

Syntheses and characterization of organoimido complexes of tantalum; potential single-source precursors to tantalum nitride

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Abstract—New single-source precursor to tantalum nitride thin films, $(\text{Bu}^i\text{N})\text{Ta}(\text{NEt}_2)_3$, and related complexes, $(\text{RN})\text{Ta}(\text{NEt}_2)_3$ ($\text{R} = \text{Pr}^i$ and Pr^n), were prepared by reacting corresponding $(\text{RN})\text{TaCl}_3\text{py}_2$ complexes ($\text{R} = \text{Bu}^i$, Pr^i and Pr^n) with LiNEt_2 in hydrocarbon solvents. The structure of $(\text{Bu}^i\text{N})\text{TaCl}_3\text{py}_2$ was determined by X-ray crystallography. © 1998 Elsevier Science Ltd. All rights reserved

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Imido ligands, $=\text{NR}$, can stabilize early transition metals in high-oxidation states by metal-nitrogen π -bonding [1]. There are many interesting reactions involving these complexes. For example, use of these complexes in homogeneous catalysis, such as olefin metathesis, has been explored [2]. Recently, imido complexes have been employed as precursors to metal nitride and carbonitride thin films by chemical vapor deposition (CVD) [3–6]. For example, cubic phase tantalum nitride thin films can be grown from an ethylimido complex of tantalum, $(\text{EtN})\text{Ta}(\text{NEt}_2)_3$ [3]. The metal-nitrogen multiple bond of this molecule is speculated to play a major role for the preservation of nitrogen atoms into the solids. However, $(\eta^2\text{-EtN}=\text{CHMe})\text{Ta}(\text{NEt}_2)_3$, a precursor of $(\text{EtN})\text{Ta}(\text{NEt}_2)_3$, is always in presence with $(\text{EtN})\text{Ta}(\text{NEt}_2)_3$ [7]. Due to their similar physical properties, complete separation of one from the other is difficult. This makes reaction pathway elucidation complex. The use of other similar organoimido tantalum complexes, such as $(\text{Bu}^i\text{N})\text{Ta}(\text{NMe}_2)_3$, has been considered [8]. The yield of $(\text{Bu}^i\text{N})\text{Ta}(\text{NMe}_2)_3$, however, is low in our hands. Here in we report the systematic syntheses and characterization of $(\text{RN})\text{Ta}$ -

Cl_3py_2 (**1a**, $\text{R} = \text{Bu}^i$; **1b**, $\text{R} = \text{Pr}^i$; **1c**, $\text{R} = \text{Pr}^n$; $\text{py} =$ pyridine). These complexes can be converted into $(\text{RN})\text{Ta}(\text{NEt}_2)_3$ (**2a**, $\text{R} = \text{Bu}^i$; **2b**, $\text{R} = \text{Pr}^i$; **2c**, $\text{R} = \text{Pr}^n$), all of which are volatile liquids at room temperature. These properties make them good candidates for CVD applications; for example, **2a** has been employed successfully as a single-source precursor to grow tantalum nitride thin films by CVD for electronic device applications [9–11].

RESULTS AND DISCUSSION

The air- and moisture-sensitive organoimido complexes $(\text{RN})\text{TaCl}_3\text{py}_2$ were conveniently prepared in good yields by reacting TaCl_5 with the corresponding amines $\text{R}(\text{Me}_2\text{Si})\text{NH}$ and py in hydrocarbon solvents (Scheme 1). The synthetic procedure employed here parallels the methods used to prepare some other organoimido complexes of Ta, for example $(\text{Me}_2\text{SiN})\text{TaCl}_3\text{L}_2$ and $[\text{TaCl}(\mu\text{-Cl})(\text{NBu}^i)(\text{NHBu}^i)(\text{NH}_2\text{Bu}^i)]_2$ [12, 13].

