β-(Triphenylsilyl)styrene.[36] A dry Schlenk tube was charged with **2c** (17 mg, 0.012 mmol), triphenylsilane (3.9 g, 15 mmol), phenylacetylene (2.2 mL, 19.7 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 11 h. The ^1H NMR of the crude material showed evidence of Z product (approximately 1:1 mixture); however, the mixture was distilled (200 °C (ca. 0.1 Torr)) to yield only (E)-β-(triphenylsilyl)-styrene (1.6 g, 25% yield).

Reactions with Other Bis(olefin) Complexes. Complexes **1c**, TpIr-$(C_2H_4)_2$, and $(Cp-d_5)Ir(C_2H_4)_2$[37] were not catalyst precursors for the hydrosilylation of phenylacetylene with triethylsilane at 25 °C in CH_2Cl_2. Both **1c** and $TpIr(C_2H_4)_2$ undergo reaction with the silane/alkyne mixture but do not catalyze the hydrosilylation. $(Cp-d_5)Ir(C_2H_4)_2$ remains unchanged under the reaction conditions. $IndIr(coe)_2$ is a catalyst for the reaction, but it proceeds more slowly than reactions catalyzed by **2a**.

Catalysis with IndIr(coe)₂. A dry Schlenk tube was charged with $IndIr(coe)_2$ (13 mg, 0.023 mmol), triethylsilane (3.7 mL, 23.2 mmol), phenylacetylene (3.7 mL, 33.7 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 7.5 h. The mixture was transferred to a

round-bottom flask and the product distilled (80 °C (ca. 0.1 Torr)) to yield β-(triethylsilyl)acetylene (Z:E = 52:1, 1.02 g, 20% yield, 203 turnovers, 27 turnovers/h).

Deuterium Labeling Studies. β-Deuterio-β-(triethylsilyl)styrene (92% *d*). A dry Schlenk tube was charged with **2c** (10 mg, 0.012 mmol), triethylsilane (0.67 mL, 4.1 mmol), phenylacetylene (92% PhC≡CD, 0.6 mL, 2.2 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 4.5 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (80 °C (ca. 1 Torr)) to yield β-deuterio-β-(triethylsilyl)styrene (92% d_2). ^2H NMR (CHCl₃, 76.77 Hz): δ 5.83 (d, J_{H-D} = 1.8 Hz). ^1H NMR shows about 8% β-(triethylsilyl)styrene by integration.

A dry Schlenk tube was charged with **2c** (11 mg, 0.013 mmol), triethylsilane (>99% R₃SiD, 0.67 mL, 4.1 mmol), phenylacetylene (92% PhC≡CD, 0.58 mL, 2.1 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 4.5 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (80 °C (ca. 1 Torr)) to yield α,β-dideuterio-β-(triethylsilyl)styrene (92% d_2). ^2H NMR (CHCl₃, 76.77 Hz): δ 7.49 (s), 5.83 (s). ^1H NMR shows about 8% α,β-dideuterio-β-(triethylsilyl)styrene by integration.

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Ladder Structure of [('BuCH₂)₂TaN]₅·NH₃·2C₇H₈ and Its Relationship to Cubic TaN

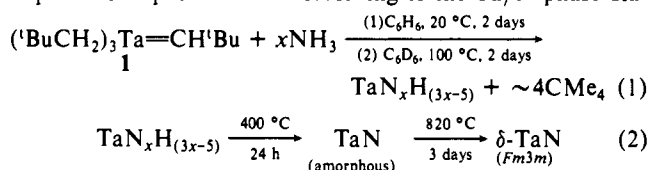**Mark M. Banaszak Holl,**[†] **Peter T. Wolczanski,**[*,‡] **and Gregory D. Van Duyne**

Contribution from the Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York 14853. Received December 18, 1989

Abstract: Ammonolysis of ('BuCH₂)₃Ta=CH'Bu (**1**) at 20 °C produced an intermediate pentamer, [('BuCH₂)₂TaN]₅ (**2**, ~40%); further reaction generated an orange precipitate. Thermolysis of the latter at 400 °C and then 820 °C produced cubic TaN (*Fm3m*, a = 4.300 (2) Å) at temperatures and pressures substantially below those of conventional nitriding procedures. Ammonolysis of ('BuCH₂)₂Ta(NMe₂)₃ (**3**) provided an alternative (19%), route to **2**. ^1H, ^{13}C, and ^{15}N NMR spectra of **2** indicated C_{2v} symmetry, and X-ray crystallographic characterization of [('BuCH₂)₂TaN]₅·NH₃·2C₇H₈ (**2·NH₃·2C₇H₈**) revealed a roughly planar ladder structure of alternating ('BuCH₂)₂TaN units. The interior nitrogens adopt a T-shaped coordination geometry and an NH₃ is weakly bound to an exterior Ta atom. Crystal data (**2·NH₃·2C₇H₈**): triclinic *P1̄*, λ(Mo Kα), μ = 7.068 mm⁻¹, a = 11.616 (2) Å, b = 15.407 (3) Å, c = 23.172 (6) Å, α = 106.120 (17)°, β = 99.060 (18)°, γ = 100.170 (16)°, T = -20 °C, Z = 2, V = 3829.6 (12) Å³, R = 0.083, R_w = 0.098, 7346 (72.8%) reflections where $|F_o| \geq 3\sigma(F_o)$. The conformation of **2·NH₃·2C₇H₈** reflects the motif of cubic TaN, rather than the thermodynamically expected hexagonal form, hence the framework of this ceramic may be dictated by the geometry of the molecular precursor.

Introduction

Organotransition-metal complexes are promising as precursors in the formation of solid-state materials.[1] Solution methods leading to aggregates, solids,[2–4] and polymeric materials[5–7] are inherently advantageous because the conditions employed are mild relative to conventional solid-state syntheses. Potential advances include low-temperature routes to known compounds in addition to the rational design of new, kinetically stable materials.

