New Volatile Tantalum Imido Precursors with Carboxamide Ligands

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ABSTRACT: A series of Ta(V) tBu-imido/N-alkoxy carboxamide complexes, TaCl₂(NBu)(pyridine)(edpa) (1), TaCl₂(NBu)(edpa)₂ (2), Ta(NBu)(edpa)₃ (3), TaCl₂(NBu)(pyridine)(mdpa) (4), and Ta(NBu)(mdpa)₃ (5), were successfully synthesized by metathesis reactions between Ta(N(Bu)Cl₃(py)₂ and several equivalents of Na(edpa) (edpaH = N-ethoxy-2,2-dimethylpropanamide) and Na(mdpa) (mdpaH = N-methoxy-2,2-dimethylpropanamide). Furthermore, complexes 3 and 5 were simply transformed to new dimeric structures [Ta(μ₂-O)(edpa)₃]₂ (6) and [Ta(μ₂-O)(mdpa)₃]₂ (7) with the elimination of the NBu imido group by air exposure. Compounds 1–7 were characterized by 1H and 13C nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, elemental analysis, thermogravimetric analysis (TGA), and single-crystal X-ray diffraction. Single-crystal X-ray diffraction analysis revealed that complexes 3 and 5 have a distorted pentagonal bipyramidal geometry around the central Ta atom, with three monoanionic bidentate N-alkoxy carboxamide ligands and one tBu imido ligand saturating the coordination of tantalum ions. TGA revealed that complexes 3 and 5 have superior thermal characteristics and stability. These complexes could potentially be applied as precursors for tantalum oxide thin films.

INTRODUCTION

Tantalum oxide (Ta₂O₅) is a dielectric material with excellent chemical, physical, and thermal stability, a high refractive index (~2.2), high dielectric constants (~15 for an amorphous film and ~50 for a crystalline film), good dielectric breakdown strength, a wide optical band gap (~4.3 eV), and low leakage currents.1–5 Owing to these fascinating properties, Ta₂O₅ thin films have a wide range of applications, such as copper diffusion barriers, antireflective coatings, corrosion-resistant coatings, optical waveguides, alternative gate dielectrics in metal oxide semiconductor devices, thin-film transistors (TFTs), and high-k dielectric in dynamic random access memory.4–6 In addition, Ta-based oxides have also recently received considerable attention for resistive random access memory (ReRAM) applications because of their superior device performance, endurance, and switching speed in comparison with other transition metal oxides.7–9

Ta₂O₅ thin films have been fabricated using various methods such as sputtering, electrospray deposition, electron beam evaporation, chemical vapor deposition (CVD), photo-CVD, and atomic layer deposition (ALD).9–14 In particular, ALD is the most advanced technique for the fabrication of thin films because it allows the precise control of the thickness, uniformity over a large area, and conformity, which are requirements for most of the abovementioned applications.

The fabrication of Ta₂O₅ by ALD and CVD has been compared with other transition metal oxides.7,8 In particular, ALD is an appropriate technique for the fabrication of high thermal stability.2,21,22 However, efforts have been dedicated to introducing imido groups such as Ta(NBu)(NEt)₃ and Ta(NBu)(dmamp)₂(CH₃) (dmampH = 1-dimethylamino-2-methyl-2-propanol) with high thermal stability.21,22 Our study is focused on the development of novel tantalum precursors by introducing an imido ligand and N-alkoxy carboxamide ligands with high tunability on both sides of the amide group. The imido ligand has several advantages from a precursor perspective. First, it was reported by several research groups that imido groups containing tantalum complexes have superior thermal characteristics and stability.23–25

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Scheme 1. Synthesis of Complexes 1–5

