Inorg. Chem. **1994**, *33*, 1227–1229

Notes

$[TiCl_4(NH_3)_2]$: An Improved Single-Source Precursor to Titanium Nitride Films. Crystal and Molecular Structure of $[TiCl_4(TPPO)_2]$ (TPPO = Tripiperidinophosphine Oxide)

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Received July 28, 1993

Introduction

Titanium nitride is an extremely hard, high-melting, chemically inert material and has applications in microelectronics, as solar control coatings for glass, as hard coatings for tools, and as decorative gold-colored coatings.[2] Chemical vapor deposition (CVD) routes available for titanium nitride films can be divided into two broad classes. Multiprecursor systems include the CVD reaction between titanium tetrachloride, nitrogen, and hydrogen at ≥1000 °C,[3] titanium tetrachloride and ammonia at 550 °C,[4] titanium tetrachloride and aliphatic amines at ≥475 °C,[5] and tetrakis(dialkylamido)titanium(IV) complexes and ammonia at temperatures between 200 and 450 °C.[6] The second class utilizes the gas-phase decomposition of single-source precursors tetrakis(dialkylamido)titanium(IV)[7a] and titanocene diazide $(Cp_2Ti(N_3)_2)$.[7b,8] Unfortunately, both of these single-source precursors provide low-quality films that are heavily contaminated with carbon and oxygen.[7b,9] The use of a single-source precursor in the deposition of titanium nitride films is potentially advantageous, since the precursor eliminates the various problems associated with mixing two or more gaseous precursors in a CVD reactor (e.g., powder formation,[4,10] maintenance of reactive species over the substrate in a low pressure reactor, etc.), provides precise control over reagent stoichiometry with concomitant waste reduction, and avoids the use of highly corrosive liquids and gases (e.g., titanium tetrachloride, ammonia, etc.). We recently reported that the complex $[TiCl_2(NtBu)(NH_2tBu)_2]_3$ comprises the first single-source precursor to high-quality titanium nitride films and provides films with ≤2% carbon and chlorine impurities.[11] Herein we report that the complex $[TiCl_4(NH_3)_2]$ comprises a single-source precursor to high quality titanium nitride films at temperatures of ≥475 °C. This complex represents an improvement over our previously reported precursor, since it does not contain carbon and provides films with ≤2% chlorine contamination.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of argon or nitrogen using a glovebox or Schlenk techniques. Dichloromethane was distilled from calcium hydride. Diethyl ether was distilled from a purple solution of sodium benzophenone ketyl. Chloroform-*d* was purified by vacuum transfer from activated 4-Å molecular sieves. Titanium tetrachloride, ammonia, and tripiperidinophosphine oxide were used as received from the Aldrich Chemical Co.

^1H NMR and $^{13}C\{^1H\}$ NMR spectra were obtained on a General Electric QE-300 or GN-300 spectrometer. The ^{15}N CP/MAS spectrum was run by Spectral Data Service, Inc., Champaign, IL. Infrared spectra were collected on a Nicolet DX-20 spectrophotometer using Nujol as the medium. Elemental analyses were performed by Midwest Microanalysis, Indianapolis, IN. Melting points were obtained on a Haake Buchler HBI digital melting point apparatus and are uncorrected. The film analyses were obtained as previously described.[11b]

Preparation of $[TiCl_4(NH_3)_4]$ (1). A 500-mL Schlenk flask was charged with titanium tetrachloride (3.0 mL, 27.4 mmol), dichloromethane (120 mL), and a stir bar and was fitted with a rubber septum. Anhydrous ammonia was bubbled through this solution for 0.5 h at 23 °C. The resultant deep yellow suspension was stirred for 1 h, and the volatiles were pumped off to afford **1** as a deep yellow solid (6.15 g, 87% based upon titanium tetrachloride): dec range 210–240 °C; IR (Nujol, cm^{-1}) 3308 (s), 3239 (s), 3137 (s), 3040 (s), 1759 (m, broad), 1657 (w), 1593 (s), 1399 (vs), 1255 (s), 1233 (s), 1094 (w), 976 (s), 901 (m), 874 (m), 799 (w). Anal. Calcd for $N_4H_{12}Cl_4Ti$: H, 4.69; N, 21.73. Found: H, 4.95; N, 21.51.