Recently, thermolysis of "$TaN_xH_{(3x-5)}$", a precipitate derived from ammonolysis of ('BuCH₂)₃Ta=CH'Bu (**1**),[8] was shown to yield cubic tantalum nitride (*Fm3m*, a = 4.300 (2) Å) via the sequence in eqs 1 and 2.[9] According to the Ta/N phase dia-

$$('BuCH_2)_3Ta{=}CH'Bu + xNH_3 \xrightarrow[\text{(2) } C_6D_6, \text{ 100 °C, 2 days}]{\text{(1)}C_6H_6, \text{ 20 °C, 2 days}}$$
$$\mathbf{1}$$

$$TaN_xH_{(3x-5)} + {\sim}4CMe_4 \quad (1)$$

$$TaN_xH_{(3x-5)} \xrightarrow[\substack{24 \text{ h}}]{400 \text{ °C}} \underset{\text{(amorphous)}}{TaN} \xrightarrow[\substack{3 \text{ days}}]{820 \text{ °C}} \underset{(Fm3m)}{\delta\text{-TaN}} \quad (2)$$

gram,[10] hexagonal tantalum nitride ($P6/mmm$)[11] is the expected thermodynamic product under the conditions employed. The

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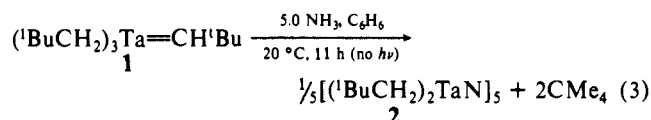
diagram, which was compiled from various sources, suggests that rather extreme conditions are necessary to prepare cubic TaN[12] from the elements (e.g., >1500 °C, >1 atm N$_2$); consequently, the solution and subsequent thermolytic methods delineated above comprise a low-temperature route to a metastable product. Furthermore, it seemed plausible that structural elements critical to the formation of the cubic phase were established in the precipitate and its soluble precursors. Presented herein are the isolation and structural characterization of an oligomeric precursor to $TaN_xH_{(3x-5)}$ and a discussion of its structural relationship to cubic and hexagonal tantalum nitride.
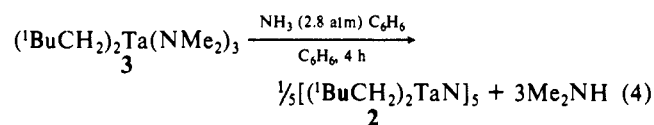
Results and Discussion

Synthesis of [(^{t}BuCH$_2$)$_2$TaN]$_5$ (2). Upon monitoring the ammonolysis of (^{t}BuCH$_2$)$_3$Ta=CH^{t}Bu (1) by ^{1}H NMR (eq 1), the presence of a major intermediate was revealed, prompting efforts toward the isolation of this precursor to $TaN_xH_{(3x-5)}$. Treatment of a light-protected benzene solution of **1** with 5.0 equiv of NH$_3$ for 11 h (eq 3), followed by precipitation from hexane, afforded

$$(^tBuCH_2)_3Ta\!=\!CH^tBu \xrightarrow[\text{20 °C, 11 h (no } h\nu)]{\text{5.0 NH}_3,\ C_6H_6}$$
$$\mathbf{1}$$

$$\tfrac{1}{5}[(^tBuCH_2)_2TaN]_5 + 2CMe_4 \quad (3)$$
$$\mathbf{2}$$

oligomer **2** in ~40% isolated yield. When quenched with methanol, 2.0 equiv of CMe$_4$/Ta were released, consistent with the formula [(^{t}BuCH$_2$)$_2$TaN]$_n$ (2). Spectroscopic evidence alluded to a pentameric structure of C_{2v} symmetry. Three ^{t}Bu resonances were observed (^{1}H NMR, C$_6$D$_6$) in a 2:2:1 ratio (δ 1.42, 1.33, 1.04) accompanied by two sets of diastereotopic methylene protons (δ 0.84, 1.58, J = 13.6 Hz; δ 1.43, 1.95, J = 13.5 Hz) and a CH$_2$ singlet (δ 1.57); ^{13}C{^{1}H}-NMR spectra corroborated the 2:2:1 pattern. ^{15}N{^{1}H}-NMR spectra of **2**-^{15}N$_5$, prepared from **1** and ^{15}NH$_3$, displayed an ~2:2:1 set of resonances at δ 277.6, 158.6, and 116.2. In addition, a broad feature at δ -360 was tentatively assigned as solvated ^{15}NH$_3$ undergoing exchange with bound ammonia.

Each time the light- and temperature-sensitive pentamer (**2**) was isolated, subtle variations in its spectra were noted, including the observation of free benzene by ^{1}H NMR and the sporadic appearance of a weak 3373-cm^{-1} band in the IR, consistent with variable amounts of bound NH$_3$. Several absorptions in a region

$$(^tBuCH_2)_2Ta(NMe_2)_3 \xrightarrow[\text{C}_6\text{H}_6,\ 4\ h]{\text{NH}_3\ (2.8\ atm)\ C_6H_6}$$
$$\mathbf{3}$$