Scheme 1: Synthesis of Complexes 1–5

**RESULTS AND DISCUSSION**

**Synthesis.** As shown in Scheme 1, the reaction of TaCl(NBu)(pyridine) with 1 equiv of Na(edpa) afforded a pale yellow liquid, TaCl(NBu)(py)(edpa) (1) in 88% yield. A similar reaction with 2 and 3 equiv of Na(edpa) afforded TaCl(NBu)(edpa) (2) and Ta(NBu)(edpa) (3) as pale yellow and yellow-brown liquids in 80 and 85% yields, respectively. Complexes 2 and 3 were purified by vacuum distillation (100 °C/0.5 Torr and 110 °C/0.5 Torr). Complex 3 was converted to Crystalline powder as the temperature decreased to room temperature owing to its low melting point (35 °C). TaCl(NBu)(py)(mdpa) (4) and Ta(NBu)(mdpa) (5) were synthesized by a similar procedure using Na(mdpa) instead of Na(edpa). Complexes 4 and 5 were obtained as a yellow liquid and a white crystalline powder, respectively, and complex 5 was purified by vacuum sublimation (100 °C/0.5 Torr). All of the compounds were stable under inert conditions. The prepared complexes were highly soluble in organic solvents as well as toluene, tetrahydrofuran (THF), and diethyl ether. The 1H NMR spectrum of complex 1 in the benzene-d6 solution showed an upfield shift of the 1Bu protons from the imido group (NC(CH3)3) from 1.47 to 1.41 ppm and the edpa ligand (CC(CH3)3) from 1.31 to 1.13 ppm compared to that of the free ligand. Furthermore, the ethoxy (1.12 (OCH2CH3) and 4.68 (OCH2CH3)); and pyridine (6.39 (H2) and 6.67 (H2)) and pyridine (6.37 (H2)), peaks shifted with respect to Na(edpa) (1.28 (OCH2CH3) and 4.03 ppm (OCH2CH3)) and free pyridine (6.66 (H2), 6.98 (H2), and 8.53 (H2)). In the case of complex 2, the signals for the 1Bu group in the imido and edpa ligands appeared at 1.28 and 1.35 ppm, respectively. These peaks were shifted upfield and downfield relative to those of the relevant starting materials, respectively, indicating that the nitrogen in the imido group was bound to the tantalum center. The ethoxy peaks were shifted to 1.32 ppm (OCH2CH3) and 4.67 ppm (OCH2CH3). The 1H NMR spectrum of complex 3 showed two singlet signals about 1Bu groups at 1.27 (NC(CH3)3) and 1.34 (CC(CH3)3). Furthermore, the broad ethoxy signals appeared at 1.25 ppm for OCH2CH3 and 4.00 and 4.52 ppm for OCH2CH3, where the CH2 of the broad ethoxy group showed two resonances as a 2:1 ratio at room temperature. The 1H NMR spectrum of complex 4 showed three singlet peaks and 1 equiv pyridine peaks at 1.11 (CC(CH3)3), 1.41 (NC(CH3)3), 4.21 (OCH2), 6.37 (py, H2), 6.67 (py, H2), and 8.75 (py, H2) ppm. The 1Bu peaks of the complexes were shifted upfield and the methoxy peaks were shifted downfield. The 1H NMR spectrum of complex 5 showed three singlets at 1.24, 1.31, and 4.14 ppm, corresponding to the NC(CH3)3, CC(CH3)3, and OCH3 groups. In the case of complex 5, the 1Bu peak from the imido group shifted upfield, while the other peaks were shifted downfield with respect to those of the starting materials. Additionally, the low-temperature 1H NMR spectra of 5 in toluene-d8 showed a broad singlet signal related to the methoxy group at room temperature. However, the methoxy signal was split into two broad singlet resonances as a 2:1 ratio at 4.12 and 3.56 ppm at −5 and 5 °C (Figure S11). The reaction of TaCl(NBu)(py)2 with 2 equiv of Na(mdpa) afforded a mixture of Ta(NBu)(mdpa)3, TaCl(NBu)(mdpa)2, and TaCl(NBu)(py)(mdpa), as confirmed by 1H NMR spectroscopy, and the mixtures were not isolated pure products (Figure S12).

**Crystal Structure.** X-ray-quality single crystal 3 could be grown from the distillate of complex 3 at room temperature, and crystal 5 was obtained from a saturated toluene solution at −30 °C. The selected bond lengths and angles of the complexes are listed in Table 1 and structure refinement data are listed in Table 2. As shown in Figures 1 and 2, the Ta metal center is surrounded by three N-alkoxy carboxamide ligands and one 1Bu imido group and has [O3N1] seven coordination. The carboxamide ligands acted as a monoanionic bidentate, which was evident by the relatively short Ta–O bond lengths (1.21–O2: 2.048(8), Ta1–O4: 2.042(7), and Ta1–O5: 2.060(7) for 3 and Ta1–O2: 2.040(13) and Ta1–O4: 2.0565(18) for 5) in comparison with coordinated Ta–O (1.21–O1: 2.263(8), Ta1–O3: 2.267(8), and Ta1–O6: 2.260(7) for 3 and Ta1–O1: 2.2854(14) and Ta1–O3: 2.2673(19) for 5). The 1Bu imido group and one oxygen atom of the carboxamide ligand are located in axial positions with devoted bond angles (172.4(3) and 172.25(9)°) from the ideal angle (180°), while the other oxygen atoms form the...
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 3 and 5