Preparation of $[TiCl_4(NH_3)_2]$ (2). Complex **1** (0.25 g, 0.97 mmol) was placed into a sublimation tube and was sublimed (80 °C, 0.1 mmHg) for 1 h. A deep yellow sublimate was observed in the cooler parts of the tube. Analytically pure **2** was isolated as a deep yellow solid by scraping the sublimate off the sublimation tube (0.168 g, 77% based upon **1**): mp 240 °C dec; ^{15}N NMR (CP/MAS, NH_4Cl = 0 ppm) −1.21 (s); IR (Nujol, cm^{-1}) 3318 (s), 3231 (s), 3144 (s), 3046 (s), 1591 (m), 1400 (s), 1255 (s), 1238 (s), 851 (w), 678 (m). Anal. Calcd for $H_6N_2Cl_4Ti$: H, 2.70; N, 12.52. Found: H, 2.90; N, 12.73.

Preparation of $[TiCl_4(TPPO)_2]$ (3). A 100-mL Schlenk flask was charged with **2** (0.1 g, 0.45 mmol), dichloromethane (10 mL), and a stir bar and was fitted with a rubber septum. A solution of tripiperidinophosphine oxide (0.27 g, 0.90 mmol) in dichloromethane (10 mL) was added via a cannula to the above solution. A slow reaction ensued over 48 h to give a yellow turbid solution. This solution was filtered through a 2-cm pad of Celite on a medium glass frit to afford a clear, yellow solution. Diethyl ether (70 mL) was carefully layered onto the dichloromethane layer, and the system was allowed to equilibrate for 24 h. The solvent was decanted by a cannula, and the crystals were vacuum-dried to afford **3** as large yellow crystals (0.26 g, 73% based upon **2**): mp >250 °C; IR (Nujol, cm^{-1}) 3161 (w), 2987 (m), 2691 (w), 2662 (w), 1450 (s), 1437 (s), 1363 (m), 1322 (m), 1288 (w), 1279 (m), 1270 (w), 1257 (w), 1207 (s), 1168 (s), 1164 (s), 1121 (s), 1110 (s), 1078 (s), 1062 (s), 1049 (s), 1042 (s), 1025 (s), 1006 (s), 969 (s), 958 (s), 950 (s), 898 (m), 855 (m), 848 (s), 833 (m), 811 (w), 731 (s), 725 (s), 671 (s), 578 (m), 567 (m), 556 (m); ^1H NMR ($CDCl_3$, 23 °C, δ) 3.30 (broad s, NCH_2), 1.70 (broad s, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 46.60 (s, NCH_2), 26.00 (s, NCH_2CH_2), 23.80 (s, $NCH_2CH_2CH_2$). Anal. Calcd

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0020-1669/94/1333-1227$04.50/0

Table 1. Experimental Crystallographic Data for 3

chem formula	$C_{30}H_{60}Cl_4N_6O_2P_2Ti$	Z	2
fw	788.5	T (°C)	26
space group	$P2_1/c$	ρ_{calcd} (g cm^{-3})	1.330
a (Å)	9.666(4)	λ (Å)	0.710 73
b (Å)	14.597(4)	μ (cm^{-1})	6.05
c (Å)	14.683(4)	$R(F_o)^a$ (%)	4.71
β (deg)	108.14(3)	$R_\omega(F_o)^a$ (%)	5.32
V (Å^3)	1968.7(11)		

[a] $R(F_o) = (\sum|\Delta F|/\sum|F_o|)$; $R_\omega(F_o) = [\sum_w|\Delta F|^2)/\sum_w F_o^2]^{1/2}$.

for $C_{30}H_{60}Cl_4N_6O_2P_2Ti$: C, 45.79; H, 7.67. Found C, 43.37; H, 7.60 (not analytically pure).

X-ray Crystal Structure of 3. Crystallographic data are collected in Table 1. A suitable yellow block was grown by slow diffusion of diethyl ether into a dichloromethane solution of 3 at ambient temperature. A specimen was sealed in a glass capillary and was found to have $2/m$ Laue symmetry by photographic methods. Data were collected to the limit of availability (ca. 2θ(Mo Kα) = 52°). The structure was solved intuitively by placing a titanium atom at the origin. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized, isotropic contributions. All computations used the SHELXTL-PLUS software library of programs (G. Sheldrick, Siemens XRD, Madison WI). Further data are contained in the supplementary material.