$$\tfrac{1}{5}[(^tBuCH_2)_2TaN]_5 + 3Me_2NH \quad (4)$$
$$\mathbf{2}$$

expected for Ta–N stretching vibrations (886, 819, 803, 759, 717 cm^{-1}) were observed to shift when the pentamer was prepared from ^{15}NH$_3$ (**2**-^{15}N$_5$). Mass spectral data (FABS) were consistent with loss of neopentyl units from a pentameric formulation. Fur-
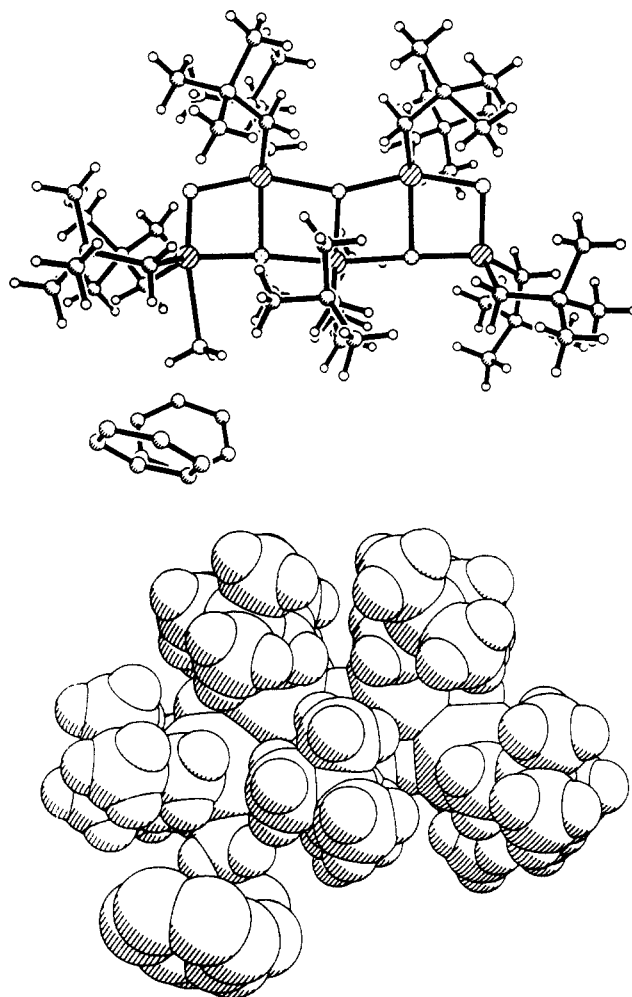
Figure 1. Molecular structure and space-filling view of [(^{t}BuCH$_2$)$_2$TaN]$_5$·NH$_3$·2C$_7$H$_8$ (2·NH$_3$·2C$_7$H$_8$). Due to a disorder, the toluene methyl groups are not shown.

thermore, ammonolysis of (^{t}BuCH$_2$)$_2$Ta(NMe$_2$)$_3$ (**3**, eq 3), [13] synthesized from [(Me$_2$N)$_3$TaCl$_2$]$_2$[14] and 2.0 equiv of ^{t}BuCH$_2$Li, provided an alternative, albeit low yield (19%), route to **2**.

Structure of [(^{t}BuCH$_2$)$_2$TaN]$_5$·NH$_3$·2C$_7$H$_8$ (2·NH$_3$·2C$_7$H$_8$). A single crystal of the pentamer, obtained from toluene solution via eq 3, proved amenable to an X-ray structure determination. As Figure 1 illustrates, a ladder geometry is observed,[15-17] although the spectroscopically apparent C_{2v} symmetry is disrupted by an ammonia bound to a terminal Ta, hence the formulation [(^{t}BuCH$_2$)$_2$TaN]$_5$·NH$_3$·2C$_7$H$_8$ (2·NH$_3$·2C$_7$H$_8$). In order to account for the higher symmetry observed in the NMR studies, it is necessary to invoke the rapid dissociation of the ammonia. The π-systems of both toluene molecules interact with the protons of the bound NH$_3$ in a fashion reminiscent of bonds between RNH$_3$$^+$ units and aromatic residues in proteins.[18]

The middle and adjacent tantalums are trigonal-bipyramidal with the neopentyl groups occupying sterically favorable equatorial

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Table I. Selected Interatomic Distances (Å) and Angles (deg) for [(tBuCH2)2TaN]5·NH3·2C7H8 (2·NH3·2C7H8)[a]

Ta1-N1	1.864 (27)	Ta1-N2	1.955 (20)	Ta1-N6	2.508 (28)
Ta2-N1	1.957 (22)	Ta2-N2	2.120 (24)	Ta2-N3	2.121 (21)
Ta3-N2	2.006 (21)	Ta3-N3	1.937 (25)	Ta3-N4	2.085 (20)
Ta4-N3	2.020 (20)	Ta4-N4	2.167 (24)	Ta4-N5	1.948 (22)
Ta5-N4	1.874 (20)	Ta5-N5	1.836 (26)	Ta1-Ta2	2.894 (2)
Ta2-Ta3	3.045 (2)	Ta3-Ta4	3.092 (2)	Ta4-Ta5	2.860 (2)
Ta1-C1	2.165 (21)	Ta1-C1A	2.227 (24)	Ta2-C2	2.085 (23)
Ta2-C2A	2.133 (30)	Ta3-C3	2.223 (23)	Ta3-C3A	2.058 (38)
Ta4-C4	2.141 (26)	Ta4-C4A	2.074 (35)	Ta5-C5	2.051 (33)
Ta5-C5A	2.175 (33)				
N1-Ta1-N2	89.0 (10)	N1-Ta1-N6	169.7 (10)	N2-Ta1-N6	82.1 (9)
N1-Ta2-N2	82.0 (10)	N1-Ta2-N3	161.9 (10)	N2-Ta2-N3	80.1 (9)
N2-Ta3-N3	87.6 (9)	N2-Ta3-N4	171.0 (10)	N3-Ta3-N4	83.7 (9)
N3-Ta4-N4	79.7 (9)	N3-Ta4-N5	158.1 (11)	N4-Ta4-N5	80.3 (9)
N4-Ta5-N5	91.6 (10)	Ta1-N1-Ta2	98.5 (12)	Ta1-N2-Ta2	90.4 (9)
Ta1-N2-Ta3	174.0 (13)	Ta2-N2-Ta3	95.1 (9)	Ta2-N3-Ta3	97.1 (9)
Ta2-N3-Ta4	160.1 (13)	Ta3-N3-Ta4	102.7 (11)	Ta3-N4-Ta4	93.3 (9)
Ta3-N4-Ta5	167.5 (12)	Ta4-N4-Ta5	89.8 (8)	Ta4-N5-Ta5	98.2 (10)
C1-Ta1-N1	102.8 (10)	C1-Ta1-N2	126.8 (9)	C1-Ta1-N6	78.8 (10)
C1A-Ta1-N1	104.3 (10)	C1A-Ta1-N2	109.8 (8)	C1A-Ta1-N6	83.6 (9)
C2-Ta2-N1	103.6 (10)	C2-Ta2-N2	123.7 (10)	C2-Ta2-N3	88.9 (9)
C2A-Ta2-N1	95.4 (10)	C2A-Ta2-N2	118.5 (10)	C2A-Ta2-N3	90.4 (10)
C3-Ta3-N2	95.1 (9)	C3-Ta3-N3	127.1 (9)	C3-Ta3-N4	88.4 (9)
C3A-Ta3-N2	94.0 (13)	C3A-Ta3-N3	123.7 (12)	C3A-Ta3-N4	92.8 (13)
C4-Ta4-N3	90.3 (9)	C4-Ta4-N4	128.1 (10)	C4-Ta4-N5	94.9 (10)
C5-Ta5-N4	105.6 (12)	C5-Ta5-N5	114.7 (11)		
C5A-Ta5-N4	120.6 (9)	C5A-Ta5-N5	106.9 (13)		

