysis of **1-4** were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker APEXII CCD area detector using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 100(1) K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,¹¹ producing a listing of non-averaged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL¹² program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.⁷ All calculations were performed using SHELXS¹³ and SHELXL.¹⁴ The structures were solved by Patterson and Fourier transform methods. All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models. For **1**, two crystallographically independent, but chemically equivalent molecules are present in the asymmetric unit. One site occupied by a pentane molecule was identified in the asymmetric unit. This site contains considerably a disordered pentane molecule and was treated by SQUEEZE as a diffuse contribution.^{15, 16} In the void space, a contribution of 53 e⁻ per unit cell was found and taken to represent one pentane molecule in the asymmetric unit, giving 0.5 pentane molecules for each Ta complex. For **2**, the $[(\text{Me}_3\text{SnCl})_2(\mu\text{-X})]^-$ anion was disordered as a mixture of X = Cl and F, and the occupancies were refined as 0.81 and 0.19 respectively by the FVAR refinement. The thermal ellipsoids of $[(\text{Me}_3\text{SnCl})_2(\mu\text{-F})]^-$ were fixed by SHELXL restraint commands, DELU and SIMU. For **4**, one of the ¹Pr groups in OAr was disordered over two positions. These results were checked using the IUCr's CheckCIF routine. The alerts in the output are related to the disordered groups and crystal solvents. Some unidentified Q-peaks (> 1) still remain in these data, but those Q-peaks (> 1) are on unrealistic positions to locate any atom. The large values of the second parameter on the SHELXL weighting are due to the poor quality of crystals.

Results and Discussion

As reported by Doherty and co-workers, complex $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}\{\text{SiMe}_3\}$ is a convenient precursor prepared readily from TaCl_5 , py, and $\text{HN}\{\text{SiMe}_3\}_2$ in benzene.⁷ When $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}\{\text{SiMe}_3\}$ is treated with Li(PNP) in toluene at 70 °C over 18 hours, complex $(\text{PNP})\text{Ta}=\text{N}\{\text{SiMe}_3\}\text{Cl}_2$ (**1**) can be isolated in nearly quantitative yield (94% isolated yield) after subsequent workup of the reaction mixture (Scheme 1). Some signature spectroscopic features for **1** include the presence of a shifted trimethylsilyl group (¹H NMR: 0.05 ppm) when compared to $\text{Cl}_3(\text{py})_2\text{Ta}=\text{N}\{\text{SiMe}_3\}$ (0.37 ppm), as well as the observation of two doublets (42.88 and 46.98 (d, ²J_{pp} = 140 Hz) in the ³¹P{¹H} NMR spectrum. A solid state structural analysis confirms its monomeric and six-coordinate nature in addition to a short Ta–N_{imide} bond of 1.791(3) Å (Figure 1) and a linear Ta–N–Si angle (166.56(19)°). Such distance and angle are comparable to other reported trimethylsilyl imide tantalum complexes having a terminal imide group.¹⁸ The PNP ligand adopts a meridional configuration with the P–Ta–P being distorted from linearity (146.35(2)°). The chloride groups are cisoid (83.61(3)°) with the imide group occupying the meridional plane (orthogonal to the (PNP)Ta plane) defined by $\text{TaCl}_2\text{N}_{\text{imide}}$ atoms.

Scheme 1. Synthesis of complexes **1** and **2**.

Not surprisingly, complex **1** is thermally quite stable so we decided to take advantage of the strong Si–F bond dissociation enthalpy by replacing Cl with F. Unfortunately, multiple attempts to cleanly replace the chloride ligands in **1** with an anhydrous and fluoride source such as FSnMe_3 resulted in complicated mixtures out of which we could marginally obtain a few crystals of the fluoride salt-like species $[(\text{PNP})\text{Ta}=\text{N}\{\text{SiMe}_3\}]_2(\mu_2\text{-F})_3][\text{Me}_3\text{ClSn}(\mu_2\text{-X})\text{SnClMe}_3]$ (**2**) ($\text{X}^- = \text{F}$ or Cl) shown in Scheme 1. Although we were unable to obtain reliable spectroscopic data due to the presence of numerous side-products,¹⁹ we managed to obtain single crystals of **2** and a solid state X-ray diffraction study revealed this species to be a discrete salt where all three fluoride ligands bridged the two Ta(V) centers (Figure 1). Although we were able to establish connectivity of this