Single crystals of **1a** were grown from a toluene solution at -15°C . An ORTEP of **1a**, from an X-ray diffraction study, is shown in Fig. 1. Bond distances and bond angles are listed in Table 1. **1a** has a distorted octahedral geometry. The distance between Ta

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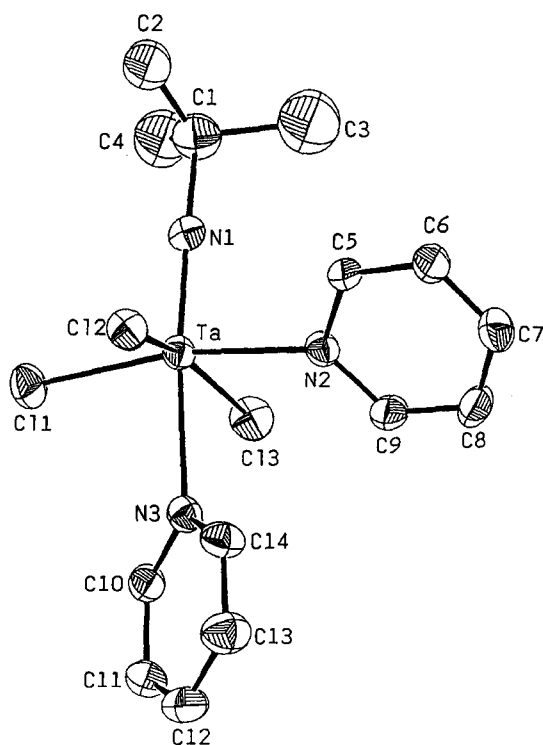


Fig. 1. ORTEP drawing of $(\text{Bu}'\text{N})\text{TaCl}_3\text{py}_2$ (**1a**) showing the atom numbering scheme. Only one orientation of the disordered Bu' group is shown.

Table 1. Selected bond distances and bond angles of **1a**

Bond Distance (Å)		Bond Angle (°)	
Ta-Cl(1)	2.368(2)	Cl(1)-Ta-Cl(2)	92.96(7)
Ta-Cl(2)	2.406(2)	Cl(1)-Ta-Cl(3)	93.77(7)
Ta-Cl(3)	2.382(2)	Cl(1)-Ta-N(1)	99.3(2)
Ta-N(1)	1.745(5)	Cl(1)-Ta-N(2)	168.8(1)
Ta-N(2)	2.273(5)	Cl(1)-Ta-N(3)	86.4(1)
Ta-N(3)	2.452(5)	Cl(2)-Ta-N(3)	160.84(7)
N(1)-C(1)	1.475(1)	Cl(2)-Ta-N(1)	99.6(2)
		Cl(2)-Ta-N(2)	84.6(1)
		Cl(2)-Ta-N(3)	81.5(1)
		Cl(3)-Ta-N(1)	97.0(2)
		Cl(3)-Ta-N(2)	85.4(1)
		Cl(3)-Ta-N(3)	81.1(1)
		N(1)-Ta-N(2)	91.9(2)
		N(1)-Ta-N(3)	174.1(2)
		N(2)-Ta-N(3)	82.4(2)
		Ta-N(1)-C(1)	175.0(5)

and N(1) is short, 1.745(5) Å while the Ta-N(1)-C(1) angle is almost linear, 175.0(5)°. This closely resembles $(\text{PhN})\text{TaCl}_3\text{THF}(\text{PEt}_3)$, which has a Ta-N distance of 1.765(5) Å and a Ta-N-C angle of 173.3(4)° [14]. The Ta-N(3) distance, 2.452(5) Å, is significantly longer than the Ta-N(2) distance, 2.273(5) Å, reflecting the

strong trans influence of the imido ligand. The structure of **1a** derived from solution NMR spectra, which show two sets of non-equivalent py signals, is consistent with the diffraction results. Since **1b** and **1c** showed very similar NMR spectra in the py region, they are thought to be isostructural with **1a**.