Results and Discussion

Complexes of the formula $[TiCl_4(NH_3)_n]$ (n = 2–8) have been previously claimed.[12] We have found that treatment of titanium tetrachloride with excess ammonia in dichloromethane at ambient temperature affords an insoluble yellow powder, with an approximate composition of $[TiCl_4(NH_3)_4]$ (**1**, ca. 87%, eq 1) as determined by microanalysis. Sublimation of this crude material (80 °C, 0.1 mmHg) yielded analytically pure yellow flakes of $[TiCl_4(NH_3)_2]$ (**2**, 77%, eq 1). Complex **2** was insoluble in all common solvents and was characterized by solid-state ^{15}N NMR spectroscopy, infrared spectroscopy, and microanalysis. The solid-state ^{15}N NMR spectrum of **2** showed a singlet at −1.21 ppm (NH_4Cl = 0 ppm), which indicated that the nitrogen magnetic environment in **2** is similar to that in ammonium chloride.[13] The infrared spectrum of **2** showed strong N–H stretches at 3318, 3231, 3144, and 3046 cm^{-1}, which are indicative of strong N–H···Cl hydrogen bonding.[14] No bands attributable to the ammonium ion were present. Other absorptions were observed at 1591 cm^{-1} (m, N–H bending), 1255 and 1238 cm^{-1} (s, NH_3 symmetric deformation), and 678 cm^{-1} (m, NH_3 rocking vibrations). The infrared spectrum of **2** is consistent with the formulation as an ammine complex and is inconsistent with other nitrogen ligand types.[15]

$$\begin{tikzcd}
TiCl_4 + \text{excess}\,NH_3 \arrow[r, "\substack{CH_2Cl_2\\ 23\ ^\circ C}", "87\%"'] & \underset{1}{[TiCl_4(NH_3)_4]} \quad (1) \arrow[d, "\substack{\text{sublime,}120\ ^\circ C\\ 0.1\ mmHg\\ 77\%}"] \\
\underset{3}{[TiCl_4(OP(C_5H_{10}N)_3)_2]} & \underset{2}{[TiCl_4(NH_3)_2]} \arrow[l, "\substack{2\ (C_5H_{10}N)_3P{=}O\\ CH_2Cl_2,\ 23\ ^\circ C}"', "48\ h,\ 75\%"]
\end{tikzcd}$$

In order to obtain a chemical characterization, **2** was treated with 2 equiv of tripiperidinophosphine oxide (TPPO). A slow reaction ensued (ca. 48 h, due to the insolubility of **2**) and resulted in the complex $[TiCl_4(TPPO)_2]$ (**3**), which could be isolated in 70–75% yield as yellow crystals by layering the reaction medium with diethyl ether. Complex **3** was fully characterized by spectroscopic and analytical techniques, and the X-ray crystal structure was determined (vide infra). On the basis of this chemical reaction and the spectral data, we propose the monomeric formulation $[TiCl_4(NH_3)_2]$ for **2**. The insolubility of **2** may be attributable to intermolecular N–H···Cl hydrogen bonding.

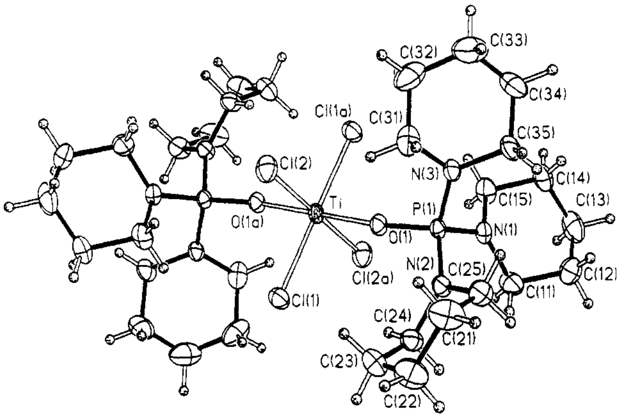

Figure 1. Perspective View of 3.