[a] C# and C#A refer to the methylene carbons of the neopentyl groups.

positions. Four-coordinate Ta5 has a distorted tetrahedral environment, while Ta1 deviates slightly from tbp due to weak axial bonding of the NH3. A rare T-shaped coordination is adopted by the interior μ_3-nitrides,[16,19,20] while the exterior μ_2-nitrides are similar to those of [Cp*MeTaN]3 (Cp* = η^5-C5Me5)[9] and related complexes.[21-23] As indicated in Figure 2, the ladder is roughly planar, with a 0.028-Å mean deviation of Ta atoms and a corresponding 0.126-Å variation of the nitrogens. A slight helical twist of 12.8° accounts for the discrepancy, presumably due to long-range steric influences of the neopentyl groups, although each Ta2N2 "square" is virtually planar. A related tetranuclear complex, Mo4(μ_3-N)2(μ_2-O-i-Pr)2(O-i-Pr)10,[16] which contains two nitrides with T-shaped coordination, exhibits similar minor deviations from a flat geometry.

The four parallel, interior Ta-N bond lengths average 2.06 (5) Å while the related exterior set averages 1.94 (4) Å.[24] In contrast, the perpendicular Ta-N "rungs" of the ladder alternate in distance; the middle Ta3-N3 length of 1.94 (3) Å is significantly shorter than Ta2-N2 (2.12 (2) Å) and Ta4-N4 (2.18 (2) Å), whereas the outer nitride bonds reflect greater multiple bonding to four-coordinate Ta5 (1.84 (3) Å) and Ta1 (1.86 (3) Å),[9,21-23] whose bond to NH3 is extremely long (2.51 (3) Å). The dramatic differences in the interior perpendicular bonds cannot be so easily rationalized. Despite the sterically congested environment of Ta3, equatorial Ta3-N3 (1.94 (3) Å) is significantly shorter than its axial partners, perhaps due to stronger N(pπ) → Ta(dπ) bonding.[25] In comparison, equatorial Ta2-N2 (2.12 (2) Å) and Ta4-N4 (2.17 (2) Å) are longer than the axial nitride bonds to

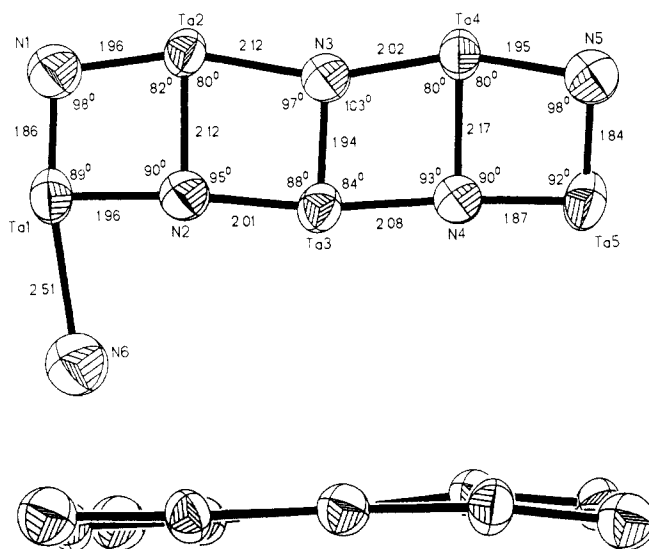(19) Ciechanowicz, M.; Griffith, W. P.; Pawson, D.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1971**, 876.

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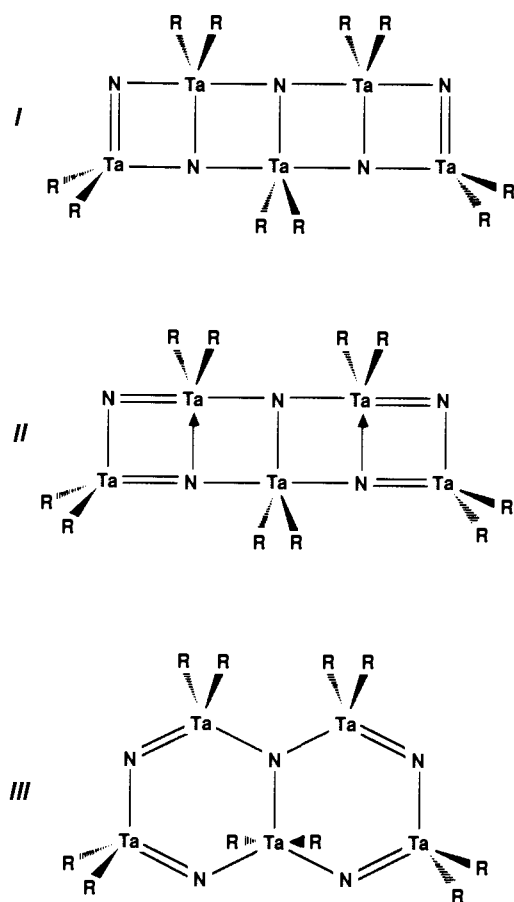
Figure 2. The ladder core of [(tBuCH2)2TaN]5·NH3·2C7H8 (2·NH3· 2C7H8) including a side view that reveals the helical twist (N1-N5 in the forefront). Standard deviations on the bond distances and angles are 0.02-0.03 Å and 1.0°.