| Bond Lengths (Å) | Ta(N'Bu)(edpa)$_3$ (3) | Ta(N'Bu)(mdpa)$_3$ (5) |
|-----------------|-------------------------|------------------------|
| Ta1−N1         | 1.773(9)                | 1.761(2)               |
| Ta1−O1         | 2.263(8)                | 2.2854(14)             |
| Ta1−O2         | 2.048(8)                | 2.0404(13)             |
| Ta1−O3         | 2.267(8)                | 2.2673(19)             |
| Ta1−O4         | 2.042(7)                | 2.0565(18)             |
| Ta1−O5         | 2.060(7)                |                        |
| Ta1−O6         | 2.260(7)                |                        |

| Bond Angles (deg) | Ta(N'Bu)(edpa)$_3$ (3) | Ta(N'Bu)(mdpa)$_3$ (5) |
|------------------|-------------------------|------------------------|
| N1−Ta1−O1        | 92.5(3)                 | 91.23(4)               |
| N1−Ta1−O2        | 104.8(4)                | 103.20(7)              |
| N1−Ta1−O3        | 90.9(4)                 | 172.25(9)              |
| N1−Ta1−O4        | 101.0(4)                | 102.41(9)              |
| N1−Ta1−O5        | 102.5(3)                | 82.89(5)               |
| N1−Ta1−O6        | 172.4(3)                | 69.84(6)               |
| O1−Ta1−O2        | 67.6(3)                 | 74.96(7)               |
| O1−Ta1−O4        | 67.9(3)                 | 73.85(4)               |
| O1−Ta1−O6        | 70.0(3)                 | Ta1−N1−C1 174.4(2)    |
| O2−Ta1−O4        | 73.5(3)                 |                        |
| O3−Ta1−O5        | 74.6(3)                 |                        |
| Ta1−N1−C1        | 174.4(2)                |                        |

Table 2. X-ray Data Collection and Structure Refinement for Complexes 3 and 5

| Empirical formula | C$_{25}$H$_{50}$N$_4$TaO$_6$ | C$_{22}$H$_{48}$N$_4$TaO$_6$ |
|------------------|-----------------------------|-----------------------------|
| Formula weight   | 683.64                      | 645.59                      |
| Temperature (K)  | 100(1)                      | 100(1)                      |
| Crystal system   | monoclinic                  | orthorhombic                |
| Space group      | P2$_1$/n                    | Pnma                        |
| a (Å)            | 11.4733(3)                  | 16.2677(2)                  |
| b (Å)            | 16.5773(4)                  | 16.0705(2)                  |
| c (Å)            | 17.1424(4)                  | 11.2870(2)                  |
| α (deg)          | 90                          | 90                          |
| β (deg)          | 90                          | 90                          |
| γ (deg)          | 90                          | 90                          |
| V (Å$^3$)        | 3244.36(14)                 | 2950.76(7)                  |
| Z                | 4                           | 4                           |
| $\rho$ (mg m$^{-3}$) | 1.400                      | 1.453                       |
| $\mu$ (mm$^{-1}$) | 3.427                      | 3.763                       |
| F(000)           | 1396                        | 1316                        |
| θ range (deg)    | 1.71−25.45                  | 4.03−25.79                  |
| No. of reflections collected | 43,467                        | 38,808                        |
| No. of reflections independent | 6001                        | 2920                        |
| No. of reflections with I > 2$\sigma$(I) | 5959                        | 2920                        |
| $\bar{R}_{	ext{merge}}$ | 0.7452                      | 0.963                       |
| $\bar{R}_{	ext{intensity}}$ | 0.4625                      | 0.574                       |
| No. of parameters | 409                         | 175                         |
| Goodness of fit on F2 | 1.1031                    | 1.0435                      |
| R$^2$            | 0.0636                      | 0.0148                      |
| wR$_{2}^{b}$     | 0.1570                      | 0.0377                      |
| Maximum in $\Delta\rho$ (e Å$^{-3}$) | 3.4901                      | 0.3736                      |
| Minimum in $\Delta\rho$ (e Å$^{-3}$) | $-3.2538$                  | $-0.5428$                   |

$\bar{R} = \left( \sum |F_{o}| - |F_{c}| / \sum |F_{o}| \right)$. $wR_{2} = \left( \sum w(F_{o}^2 - F_{c}^2)^2 / \right) / \sum \left[ w(F_{o}^2) \right]^{1/2}$. 