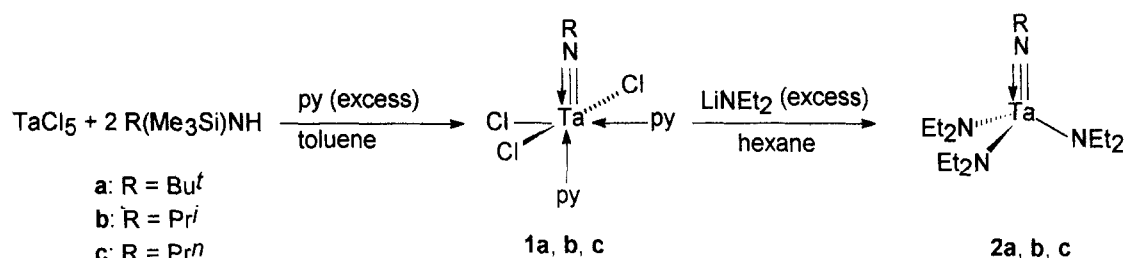
The complexes $(\text{RN})\text{TaCl}_3\text{py}_2$ react with LiNET_2 to generate $(\text{RN})\text{Ta}(\text{NET}_2)_3$ in good yield (Scheme 1). The three complexes are air- and moisture-sensitive liquids. In a mass spectrometer, they all showed M^+ signals corresponding to the m/z values for the $(\text{RN})\text{Ta}(\text{NET}_2)_3^+$ ions. NMR data show resonance signals which can be assigned to the alkyl groups on the imido and the amido ligands. Based on the data, **2** are proposed to have structures resembling those of tris(dimethylamido)(tertbutylimido)tantalum(V) and tris(dimethylamido)(2,6-diisopropylphenylimido)niobium(V) [8, 15]. Being volatile liquids at 60°C under vacuum is a significant advantage for **2** to be considered as CVD precursors. **2a** has been employed successfully as a single-source precursor to deposit good quality tantalum nitride thin films for electronic device applications [9–11]. Investigations are underway to study the potential applications of **2b** and **2c** as the CVD precursors to TaN thin films.

EXPERIMENTAL

All chemicals and solvents were manipulated under dry and oxygen-free environments. TaCl_5 was purchased from Strem and used without further purification. RNH_2 and pyridine were supplied by Merck and degassed before use. Me_3SiCl was obtained from Janssen and used as received. LiNET_2 was prepared from HNET_2 and Bu^nLi (Janssen) in hexane. All ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 300 and 75-MHz, respectively, on a Varian Unity-300 spectrometer at +25°C. Mass spectra were measured (Vacuum Generator Trio-2000) by the direct insertion method. Elements were analyzed with a Heraeus CHN-O-Rapid Analyzer.

Preparation of $(\text{Bu}'\text{N})\text{TaCl}_3\text{py}_2$ **1a**

To $\text{Bu}'(\text{Me}_3\text{Si})\text{NH}$ (2.3 cm³, 12 mmol), prepared *in situ* by reacting Me_3SiCl (1.5 cm³, 12 mmol) with $\text{Bu}'\text{NH}_2$ (2.6 cm³, 25 mmol) in toluene (100 cm³), TaCl_5 (2.0 g, 5.5 mmol) was added. After the mixture was stirred for 1 h at room temperature, pyridine (1.6 cm³, 21 mmol) was added. The mixture was stirred overnight then filtered. A yellow solid was separated after the filtrate was concentrated (2.4 g, 85% based on Ta). Recrystallization from toluene at -15°C gave large crystals suitable for X-ray structural analysis. ^1H NMR (benzene-*d*₆): 1.53 (s, 9H, Me_3CN), 6.27 (t, 2H, *m*- $\text{C}_6\text{H}_5\text{N}$), 6.52 (br, 2H, *m*- $\text{C}_6\text{H}_5\text{N}$), 6.67 (t, 1H, *p*- $\text{C}_6\text{H}_5\text{N}$), 6.84 (br, 1H, *p*- $\text{C}_6\text{H}_5\text{N}$), 8.89 (d, 2H, *o*- $\text{C}_6\text{H}_5\text{N}$), 9.18 (br, 2H, *o*- $\text{C}_6\text{H}_5\text{N}$). ^{13}C NMR (chloroform-*d*): 31.6 (Me_3CN), 66.2 (Me_3CN), 124.2 (*m*-



Scheme 1. Syntheses of 1 and 2.

C₆H₅N), 124.5 (m-C₆H₅N), 139.2 (p-C₆H₅N), 140.6 (p-C₆H₅N), 151.6 (o-C₆H₅N), 152.9 (o-C₆H₅N). Mass (EI, m/z, ³⁵Cl, ¹⁸¹Ta): 342 [M-2 py-Me]⁺. Anal. Calcd. for TaC₁₄H₁₉N₃Cl₃: C, 32.54; H, 3.68; N, 8.13. Found: C, 32.50; H, 3.84; N, 8.02.