material, the solid state structure of complex **2** suffers from occupancy disorder in the X bridging group (81 (Cl):19 (F)) in the counter anion $[\text{Me}_3\text{ClSn}(\mu_2\text{-X})\text{SnClMe}_3]^-$.

Figure 1. Solid state structural diagrams for complexes **1** (left), cationic part (middle) and anionic part (right top X = Cl, bottom X = F) of **2** displaying thermal ellipsoids at the 50% probability level. For complex **1**, H-atoms, and residual solvent (pentane) have been excluded for clarity. For complex **2**, H-atoms, and substitutions (ⁱPr and Me groups) of PNP have been omitted for clarity. Selected metrical parameters (distance in Å and angles in °) for **1**: Ta1–Cl1, 2.5331(9); Ta1–Cl2, 2.4075(9); Ta1–P1, 2.6352(9); Ta1–P2, 2.6236(9); Ta1–N1, 2.2098(3); Ta1–N2, 1.791(3); Cl1–Ta1–Cl2, 83.61(3); Cl1–Ta1–P1, 89.82(3); Cl1–Ta1–P2, 84.05(3); Cl1–Ta1–N1, 86.04(8); Cl1–Ta1–N2, 169.36(10); Cl2–Ta1–P1, 90.13(3); Cl2–Ta1–P2, 121.78(3); Cl2–Ta1–N1, 159.54(8); Cl2–Ta1–N2, 93.40(10); P1–Ta1–P2, 146.35(3); P1–Ta1–N1, 72.21(8); P1–Ta1–N2, 100.42(10); N1–Ta1–N2, 99.77(12); Ta1–N2–Si1, 166.56(19). For **2**: Ta1–F1, 2.146(2); Ta1–F2, 2.278(2); Ta1–F3, 2.075(2); Ta1–P1, 2.6657(11); Ta1–P2, 2.6618(12); Ta1–N1, 2.160(4); Ta1–N3, 1.789(4); Ta2–F1, 2.137(2); Ta2–F2, 2.073(2); Ta2–F3, 2.278(2); Ta2–P3, 2.6480(11); Ta2–P4, 2.6639(11); Ta2–N2, 2.165(3); Ta2–N4, 1.786(3); Sn1A–Cl1A, 2.4982(18); Sn1A–Cl3A, 2.7719(18); Sn2A–Cl2A, 2.505(5); Sn2A–Cl3A, 2.817(2); Ta1–F1–Ta2, 102.18(10); Ta1–F2–Ta2, 99.87(9); Ta1–F3–Ta2, 99.80(9); Ta1–N3–Si1, 169.5(2); Ta2–N2–Si2, 165.7(2); Cl1A–Sn1A–Cl3A, 177.53(6); Sn1A–Cl3A–Sn2A, 121.56(7); Cl2A–Sn2A–Cl3A, 173.85(11).