Figure 1. Crystal structure of Ta(N'Bu)(edpa)$_3$ (3) without disorder. H atoms are omitted for clarity. Color code: Ta, green; N, blue; O, red; and C, gray.

Figure 2. Crystal structure of Ta(N'Bu)(mdpa)$_3$ (5). H atoms are omitted for clarity. Color code: Ta, green; N, blue; O, red; and C, gray.

equatorial plane of the pentagonal bipyramid. The bond angle between the nitrogen atom in the imido group and the five oxygen atoms in the equatorial plane are in ranges of 90.9−104.8° for compound 3 and 91.23−103.20° for compound 5 similar to the reported distorted pentagonal bipyramid geometry complexes. In particular, one oxygen atom in the equatorial plane from the axial chelating carboxamide is slightly distorted with the plane composed of four other equatorial oxygen atoms in the range of known distorted pentagonal bipyramid geometry complexes (25.21 and 26.80°). The equatorial site bond angles were 358.3° for compound 3 and 358.5° for compound 5, which approximate the ideal angle of 360°. The Ta−N−C unit of the imido ligand was nearly linear.
The Ta–N bond length is in the range of known Ta–NBu imido complexes (1.773(9) and 1.761(2) Å). The Ta–N bond length is in the range of known Ta–NBu imido complexes (1.773(9) and 1.761(2) Å). Moreover, complexes 3 and 5 were transformed into dimeric structures [Ta(μ2−O)(edpa)3]2 (6) and [Ta(μ2−O)−(mdpa)3]2 (7) by eliminating the tBu imido group when exposed to air for 1 day (Scheme 2). Complexes 6 and 7 were obtained as a white crystalline powder and purified via recrystallization from a saturated toluene solution at −30 °C.

The reaction between the imido group and water is well known in numerous studies. Complexes 6 and 7 were characterized by 1H NMR spectroscopy, EA, FT-IR, and single-crystal X-ray analysis (Tables S1 and S2 and Figures S13−S16 and 3). The 1H NMR spectrum of complex 6 showed only edpa ligand peaks at 0.90 (s, 9H, CC(CH3)3), 1.05 (t, 3H, OCH2CH3), and 3.76 ppm (q, 2H, OC(CH3)2). Complex 7 also showed only two singlet peaks at 0.90 (s, 9H, CC(CH3)3) and 3.50 ppm (s, 3H, OCH3), the corresponding mdpa ligands. Single-crystal X-ray diffraction revealed that complex 6 crystallized in monoclinic C2/c. The Ta metal centers were saturated with three edpa ligands and two bridging oxygens; edpa ligands act as monoanionic bidentate ligands, as evidenced by the relatively short Ta–O bond lengths (Ta1–O1, 2.0345(19), Ta1–O3, 2.031(2), and Ta1–O5, 1.9981(19)) in comparison with coordinated Ta–O (Ta1–O2, 2.274(2), Ta1–O4, 2.323(2), and Ta1–O6, 2.3916(19)). Complex 6 formed a dimer with an oxygen atom bridging the two metal centers in the complexes via μ2−O bonding.

Figure 3. Crystal structure of [Ta(μ2−O)(edpa)3]2. H atoms are omitted for clarity. Color code: Ta, green; N, blue; O, red; and C, gray.