Table 2. Bond Lengths (Å) and Selected Bond Angles (°) for 3

Ti–Cl(1)	2.341(1)	Ti–Cl(2)	2.343(1)
Ti–O(1)	1.923(3)	Ti–Cl(1A)	2.341(1)
Ti–Cl(2A)	2.344(1)	Ti–O(1A)	1.923(3)
P(1)–O(1)	1.518(3)	P(1)–N(1)	1.618(4)
P(1)–N(2)	1.623(3)	P(1)–N(3)	1.619(3)
N(1)–C(11)	1.469(5)	N(1)–C(15)	1.478(6)
N(2)–C(24)	1.471(5)	N(2)–C(25)	1.450(6)
N(3)–C(31)	1.466(6)	N(3)–C(35)	1.476(6)
C(11)–C(12)	1.524(8)	C(12)–C(13)	1.507(8)
C(13)–C(14)	1.513(8)	C(14)–C(15)	1.516(8)
C(21)–C(22)	1.520(8)	C(21)–C(25)	1.504(7)
C(22)–C(23)	1.516(8)	C(23)–C(24)	1.497(7)
C(31)–C(32)	1.517(7)	C(32)–C(33)	1.511(10)
C(33)–C(34)	1.514(9)	C(34)–C(35)	1.507(6)
Cl(1)–Ti–Cl(2)	90.0(1)	Cl(1)–Ti–O(1)	90.3(1)
Cl(2)–Ti–O(1)	90.8(1)	Cl(1)–Ti–Cl(1A)	180.0(1)
Cl(2)–Ti–Cl(1A)	90.0(1)	O(1)–Ti–Cl(1A)	89.7(1)
Cl(1)–Ti–Cl(2A)	90.0(1)	Cl(2)–Ti–Cl(2A)	180.0(1)
O(1)–Ti–Cl(2A)	89.2(1)	Cl(1A–Ti–Cl(2A)	90.0(1)
Cl(1)–Ti–O(1A)	89.7(1)	Cl(2)–Ti–O(1A)	89.2(1)
O(1)–Ti–O(1A)	180.0(1)	Cl(1A)–Ti–O(1A)	90.3(1)

The X-ray crystal structure of **3** was determined in order to unequivocally establish its identity and geometry. Figure 1 shows a perspective view of **3**, Table 1 gives crystallographic data, Table 2 contains selected bond lengths and angles, and Table 3 gives the atomic positional parameters. The structure exhibits an ideal octahedral geometry about the titanium atom and reveals trans-TPPO ligands. The titanium–chlorine bond lengths are 2.341(1) (Ti–Cl(1)) and 2.343(1) Å (Ti–Cl(2)). The titanium–oxygen bond length (Ti–O(1), 1.923(3) Å) is shorter than a titanium–oxygen single bond and clearly contains a significant π-bonding component. A strong titanium–oxygen bond is also manifested by a nearly linear titanium–oxygen–phosphorus bond (Ti–O(1)–P(1) = 165.1(2)°). The related molecules $[TiCl_4(POCl_3)_2]$[16] and $[TiCl_4(POCl_3)]_2$[17] have been crystallographically characterized and possess coordination spheres similar to that of **2**.

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Table 3. Atomic Positional Parameters for 3

atom	*x*	*y*	*z*
Ti	5000	0	5000
Cl(1)	3727(1)	828(1)	3630(1)
Cl(2)	6951(1)	1027(1)	5280(1)
P(1)	3399(1)	1076(1)	6476(1)
O(1)	4132(3)	736(2)	5763(2)
N(1)	2430(3)	319(2)	6806(2)
N(2)	2363(4)	1929(2)	5974(2)
N(3)	4660(3)	1381(2)	7442(2)
C(11)	832(5)	287(4)	6457(3)
C(12)	248(5)	30(5)	7275(4)
C(13)	907(6)	–850(4)	7753(4)
C(14)	2552(6)	–821(3)	8064(3)
C(15)	3097(6)	–553(3)	7238(3)
C(21)	2375(7)	3593(3)	6080(4)
C(22)	1560(7)	3645(4)	5014(4)
C(23)	1843(6)	2801(4)	4497(4)
C(24)	1517(5)	1943(3)	4950(3)
C(25)	2055(5)	2706(3)	6496(3)
C(31)	5995(5)	1833(4)	7405(4)
C(32)	7306(6)	1427(5)	8155(5)
C(33)	7137(7)	1450(5)	9144(5)
C(34)	5706(6)	1037(4)	9153(4)
C(35)	4457(5)	1475(3)	8393(3)