Preparation of (PrⁿN)TaCl₅py₂ **1b** and (PrⁿN)TaCl₅py₂ **1c**

By using Prⁱ(Me₃Si)NH and Prⁿ(Me₃Si)NH, **1b** and **1c** were synthesized by a procedure similar to the one used to prepare **1a**.

1b ¹H NMR (benzene-*d*₆): 1.38 (d, 6H, Me₂CHN), 5.22 (m, 1H, Me₂CHN), 6.28 (t, 2H, m-C₆H₅N), 6.59 (br, 2H, m-C₆H₅N), 6.82 (t, 1H, p-C₆H₅N), 6.92 (br, 1H, p-C₆H₅N), 8.81 (d, 2H, o-C₆H₅N), 9.15 (br, 2H, o-C₆H₅N). ¹³C NMR (chloroform-*d*): 25.1 (Me₂CHN), 61.9 (Me₂CHN), 124.3 (m-C₆H₅N), 124.7 (m-C₆H₅N), 139.0 (p-C₆H₅N), 140.2 (p-C₆H₅N), 151.6 (o-C₆H₅N), 152.8 (o-C₆H₅N). Mass (EI, m/z, ³⁵Cl, ¹⁸¹Ta): 343 [M-2 py]⁺. Anal. Calcd. for TaC₁₃H₁₇N₃Cl₃: C, 31.06; H, 3.38; N, 8.36. Found: C, 30.95; H, 3.72; N, 8.21.

1c ¹H NMR (benzene-*d*₆): 1.02 (t, 3H, MeCH₂CH₂N), 1.62 (m, 2H, MeCH₂CH₂N), 5.02 (t, 2H, MeCH₂CH₂N), 7.34 (m, 4H, m-C₆H₅N), 7.81 (t, 1H, p-C₆H₅N), 7.90 (t, 1H, p-C₆H₅N), 8.77 (d, 2H, o-C₆H₅N), 8.88 (br, 2H, o-C₆H₅N). ¹³C NMR (chloroform-*d*): 12.0 (MeCH₂CH₂N), 26.2 (MeCH₂CH₂N), 63.1 (MeCH₂CH₂N), 124.4 (m-C₆H₅N), 124.8 (m-C₆H₅N), 138.6 (p-C₆H₅N), 140.1 (p-C₆H₅N), 151.5 (o-C₆H₅N), 152.5 (o-C₆H₅N). Mass (EI, m/z, ³⁵Cl, ¹⁸¹Ta): 343 [M-2 py]⁺. Anal. Calcd. for TaC₁₃H₁₇N₃Cl₃: C, 31.06; H, 3.38; N, 8.36. Found: C, 30.71; H, 3.43; N, 8.23.

Preparation of (BuⁿN)Ta(NEt₂)₃ **2a**

To **1a** (2.4 g, 4.6 mmol) suspended in hexane (100 cm³), LiNEt₂ (1.8 g, 23 mmol) suspended in hexane (50 cm³) was added slowly. The mixture turned brown gradually as it was stirred overnight. After filtration, the filtrate was concentrated to a brown liquid. Purification by vacuum distillation (60 °C, 10⁻¹ mm Hg) gave a yellow liquid (1.4 g, 65% based on Ta). ¹H NMR (benzene-*d*₆): 1.15 (t, 18H, MeCH₂N), 1.43 (s, 9H, Me₃CN), 3.47 (q, 12H,

MeCH₂N). ¹³C NMR (benzene-*d*₆): 17.2 (MeCH₂N), 34.5 (Me₃CN), 47.6 (MeCH₂N), 66.2 (Me₃CN). Mass (EI, m/z, ¹⁸¹Ta): 468 [M]⁺. A satisfactory carbon analysis was not obtained. Anal. Calcd. for TaC₁₆H₃₉N₄: C, 41.02; H, 8.39; N, 11.96. Found: C, 40.35; H, 8.30; N, 11.93.

Preparation of Ta(NPrⁱ)(NEt₂)₃ **2b** and Ta(NPrⁿ)(NEt₂)₃ **2c**

2b and **2c** were synthesized by a procedure similar to the one used to prepare **2a**.