Thermogravimetric Analysis. The TGA of complexes 1−7 was conducted from room temperature to 800 °C under a constant flow of nitrogen gas (Figure 4). The TGA traces of 1, 2, 4, 6, and 7 exhibited multistep weight losses with 32−36% residual weight. The residues of 1, 2, 4, 6, and 7 were slightly less than the calculated residues for tantalum oxide (Ta2O5: 40.4, 38.3, 41.5, 35.5, and 44.9). In contrast, the TGA traces of complexes 3 and 5 primarily displayed single-step weight losses (82 and 86%, respectively), which began at 120 and 200 °C, respectively. The residual weight was less than the calculated value because of the vaporization of 3 and 5 before decomposition (Ta2O5: 34 and 32%). Consequently, complexes 3 and 5 have excellent thermal characteristics compared to complexes 1, 2, and 4, which undergo a single-step weight loss and are likely to vaporize before decomposition. TGA data
of Ta amino-alkoxide precursors previously reported by our laboratory such as Ta(N'Bu)(damp)_2Cl and Ta(N'Bu)_(damp)_2CH_3 showed weight losses at 180–300 and 200–320 °C, with residues of 40 and 32%, respectively.\(^\text{22}\) Thermal characteristics and volatility of 3 and 5 are better than our Ta amino-alkoxide precursors. Thereby we suggest 3 and 5 as suitable precursors to deposit tantalum-based oxide thin films.

**CONCLUSIONS**

In summary, we successfully synthesized and characterized a series of new Ta(V) 1Bu-imido/Na-alkoxy carboxamide complexes, TaCl_2(N'Bu)(pyridine)(edpa) (1), TaCl_2(N'Bu)-(edpa)_2 (2), Ta(N'Bu)(edpa)_3 (3), TaCl_2(N'Bu)(pyridine)-(mdpa) (4), and Ta(N'Bu)(mdpa)_3 (5), for the fabrication of tantalum-based oxide materials. Complexes 1, 2, and 4 were obtained as liquids, while complexes 3 and 5 were obtained as crystalline powders. Furthermore, complexes 3 and 5 were simply transformed into dimeric structures 6 and 7 because of their high reactivity with H_2O. Single-crystal X-ray crystallography revealed that complexes 3 and 5 had a distorted pentagonal bipyramidal geometry around the central Ta atom, with one 1Bu imido group and three bidentate N-alkoxy carboxamide ligands. The TGA trace showed clear single-step weight losses with low nonvolatile residues in complexes 3 and 5. These results indicate that complexes 3 and 5 are more suitable as CVD/ALD precursors for the fabrication of tantalum-based oxide thin films than other complexes. The study of thin-film deposition with compounds 3 and 5 as precursors is currently ongoing in our laboratory.

**EXPERIMENTAL SECTION**

**General Procedure.** All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a glovebox. All solvents were purified by the Innovative Technology PS-MD-4 solvent purification system. All reagents were purchased from Sigma-Aldrich and/or Acros. A series of N-alkoxy carboxamide-type ligands, edpaH and mdpaH, were prepared by the literature procedure.\(^\text{25}\) Na(edpa) and Na(mdpa) were prepared by the literature procedure by a modified literature method.\(^\text{25}\) TaCl_3(N'Bu)(pyridine)_2 was obtained by modifying the reported methods.\(^\text{32}\) \(^{1}H\) NMR and \(^{13}C\) NMR spectra were recorded on a Bruker DPX 500 MHz FT-NMR spectrometer. All samples for NMR measurements were contained in sealed NMR tubes and referenced using benzene-\(d_6\) as the standard. Infrared (IR) spectra were collected in the 4000–400 cm\(^{-1}\) range with a SHIMADZU IRSpirit FT-IR spectrophotometer in a 4 nm KBr window. The samples were prepared in a glovebox. Elemental analysis (EA) was performed using a Thermo Scientific Flash 2000 CHNS analyzer. Thermogravimetric analysis (TGA) was performed under a N_2 atmosphere at a scan rate of 10 °C min\(^{-1}\) using a Thermo plus EVO II TG8120 series thermogravimetry and differential thermal analysis instrument from Rigaku.

**Preparation of Starting Materials. Na(edpa).** First, edpaH (1.0 g, 6.9 mmol) was added dropwise to a NaH (0.16 g, 6.9 mmol) suspension in toluene (100 mL) at room temperature. After reacting for 12 h, the mixture was filtered. A white powder was obtained via evaporation of the filtrate in vacuo. Yield: 1.037 g (90%).\(^\text{1}\)H NMR (C_6D_6, 500 MHz): \(\delta\) 1.26 (t, 3H, OCH_2CH_3), 1.30 (s, 9H, C(CH_3)_3), 3.22 (q, 2H, OCH_2CH_3).