Successful fabrication of highly reflective, gold-colored titanium nitride films was achieved with **2** under low-pressure CVD conditions (dynamic vacuum, 0.1–0.2 mmHg total reactor pressure) using a hot-walled reactor within the temperature range 475–600 °C. Complex **2** was slowly sublimed (ca. 80 °C , 0.1 mmHg) into a heated quartz tube containing a glass or silicon substrate supported on a ceramic stage.[18] Passage of the vaporous precursor over the heated substrate resulted in films of titanium nitride. Films produced on glass substrates from **2** (ca. 4 mmol) using a 3-min deposition time afforded film thicknesses of 3650 Å at 510 °C and 3700 Å at 600 °C, as measured by scanning electron microscopy. This gives growth rates of approximately 1200 Å min^{-1} at these temperatures. Resistivities of the films were 635 $\mu\Omega$cm (510 °C) and 962 $\mu\Omega$cm (600 °C). Films deposited on glass substrates revealed nearly exclusive crystallographic (200) orientations, as shown by the X-ray diffraction pattern. X-ray photoelectron spectroscopy of a film made at 600 °C on a glass substrate divulged a 1:1 titanium:nitrogen ratio. No chlorine peaks were observed, which places an upper limit for the chlorine content of about 2%. The visible–infrared reflectance spectra of films made at 510 and 600 °C on glass substrates showed 16–22% reflectivity between 400 and 600 nm, 18–64% reflectivity between 600 and 1000 nm, and 58–74% reflectivity between 1000 and 2000 nm. The shape of the visible–infrared reflectance spectra is consistent with the dielectric function being determined by a free electron conduction mechanism.

In summary, the complex $[TiCl_4(NH_3)_2]$ comprises a volatile (sublimes ca. 80 °C, 0.1 mmHg), carbon-free precursor to high-quality films of titanium nitride possessing low chlorine contamination. This species is the second reported single-source precursor to high purity titanium nitride films, is superior to $[TiCl_2(NHtBu)_2(NH_2tBu)_{0-2}]$[11] by virtue of its enhanced volatility and lack of carbon, and should therefore be of immediate utility to the materials community. The analytical and chemical characteristics of the title complex are consistent with the mononuclear formulation $[TiCl_4(NH_3)_2]$, with strong intermolecular N–H···Cl hydrogen bonding. Interestingly, several workers who have utilized the Kurtz–Gordon process[4] (i.e., titanium tetrachloride and ammonia) for the deposition of titanium nitride films have documented the formation of a yellow powder in the deposition chamber.[10] It is nearly certain that this powder corresponds to **2**. Furthermore, **2** is probably an intermediate along the way to titanium nitride films from titanium tetrachloride and ammonia.

The success of compound **2** in providing high-quality films of titanium nitride accords a strong testament to the utility of simple coordination complexes in materials synthesis. We are continuing to explore the development of new single- source precursors to titanium nitride and related materials. In particular, halogen-free precursors are being emphasized because of the corrosion of metal substrates (e.g., steel, aluminum, etc.) by halogens at the temperatures that the CVD reactions are carried out. These studies will be reported in due course.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9123339 to C. H. W.), the Glass Division, Ford Motor Co., and the Institute for Manufacturing Research of Wayne State University for financial support.

Supplementary Material Available: Tables S1–S6, listing full experimental details for data collection and refinement, atomic coordinates, bond lengths and angles, thermal parameters, and hydrogen postional parameters for **3**, Table S7 (including spectral diagrams), giving film characterization data for the titanium nitride films, and Figure S1, showing a schematic diagram of the CVD reactor (13 pages). Ordering information is given on any current masthead page.

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(18) A schematic diagram of the CVD reactor is contained in the supplementary material.