Ta2 and Ta4, respectively. An interesting interpretation of the bonding is illustrated in Figure 3. The simplest valence bond representation of [(tBuCH2)2TaN]5 (2) consists of a ladder of TaN single bonds, with Ta=N units as the outer rungs (I). A π2 + σ2 rearrangement results in a resonance structure comprised of Ta1-N1 and Ta5-N5 single bonds adjacent to tantalum-nitrogen double bonds (II). Complete rupture of the Ta2-N2 and Ta4-N4 bonds yields an alternative geometry (III) containing Ta3N3 rings similar to those found in [Cp*RTaN]3 (R = Me, Cl).[9,21] Contributions from resonance forms I and, to a lesser extent, II may be manifested in the bond distances. The tendency to form the maximum number of Ta-N σ-interactions must play a crucial role in discriminating between I and II, which contain three five-coordinate tantalums, or naphthalene-like III, which contains a lone tbp Ta center whose neopentyl groups are forced into sterically unfavorable axial positions.

The structure of [(tBuCH2)2TaN]5 (2) may be construed as a stack of alternating (tBuCH2)2TaN monomers. A distribution

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Figure 3.

of molecules, $[(^1BuCH_2)_2TaN]_n$, would typically result from ol-igomerization of $(^1BuCH_2)_2TaN$ groups, yet a pentameric am-monia adduct $(2 \cdot NH_3 \cdot 2C_6H_6)$ was isolated in 42% yield from the ammonolysis in eq 1. Furthermore, redistribution did not occur when the pentamer was redissolved. These observations suggest that oligomerization continues up to $n = 5$, whereas the addition of another monomer is disfavored. The answer may lie in the steric requirements of the neopentyl group, whose cone angle is ap-proximately $120°$.[26] As the illustrations in Figure 1 help reveal, dimerization or trimerization of $(^1BuCH_2)_2TaN$ units generate molecular ladders possessing ample space for rotation of the neopentyl fragments. The neopentyl groups of a tetramer are also free to turn about each Ta–C bond without significant steric interactions; however, the addition of one more $(^1BuCH_2)_2TaN$ group severely restricts the movement of the neopentyls bound to the middle tantalum (Ta3). Each subsequent addition of monomer would result in similar steric consequences for an interior $(^1BuCH_2)_2TaN$ unit. The structure of $2 \cdot NH_3 \cdot 2C_7H_8$ adds credence to these arguments, since the neopentyl groups attached to Ta1 are turned away from Ta3 ($\angle(N1–Ta1–Cl,ClA) = 103.6 (11)°_{av}$, $\angle(N2–Ta1–Cl) = 126.8 (9)°$, $\angle(N2–Ta1–ClA) = 109.8 (8)°$, $\angle(N6–Ta1–Cl,ClA) = 81 (3)°_{av})$. This apparent steric repulsion opens the coordination sphere of Ta1 to ligation by the small NH_3, resulting in distorted tbp coordination, rather than the tetrahedral geometry observed for Ta5.

While it has been convenient to discuss the state of aggregation in terms of $(^1BuCH_2)_2TaN$ monomers, the actual formation of 2 is probably very complicated. A series of bimolecular con-densation reactions involving attack of Ta—CH_2^1Bu or Ta= CH¹Bu bonds by various N–H functionalities could ultimately

lead to the pentamer ladder without necessitating monomer formation. Regardless of mechanism, the degree of oligomeri-zation can be rationalized by steric arguments analogous to those above.

Relationship of 2 to TaN. The pentameric ladder of $[(^1BuCH_2)_2TaN]_5 \cdot NH_3 \cdot 2C_7H_8$ $(2 \cdot NH_3 \cdot 2C_7H_8)$ is provocative, since its conformation of edge-shared Ta_2N_2 units reflects the motif of cubic TaN, rather than the thermodynamically expected hexagonal form.[10] For reference, Figure 4 depicts two views of hexagonal $(P6/mmm)$ and one of cubic $(Fm3m)$ tantalum ni-tride.[11,12] Hexagonal TaN contains corner-shared Ta_2N_2 frag-ments but also possesses edge-shared units that propagate diag-onally and parallel to the a and b-axes, as the arrows in A and B indicate. However, these squares are substantially different than those found in 2. Consider the coplanar nitrogens of this edge-shared $[Ta_2N_2]_n$ ladder designated by the arrows in B. The tantalum atoms alternate above and below this plane of nitrogens, thus the edge-shared $[Ta_2N_2]_n$ chain is not flat, in contrast to 2. In addition, hexagonal TaN contains uninterrupted rows of tan-talums coordinated to six in-plane nitrogens, hence one-third of its Ta atoms adopts a distinctly different geometry from that manifested by the pentameric ladder (2). The rock salt structure illustrated in C clearly manifests the geometrical relationship between the interior $[Ta_2N_2]_5$ basis of pentameric 2 and cubic TaN, which is composed solely of Ta_2N_2 squares.

During the complicated conversion of $[(^1BuCH_2)_2TaN]_5$ (2) to cubic TaN, several transformations take place, including the formation of $TaN_xH_{(3x-5)}$ and the subsequent reduction of each Ta(V) to Ta(III), as previously addressed.[9] Provided the Ta_2N_2 structural units remain intact throughout the preparation of cubic tantalum nitride, the framework of this ceramic may be dictated by the geometry of the molecular precursor. An important goal of this project, the low-temperature synthesis of a kinetically stable material has been realized, if the Ta/N phase diagram compiled by Politis[10] is accurate. The Ta_2N_2 groups in 2 are readily con-verted to cubic TaN at moderate temperatures (820 °C), whereas pathways linking these units to $P6/mmm$ TaN, specifically its unique hexagonal planar TaN_6 moiety, must be energetically unfeasible. Alternatively, trace amounts of carbide may pin the structure to the cubic phase.[12] Experiments designed to establish whether a direct relationship between 2 and cubic TaN exists and further studies regarding the synthesis of polymeric and solid-state metal nitrides are underway.