To circumvent the formation of undesired salts, we resorted to protecting the metal center with an aryloxy group, akin to that used in the formation of the methyldene $(\text{PNP})\text{Zr}=\text{CH}_2(\text{OAr})^{20}$ and methyldyne $(\text{PNP})\text{Nb}\equiv\text{CH}(\text{OAr})^4$ complexes reported previously. Accordingly, treatment of **1** with NaOAr resulted in a clean transmetalation with formation of the trimethylsilylimide-aryloxy complex $(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)(\text{OAr})\text{Cl}$ (**3**) in 79% isolated yield (Scheme 2). The ^1H NMR spectrum of **3** displays a C_1 symmetry system having inequivalent tolyl methyl and broaden ⁱPr groups of the PNP ligand, in addition to showing the trimethylsilyl resonance at 0.00 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also depicts two inequivalent doublets (38.94 and 50.33 ppm, $^2J_{\text{PP}} = 129$ Hz), where the smaller coupling value suggests a more sterically crowded environment unlike in precursor **1**. As anticipated, the solid state structural diagram of **3** shown in Figure 2 displays a mononuclear, and six-coordinate Ta(V) center with a distorted P–Ta–P angle ($145.26(4)^\circ$) having twisted aryl groups on the pincer PNP to disrupt co-planarity. The aryloxy ligand is cisoid to the silylimide ($\text{N}_{\text{imide}}\text{--Ta--O}$, $99.11(15)^\circ$) and transoid to the PNP nitrogen ($\text{N}_{\text{PNP}}\text{--Ta--O}$, $167.00(13)^\circ$). The Ta–N_{imide} distance (1.809(4) Å) is slightly elongated when compared to the more electron deficient precursor **1**.

Scheme 2. Synthesis of complexes **3** and **4**.

When complex **3** is treated with FSnMe₃ in toluene over 3 hours, the imide fluoride species $(\text{PNP})\text{Ta}=\text{N}(\text{SiMe}_3)(\text{OAr})\text{F}$ (**4**) was formed quantitatively in solution (when gauged by ^{31}P NMR spectroscopy) but isolated in 75 % yield as pale brown colored solid from a pentane solution (Scheme 2). Complex **4** display several diagnostic features in the ^1H NMR spectrum such as a C_s symmetry system having equivalent tolyl methyl and ⁱPr groups of the PNP ligand. The substitution of a chloride ligand for a more electron negative halide (fluoride) resulted in downfield shift of the trimethylsilyl resonance to 0.23 ppm when compared to **3** (0.00 ppm, vide supra). The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum revealed a broad resonance ($\Delta\nu_{1/2} = 89$ Hz) at 41.88 ppm with

similar chemical shifts to other reported terminally bound Ta(V)–F systems.²¹ A solid state structural diagram of **4** (Figure 2) showed a distinctly different orientation of the monodentate ligands whereby the aryloxy is no longer transoid to the N_{PNP} (N_{PNP}–Ta–O, 103.35(11)°), but also bent at the aryloxy oxygen (Ta–O–C_{ipso}, 138.1(2)°). The six-coordinate Ta(V) center adopted a more distorted octahedral geometry with a much more distorted P–Ta–P angle (136.32(3)°) and P–Ta–N_{PNP} (71.59(8)° and 70.35(8)°) around the PNP scaffold than those observed in **3**. Figure 3 portrays an expansion of the packing diagrams of **4** and **5** emphasizing notable interactions among Ta–halide and ⁱPr methyl groups of the PNP ligand occurring between neighboring molecules (Cl–H_{ipr}; 2.73 Å and 2.90 Å, F–H_{ipr}; 2.61 Å). These Ta–X–H_{ipr} (X = halide) short contacts suggest this orientation difference around the tantalum center between complex **4** and **5** to be most likely due to packing forces occurring in solid state. The inconsistency between the C_s symmetric ¹H NMR spectrum of **4** and the C₁ symmetric solid state structure is most likely due to the fluxional behavior taking place in solution.