2b ¹H NMR (benzene-*d*₆): 1.17 (t, 18H, MeCH₂N), 1.32 (d, 6H, Me₂CHN), 3.45 (q, 12H, MeCH₂N), 4.38 (m, 1H, Me₂CHN). ¹³C NMR (benzene-*d*₆): 17.3 (MeCH₂N), 28.1 (Me₂CHN), 47.8 (MeCH₂N), 62.2 (Me₂CHN). Mass (EI, m/z, ¹⁸¹Ta): 454 [M]⁺. Satisfactory C and H analyses were not obtained. Anal. Calcd. for TaC₁₅H₃₇N₄: C, 39.65; H, 8.21; N, 12.33. Found: C, 40.35; H, 6.84; N, 12.53.

2c ¹H NMR (benzene-*d*₆): 1.04 (t, 3H, MeCH₂CH₂N), 1.19 (t, 18H, MeCH₂N), 1.70 (m, 2H, MeCH₂CH₂N), 3.44 (q, 12H, MeCH₂N), 4.16 (t, 2H, MeCH₂CH₂N). ¹³C NMR (benzene-*d*₆): 11.9 (MeCH₂CH₂N), 17.3 (MeCH₂N), 28.2 (MeCH₂CH₂N), 47.8 (MeCH₂N), 64.0 (MeCH₂CH₂N). Mass (EI, m/z, ¹⁸¹Ta): 454 [M]⁺. A satisfactory carbon analysis was not obtained. Anal. Calcd. for TaC₁₅H₃₇N₄: C, 39.65; H, 8.21; N, 12.33. Found: C, 38.29; H, 7.96; N, 12.64.

Structure determination of **1a**

A single crystal of **1a** was sealed in a glass capillary under an inert atmosphere. Data were collected on a Nonius CAD-4 using graphite-monochromated Mo K α radiation, and the structure was solved by the heavy-atom method; all data reduction and structural refinements were performed with the NRCC SDP package. Crystal data, details of data collection, and structural analysis are summarized in Table 2. The methyl groups of Buⁱ are disorder with half occupancies. They are designated as C(2), C(3), C(4) and C(2)', C(3)', C(4)', and refined isotropically. The other non-hydrogen atoms were refined with anisotropic parameters. Only hydrogen atoms of pyridine were placed in idealized positions and included in the cal-

Table 2. Crystal data and conditions for crystallographic data collection and structure refinement

Formula	C ₁₄ H ₁₉ N ₃ Cl ₃ Ta
Formula weight	516.72
Space group	P2 ₁ /c
<i>a</i> (Å)	9.664(5)
<i>b</i> (Å)	13.535(2)
<i>c</i> (Å)	14.569(3)
β (°)	90.25(3)
<i>V</i> (Å ³)	1905.5(11)
<i>Z</i>	4
ρ _{calc} , g cm ⁻³	1.769
λ (Å)	0.7107
<i>F</i> (000)	992
Unit cell determination: number; (2θ range)	25; (17.00–34.00 deg.)
Scan type	θ/2 θ
Scan width (°)	2(0.65 + 0.35tan(θ))
2 θ (max)	50.0
μ, cm ⁻¹	61.228
crystal size, mm	0.50 × 0.50 × 0.50
<i>T</i> , °C	25
Number of observed reflections (<i>I</i> > 2.0 sig(<i>I</i>))	2733
Number of unique reflections	3347
R _F ^a , R _w ^b	0.031, 0.032
GoF ^c	2.62
Refinement program	NRCVAX
Number of refined parameters	188 (2733 out of 3347 reflections.)
Minimize function	Σ(<i>w</i> (<i>F_o</i> - <i>F_c</i>) ²)
Weights scheme	(1/σ(<i>F_o</i>) ²)
<i>g</i> (2nd. extinction coefficient) × 10 ⁴	1.56(4)
(δ/σ)max	0.0480
(D-map)max.min e/Å ³	-1.260; 1.000

a, R_F = Σ(*F_o* - *F_c*)/Σ *F_o*; *b*, R_w = [Σ(*w*(*F_o* - *F_c*)²/Σ*wF_o*²)]^{1/2}; *c*, GoF = [Σ(*w*(*F_o* - *F_c*)²)/(No. of reflections - No. of parameters)]^{1/2} Standard reflections: No. 3; Decay 5%; every 3600 seconds; ¹Bu disorder.

culations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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