Experimental Section

General Considerations. All manipulations were performed with use of either glovebox or high vacuum line techniques. Ethereal and hy-drocarbon solvents were distilled under nitrogen from purple benzo-phenone ketyl and vacuum transferred from the same prior to use. Small amounts of tetraglyme (2–5 mL/L solvent) were added to hydrocarbons to solubilize the ketyl. Benzene-d_6 was dried over activated 4Å molecular sieves, vacuum transferred, and stored under N_2; THF-d_8 was dried over sodium benzophenone ketyl. Anhydrous ammonia was purchased from Matheson and distilled from sodium. $^{15}NH_3$ (Aldrich) was dried over sodium. $(^1BuCH_2)_3Ta=CH^1Bu$ $(1)^8$ and $[(Me_2N)_3TaCl_2]_2^{14}$ were pre-pared via literature methods. The procedure for $(^1BuCH_2)_2Ta(NMe_2)_3$ (3) is analogous to that of L.-S. Tan.[13]

NMR spectra were obtained by using Varian XL-200 (^1H) and XL-400 (^1H, $^{13}C\{^1H\}$, ^{15}N) spectrometers. Chemical shifts are reported relative to TMS (^1H) or benzene-d_6 (^1H, δ 7.15; $^{13}C\{^1H\}$, δ 128.00). ^{15}N spectra were referenced to natural abundance CH_3NO_2 (neat, δ 0.00)[27,28] by using a coaxial 5-mm tube containing the lock solvent; a delay of 40 s and a pulse width of 30° were employed. Infrared spectra were re-corded on a Mattson FT-IR interfaced to a AT&T PC7300 computer. Mass spectra were obtained on a Kratos MS89OMS. Analyses were obtained by Oneida Research Services, Whitesboro, NY.

Procedures. 1a. $[(^1BuCH_2)_2TaN]_5 \cdot NH_3 \cdot 2C_6H_6$ $(2 \cdot NH_3 \cdot C_6H_6)$. A 250-mL, round-bottom flask was charged with 1.011 g $(^1BuCH_2)_3Ta$-(CH^1Bu), fitted to a 287.8-mL gas bulb, and evacuated. Benzene (80 mL) was distilled into the flask and 5.0 equiv of ammonia were admitted

(25) On the basis of overlap arguments and the absence of competing π-donors in the equatorial plane, the π-interaction of N3 with $d_{x^2-y^2}/d_{xy}$ is predicted to be stronger than the corresponding interaction of N2 and N4 with d_{xz} and d_{yz}. See: Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374.
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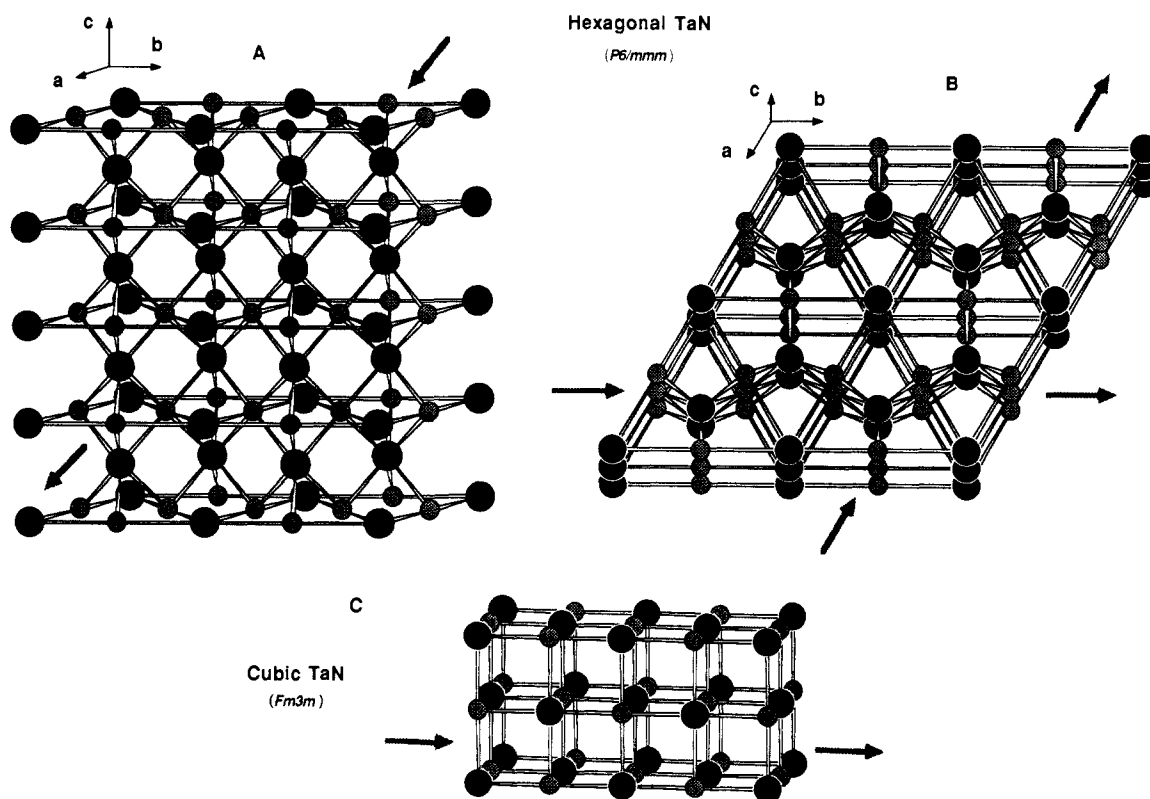
c ↑ b
a ←

A

Hexagonal TaN

(P6/mmm)

c ↑ b
a ↙

B

C

Cubic TaN

(Fm3m)

Figure 4. Two views of hexagonal (A, B: *P6/mmm*; d(Ta–N) = 2.089, 2.596 Å; d(Ta–Ta) = 2.908, 2.994, 3.438 Å) and one of cubic TaN (C; *Fm3m*; d(Ta–N) = 2.165 Å; d(Ta–Ta) = 3.062 Å) with arrows indicating rows of edge-shared Ta₂N₂ units.