**Na(mdpa).** First, mdpaH (1.0 g, 7.6 mmol) was added dropwise to a NaH (0.18 g, 7.6 mmol) suspension in toluene (100 mL) at room temperature. After reacting for 12 h, the mixture was filtered. A white powder was obtained via evaporation of the filtrate in vacuo. Yield: 0.98 g (85%).\(^\text{1}\)H NMR (C_6D_6, 500 MHz): 1.31 (s, 9H, C(CH_3)_3), 3.73 (s, 3H, OCH_3).

**Preparation of Tantalum Complexes 1–5. TaCl_2(N'Bu)-(py)(edpa) (1).** Na(edpa) (0.324 g, 1.94 mmol) was slowly added to a solution of TaCl_3(N'Bu)(py)_2 (1.00 g, 1.94 mmol) in 60 mL of toluene. The reaction mixture was allowed to stir overnight at room temperature. After filtering the mixture to remove the salts, the filtrate was concentrated in vacuo to afford the desired product. A pale yellow liquid was obtained. Yield: 0.933 g (88%); \(^{1}\)H NMR (C_6D_6, 500 MHz): \(\delta\) 1.12 (t, 3H, OCH_2CH_3), 1.13 (s, 9H, CC(CH_3)_3), 1.41 (s, 9H, NC(CH_3)_3), 4.68 (q, 2H, OCH_2CH_3), 6.40 (m, 2H, H_2 py), 6.67 (m, 1H, H_py), 8.80 (m, 2H, H_PY), 7.68 (m, 2H, H_PY), 7.69 (m, 2H, H_PY), 13C NMR (C_6D_6, 125 MHz): \(\delta\) 14.78 (OCH_2CH_3), 27.52 (CO(C(CH_3)_3)), 32.26 (NC(CH_3)_3), 35.32 (CO(CH_2CH_3)), 58.70 (OCH_2CH_3), 72.63 (NC(CH_3)_3), 124.34 (C_2 py), 139.15 (C_2 py), 151.07 (C_2 py), 171.05 (CO(CH_2CH_3)). IR (KBr, cm\(^{-1}\)): 482, 527, 553, 624, 643, 696, 761, 783, 859, 887, 1014, 1040, 1067, 1189, 1218, 1277, 1330, 1359, 1396, 1446, 1481, 1518, 1608, 2866, 2899, 2969. Anal. Calc'd for C_26H_46Cl_3Na_2TaO_7: C, 35.18; H, 5.17; N, 7.69. Found: C, 34.65; H, 5.01; N, 8.10.

**TaCl_2(N'Bu)(py)(mdpa) (2).** Na(mdpa) (0.648 g, 3.88 mmol) was slowly added to a solution of TaCl_3(N'Bu)(py)_2 (1.00 g, 1.94 mmol) in 60 mL of toluene. The reaction mixture was allowed to stir overnight at room temperature. After filtering the mixture to remove the salts, the filtrate was concentrated in vacuo to afford the desired product, and it was purified via distillation at 100 °C under 0.5 Torr to afford a pure product as a pale yellow liquid. Yield: 0.894 g (80%); \(^{1}\)H NMR (C_6D_6, 500 MHz): \(\delta\) 1.28 (s, 9H, NC(CH_3)_3), 1.32 (t, 6H, OCH_2CH_3), 1.35 (s, 18H, CC(CH_3)_3), 4.55 (br, 4H, OCH_2CH_3).\(^\text{13}\)C NMR (C_6D_6, 125 MHz): \(\delta\) 14.38 (OCH_2CH_3), 27.13 (CO(C(CH_3)_3)), 33.07 (NC(CH_3)_3), 34.93 (CO(C(CH_3)_3)), 64.13 (OCH_2CH_3), 72.23 (NC(CH_3)_3), 171.96 (CO(CH_2CH_3)). IR (KBr, cm\(^{-1}\)): 448, 525, 614, 681, 760, 780, 857, 887, 1043, 1091, 1196, 1287, 1336, 1359, 1368, 1446, 1482, 1512, 1608, 1647, 2600, 2710, 2804, 2893, 2961. Anal. Calc'd for C_26H_46Cl_3N_2TaO_7: C, 37.54; H, 6.48; N, 7.30. Found: C, 38.91; H, 6.84; N, 7.26.