Figure 2. Solid state structural diagrams for complexes **3** (left) and **4** (right) displaying thermal ellipsoids at the 50% probability level. For complexes **3** and **4**, H-atoms have been excluded for clarity. Selected metrical parameters (distance in Å and angles in °) for **3**: Ta1–Cl1, 2.5717(11); Ta1–P1, 2.6006(12); Ta1–P2, 2.6470(12); Ta1–N1, 2.137(4); Ta1–N2, 1.810(4); Ta1–O1, 1.930(3); Cl1–Ta1–P1, 90.98(4); Cl1–Ta1–P2, 77.00(4); Cl1–Ta1–N1, 82.65(10); Cl1–Ta1–N2, 176.20(12); Cl1–Ta1–O1, 84.36(10); P1–Ta1–P2, 145.26(4); P1–Ta1–N1, 73.46(10); P1–Ta1–N2, 86.57(11); P1–Ta1–O1, 106.23(9); P2–Ta1–N1, 72.73(10); P2–Ta1–N2, 103.46(12); P2–Ta1–O1, 104.87(9); N1–Ta1–N2, 93.86(12); N1–Ta1–O1, 167.00(13); N2–Ta1–O1, 99.11(15); Ta1–N2–Si1, 177.6(2); Ta1–O1–C27, 175.1(3). For **4**: Ta1–F1, 1.964(2); Ta1–P1, 2.6369(10); Ta1–P2, 2.7220(10); Ta1–N1, 2.170(3); Ta1–N2, 1.804(3); Ta1–O1, 1.985(3); F1–Ta1–P1, 72.83(7); F1–Ta1–P2, 149.81(7); F1–Ta1–N1, 126.99(11); F1–Ta1–N2, 101.65(13); F1–Ta1–O1, 79.52(10); P1–Ta1–P2, 136.32(3); P1–Ta1–N1, 71.59(8); P1–Ta1–N2, 93.45(11); P1–Ta1–O1, 138.44(8); P2–Ta1–N1, 70.35(8); P2–Ta1–N2, 86.35(10); P2–Ta1–O1, 71.82(8); N1–Ta1–N2, 118.40(13); N1–Ta1–O1, 103.35(11); N2–Ta1–O1, 122.54(13); Ta1–N2–Si1, 169.8(2); Ta1–O1–C27, 138.1(2).

Figure 3. Expanded packing diagrams for complexes **3** (left) and **4** (right) specifically showing the interactions of the halide ligands (Cl or F) with the ¹Pr methyl hydrogens.

In attempt to prepare (PNP)Ta≡N(OAr) via FSiMe₃ elimination, we subjected complex **4** to thermolytic (100 °C) and photolytic (Xe lamp with UV mirror module, 250–285 nm) conditions in C₆D₆ over 18 hours, with or without the presence of trapping substrates such as alkynes (PhC≡CH and PhC≡C-Ph) via cycloadditions. However, the extremely high fluorophilicity of tantalum prevented any reaction from occurring. Lastly, we attempted desilylation reactions of [Ta=N{SiMe₃}] moiety (in **3** and **4**) with nucleophiles such as alkyls or alkoxides,²² but these reactions resulted in demetallation reaction of the PNP ligand in addition to some unidentified products.

Conclusions

We have described the synthesis and structural features of a series tantalum (V) trimethylsilyl imide complexes bearing a pincer PNP scaffold. These trimethylsilyl imide complexes are readily accessible from a convenient precursor Cl₃(py)₂Ta=N{SiMe₃} by salt metathesis reaction of Li(PNP). A series of trimethylsilyl imide complexes gave us the best crystallographic opportunity to investigate the structural influences of halide and aryloxy ligands along with multinuclear NMR studies. Noteworthy, the introduction of the aryloxy ligand into this tantalum imide system allowed us to isolate the mononuclear trimethylsilyl imide complex having also a fluoride ligand. It is also noteworthy to mention that a mononuclear uranium complex Me₃SiN=U(N{SiMe₃}₂)₃(F) also failed to eliminate FSiMe₃ most likely due to a combination of thermodynamics as well as the transoid position of the imide and fluoride groups. Further attempts to prepare tantalum nitride species by a completely different route are ongoing.

Supporting Information

Crystallographic data for compounds **1-4** (1492696-1492699) have been submitted to The Cambridge Crystallographic Data Centre (CCDC). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. Tables, NMR spectra for complexes **1**, **3** and **4** can be found in the ESI.

Acknowledgements

We thank the University of Pennsylvania and the National Science Foundation (CHE-1152123) for financial support of this work. T.K. thanks the Japanese Society for the Promotion of Science (JSPS) for a post-doctoral fellowship (14J11968).

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Caption: The synthesis and characterization of a series of tantalum trimethylsilyl imide complexes are reported, and these explored as synthons to a molecular tantalum nitride.