via the gas bulb (total volume 538 mL). The mixture was stirred at 20 °C while protected from light. After 11 h the solvent was reduced to 8 mL, the mixture was filtered, and the residual solid was washed extensively. The benzene was removed, and the bright yellow solid redissolved in 4 mL of hexane. Cooling to –78 °C and filtering gave 342 mg of a bright yellow powder (42%). Pentamer 2·NH₃·C₆H₆ is quite light sensitive, turning olive and then brown in about 6 h. The ¹⁵N-labeled complex, [('BuCH₂)₂Ta¹⁵N]₅·¹⁵NH₃·2C₆H₆ (2[¹⁵N]₅·¹⁵NH₃·C₆H₆) was prepared as above except for the use of ¹⁵NH₃ (98% isotopic enrichment).

b, 2·NH₃·C₆H₆ via 3. A 40-mL bomb reactor was charged with 761 mg of [(Me₂N)₃TaCl₂]₂ and 307 mg of 'BuCH₂Li. The solids were washed into the bomb with 10 mL of benzene, the mixture was frozen, and an additional 15 mL of benzene was added. Sufficient ammonia was condensed into the bomb to give 2.8 atm in a 40-mL volume. The mixture was then warmed to 20 °C and stirred. After 4 h, the mixture was degassed, transferred to a 25-mL flask, and filtered. All volatiles were then removed, and 3 mL of hexane was distilled into the flask. A bright yellow solid was obtained from the solution upon cooling to –78 °C and filtering (130 mg, 19%): ¹H NMR (C₆D₆) δ 1.42, 1.33, 1.04 (C(CH₃), s, 90 H, 2:2:1), 0.84, 1.58 (CHH, d, 4 H, ²J = 13.6 Hz), 1.43, 1.95 (CHH, d, 4 H, ²J = 13.5 Hz), 1.57 (CH₂, s, 4 H); ¹³C{¹H} δ 35.65, 34.85, 36.07 (C(CH₃)₃, 2:2:1), 36.20, 35.57, 35.26 (C(CH₃)₃, 2:2:1), 105.62, 99.04, 93.07 (CH₂, 2:2:1); ¹⁵N{¹H} NMR (2-¹⁵N₅) δ –360 (ν₁/₂ ~140 Hz), 116.2 (ν₁/₂ = 11.1 Hz), 158.6 (ν₁/₂ = 6.5 Hz), 277.6 (ν₁/₂ = 11.3 Hz); IR (Nujol, cm⁻¹) ν(N–H) 3382 (w), ν(Ta–N) 886 (s), 819 (s), 803 (m), 759 (s), 717 (m); ν(¹⁵N–H) 3373 (w), ν(Ta–¹⁵N) 856 (s), 795 (s), 779 (m), 734 (s), 697 (m); MS (FABS, He, Nujol matrix, 2 (m)) found 1614.5 (m–('BuCH₂)⁺), 1472.4 (m–('BuCH₂)₂⁺), calcd 1686.2 (m⁺).

2, ('BuCH₂)₂Ta(NMe₂)₃ (3). A 25-mL, round-bottom flask was charged with 560 mg of [(Me₂N)₃TaCl₂]₂ and 228 mg of 'BuCH₂Li. The flask was evacuated, 20 mL of hexane was distilled in at –78 °C, and the mixture was stirred and allowed to warm to 20 °C. After 3 h the mixture was filtered, and white crystals of light-sensitive **3** were obtained by cooling the solution to –78 °C and filtering (200 mg, 33%): ¹H NMR (C₆D₆) δ 3.15 (N(CH₃)₂, s, 18 H), 1.13 (C(CH₃)₃, s, 18 H), 1.08 (CH₂, s, 6 H); ¹³C{¹H} δ 94.9 (N(CH₃)₂), 45.1 (CH₂), 36.9 (C(CH₃)₃), 34.8 (C(CH₃)₃). Anal. Calcd for C₁₆H₄₀N₃Ta: C, 42.19; H, 8.85; N, 9.22. Found: C, 41.11; H, 8.70; N, 9.06.

3, X-ray Crystal Structure of [('BuCH₂)₂TaN]₅·NH₃·2C₇H₈ (2· NH₃·C₇H₈). A yellow, single-crystalline prism of [('BuCH₂)₂TaN]₅· NH₃·2C₇H₈ (2·NH₃·C₇H₈), approximately 0.6 × 0.3 × 0.1 mm, was grown from toluene solution at –20 °C, protected from light, and sealed in a thin-walled Lindemann capillary. The crystal was immediately

placed in a stream of dinitrogen at –20 °C on a Syntex P2₁ diffractometer which had been modified to exclude light. Extended exposure of the crystals to light caused them to become an opaque brown. Cooling the crystals to lower temperatures or placing the crystals in an initially colder dinitrogen stream caused the crystal to crack. Precise lattice constants for a triclinic cell, determined from a least-squares fit of 21 diffractometer-measured 2θ values, were a = 11.616 (2) Å, b = 15.407 (3) Å, c = 23.172 (6) Å, α = 106.120 (17)°, β = 99.060 (18)°, γ = 100.170 (16)°, and Z = 2. The cell volume was 3829.6 (12) Å³ with a calculated density of 1.602 g/cm³ and μ = 7.068 mm⁻¹. Structure solution and subsequent refinement indicated space group P1̄. Diffraction maxima (h,±k,±l) with 0.0 ≤ 2θ ≤ 45 were measured by using variable speed 2θ–θ scans and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Total collection time was 120 h during which intensities dropped by ~10%. After correction for Lorentz, polarization, background, decomposition, and an empirical correction for absorption, 7346 (72.8%) of the unique data (10088 out of 10689 measured, Rₘₑᵣg = 0.061) were judged observed (F ≥ 3.0σ(F)). The tantalum positions were obtained from a Patterson synthesis followed by tangent formula recycling which also provided four α-carbons. Subsequent Fourier difference maps revealed the remaining positions. Hydrogens were fixed at 0.96 Å to all methyl and methylene groups and at 0.90 Å to the bound ammonia (Riding model, fixed isotropic U). Several difference map peaks were present indicating possible locations for the toluene methyl groups; attempts to model this group suggested that a rotational disorder was spread over more than two positions per ring and thus were abandoned. Full-matrix least-squares refinement of anisotropic tantalum atoms, isotropic non-hydrogen atoms, and fixed hydrogen atoms converged to crystallographic residuals of R = 0.083 and R_w = 0.098 for 7346 reflections. Anisotropic refinement of additional non-hydrogen atoms did not significantly lower the R values. The top ten remaining difference map peaks were all between 0.798 and 1.099 Å from a tantalum atom. Bond lengths in some of the neopentyl groups deviate significantly from expected values, probably indicating a degree of disorder. However, no strong difference map peaks were present indicating the presence of different conformations. It was decided not to fix the bond lengths to expected values because the added parameters would not contribute to the interesting part of the structure. The final residuals from 7346 observations and 295 parameters were R = 0.083, R_w = 0.098, and GOF = 4.68.