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**Figure 4.** TGA trace of complexes 1–7 under N_2.
Ta(N' Bu) (edpa)3. Na(edpa) (0.972 g, 5.82 mmol) was slowly added to a solution of TaCl5(N' Bu)(py)2 (1.00 g, 1.94 mmol) in 60 mL of toluene. The reaction mixture was stirred overnight at room temperature. After filtering the mixture to remove the salts, the filtrate was concentrated in vacuo to afford the desired product, and it was purified via distillation at 110 °C under 0.5 Torr to afford a pure product as a yellow-brown powder. Melting point: 35 °C. Yield: 1.129 g (85%); 1H NMR (C6D6, 500 MHz): δ 1.25 (br, 9H, OCH2CH3), 1.27 (s, 9H, NC(CH3)3), 1.41 (s, 27H, CC(CH3)3), 4.00 (br, 6H, OCH2CH3), 13C NMR (C6D6, 125 MHz): δ 15.05 (OCH2CH3), 34.76 (OCH2CH3), 63.31 (OCH2CH3), 63.02 (OCH2CH3), 61.78 (OCH2CH3), 72.30 (NCC(CH3)3), 170.74 (COCH3). IR (KBr, cm−1): 451, 487, 503, 554, 574, 613, 636, 679, 752, 886, 929, 1052, 1217, 1368, 1375, 1401, 1484, 1512, 1609, 1645, 2710, 2804, 2892, 2959. Anal. Calcld for C15H26Cl2N3TaO2: C, 33.85; H, 4.92; N, 7.90. Found: C, 36.23; H, 6.59; N, 7.09.

Preparation of Tantalum Complexes 6 and 7. Na(mdpa) (0.972 g, 5.82 mmol) was slowly added to a solution of TaCl5(N' Bu)(py)2 (1.00 g, 1.94 mmol) in 60 mL of toluene. The reaction mixture was allowed to stir overnight at room temperature. After filtering the mixture to remove the salts, the filtrate was concentrated in vacuo to afford the desired product, and it was purified via distillation at 110 °C under 0.5 Torr to afford a pure product as a yellow-brown powder. Melting point: 35 °C. Yield: 1.129 g (85%); 1H NMR (C6D6, 500 MHz): δ 1.25 (br, 9H, OCH2CH3), 1.27 (s, 9H, NC(CH3)3), 1.41 (s, 27H, CC(CH3)3), 4.00 (br, 6H, OCH2CH3), 13C NMR (C6D6, 125 MHz): δ 15.05 (OCH2CH3), 34.76 (OCH2CH3), 63.31 (OCH2CH3), 63.02 (OCH2CH3), 61.78 (OCH2CH3), 72.30 (NCC(CH3)3), 170.74 (COCH3). IR (KBr, cm−1): 451, 487, 503, 554, 574, 613, 636, 679, 752, 886, 929, 1052, 1217, 1368, 1375, 1401, 1484, 1512, 1609, 1645, 2710, 2804, 2892, 2959. Anal. Calcld for C15H26Cl2N3TaO2: C, 33.85; H, 4.92; N, 7.90. Found: C, 36.23; H, 6.59; N, 7.09.

Crystallography. Single crystal 3 was obtained via crystallization at room temperature and crystals 5 and 6 were obtained via recrystallization from toluene at −30 °C. An obtained specimen of suitable size and quality was coated with Paratone oil and mounted on a glass capillary. Reflection data were collected on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The hemisphere of the reflection data was collected as ω scans frames at 0.5° per frame and at an exposure time of 5 s per frame. The cell parameters were determined and refined using the APEX2 program.55 The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using the SADABS program.54 The compound structures were determined by direct methods and refined by full-matrix least-squares using the SHELXTL program package and Olex256 with anisotropic thermal parameters for all non-hydrogen atoms.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03659.

Crystallographic data for complex 3 (CIF)
Crystallographic data for complex 5 (CIF)
Crystallographic data for complex 6 (CIF)

H and 13C NMR spectra of complexes 1−7; 1H NMR spectrum of the TaCl(N' Bu)(mdpa)3 mixture; low-temperature 1H NMR spectra of complex 3; X-ray data collection and structure refinement for 6; and selected bond lengths and bond angles of 6 (PDF)

Accession Codes
CCDC contains the supporting crystallographic data for complexes 3 (CCDC-2091853), 5 (CCDC-2091852), and 6 (CCDC-2095437). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk

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