Syntheses, Structures, and Reactivities of Unusual Four-Membered Metallacycles Formed in Insertion Reactions of N=N=O, N=N=NR, and N=N=CR₂ with (η⁵-C₅Me₅)₂Zr(C₂Ph₂)

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Abstract: Nitrous oxide reacts with Cp*₂Zr(C₂Ph₂) (**1**, Cp* = η⁵-C₅Me₅) to afford an organometallic product in which N₂O has been incorporated *without* loss of dinitrogen. This adduct, Cp*₂Zr{N(O)NCPh=CPh} (**2**), is isolable yet thermally unstable with respect to loss of dinitrogen at ambient temperature to give the monomeric diphenyloxametallacyclobutene derivative Cp*₂Zr(OCPh=CPh) (**3**). **3** crystallizes from toluene solution in the monoclinic space group $P2_1/n$ with a = 9.194 (2) Å, b = 19.422 (4) Å, c = 16.642 (4) Å, β = 104.60 (2)°, and Z = 4. The least-squares refinement coverged to $R(F)$ = 0.051 and $R(wF)$ = 0.058 for the 1849 unique data with $Fo > 4\sigma(Fo)$. Salient metrical parameters of the four-membered oxametallacycle include the following: Zr···C(1), 2.543 (6) Å; Zr-C(2), 2.219 (7) Å, Zr-O, 2.065 (5) Å; C(1)-C(2), 1.348 (12) Å; O-C(1), 1.440 (10) Å. **3** reacts with H₂ to give the enolate hydride Cp*₂Zr(H)(OCPh=CHPh) (**8**) and with HCl to give Cp*₂ZrCl₂ and deoxybenzoin. Substrates with acidic hydrogens (H₂O, PhOH, O=CMe₂, HC≡CH, HC≡CPh, and HC≡C'Bu) react with **3** to give enolate derivatives Cp*₂Zr(X)(OCPh=CHPh) (**9**, X = OH; **10**, X = OPh; **11**, X = OC(CH₂)Me; **12**, X = C≡CH; **13**, X = C≡CPh; **14**, X = C≡C'Bu), respectively. In contrast, insertion reactions into the Zr-C bond of **3** are observed for (O=CH₂)ₓ, O=CHTol, O=CH(*n*-Hex), TolN₃, Ph₂CN₂, CO, and 'BuN≡C, affording the 5- and 6-membered metallacycles Cp*₂Zr(OCPh=CPhCH₂O) (**15**), Cp*₂Zr(OCPh=CPhCHTolO) (**16**), Cp*₂Zr{OCPh=CPhCH(*n*-Hex)O} (**17**), Cp*₂Zr{OCPh=CPhN(N=NTol)} (**18**), Cp*₂Zr{OCPh=CPhN(N=CPh₂)} (**19**), Cp*₂Zr{OCPh=CPhC(=O)} (**20**), and Cp*₂Zr{OCPh=CPhC(=N'Bu)} (**21**), respectively. *p*-Tolyl azide and diphenyldiazomethane react with **1** to afford Cp*₂Zr{N-(N₂-*p*-C₆H₄CH₃)CPh=CPh} (**4**) and Cp*₂Zr{N(N=CPh₂)CPh=CPh} (**5**), respectively; these complexes do not cleanly lose N₂ on thermolysis. **4** crystallizes from benzene solution in the monoclinic space group $P2_1/c$ with a = 9.912 (4) Å, b = 30.919 (9) Å, c = 13.583 (5) Å, β = 98.97 (2)°, and Z = 4. The least-squares refinement converged to $R(F)$ = 0.067 and $R(wF)$ = 0.064 for the 2439 unique data with $F_o > 3\sigma(F_o)$. Important metrical parameters of the planar four-membered azametallacycle include the following: Zr-C(21), 2.285 (8) Å; Zr-N(1), 2.173 (8) Å; C(21)-C(22), 1.373 (16) Å; C(22)-N(1), 1.423 (12) Å; N(1)-N(2), 1.341 (12) Å; N(2)-N(3), 1.305 (12) Å. Water adds accross a Zr-C bond of **1** to give the hydroxy vinyl species Cp*₂Zr(OH)(CPh=CHPh) (**6**), but H₂O adds across the Zr-N bond of **5** to yield Cp*₂Zr(OH){CPh=CPhNH-(N=CPh₂)} (**7**).

Introduction

During the course of our investigations on the use of nitrous oxide (N=N=O) as an oxygen atom transfer reagent in organometallic systems, we have been especially interested in studying its reactivity toward early metal (group 4), d⁰ complexes.[2,3] The impetus for focusing our initial work on this area has been 2-fold. First, since d⁰ complexes are in their highest oxidation states, oxidation of such complexes by N₂O to give metal oxo derivatives is precluded,[4] and any oxo-transfer reaction from

N₂O will necessarily involve oxidation at a ligand site. Second, it has been previously shown that organoazides (N=N=NR)[5] and diazoalkanes (N=N=CR₂),[6] molecules isoelectronic with

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