Inorg. Chem. **2002**, *41*, 4063–4067

Inorganic Chemistry

Article

Synthesis and Structures of Zirconium Amide–Iodide Complexes

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Received April 3, 2002

Zirconium amide–iodide complexes were synthesized for possible use as chemical vapor deposition precursors to zirconium nitride films. The series of six complexes $Zr(NR_2)_{4-n}I_n$ (R = Me or Et; n = 1–3) was prepared by reacting ZrI_4 and $Zr(NR_2)_4$ in hot toluene. X-ray crystallographic analyses were performed for $Zr(NMe_2)_3I$, $Zr(NEt_2)_2I_2$, and $Zr(NEt_2)I_3$. In the solid state, $Zr(NMe_2)_3I$ and $Zr(NEt_2)_2I_2$ are the discrete dimers $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ and $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$, and $Zr(NEt_2)I_3$ is the polymer of dimers $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$. In solution, $Zr(NEt_2)_3I$ is proposed to be monomeric on the basis of NMR data and a molecular weight determination. The complex $Zr(NEt_2)_3I$ is the most promising precursor candidate because of its physical properties.

Introduction

As part of a study on the use of transition metal and main group amide complexes as precursors to nitride thin films,[1] Fix, Gordon, and Hoffman found that $Zr(NEt_2)_4$ and ammonia gave polycrystalline Zr(IV) Zr_3N_4 films, a transparent insulating material, at low substrate temperatures (<450 °C) in an atmospheric pressure chemical vapor deposition (APCVD) process.[2,3] The important feature of the Zr amide complex in this process is the reactivity of the $Zr-NR_2$ bonds with ammonia, which serves to rid the zirconium precursor of the carbon-containing diethylamide ligands (i.e., $Zr-NR_2 + NH_3 \rightarrow Zr-NH_2 + HNR_2$).[2,3] Attempts to prepare Zr(III) ZrN films, a gold-colored metal, from $Zr(NEt_2)_4$ by adding hydrogen as a reducing agent to the $Zr(NEt_2)_4/NH_3$ precursor mixture in the APCVD process or by using an ammonia/argon plasma failed.[4,5] Wendel and Suhr have reported, however, that $Zr(NEt_2)_4$ and hydrogen (no ammonia) gave moderately conductive ZrN films in a parallel plate plasma reactor.[6]

The failure of $Zr(NEt_2)_4$ and ammonia to give Zr(III) nitride films in a thermal CVD process prompted us to prepare $Zr(NR_2)_{4-n}I_n$ ($n = 1-3$) complexes as possible precursors to ZrN. The rationale for synthesizing the $Zr(NR_2)_{4-n}I_n$ compounds is based on the precedent of using $Zr(NEt_2)_4/NH_3$ to prepare the Zr_3N_4 films and the relative ease with which ZrI_4 can be reduced.

Experimental Section

General Considerations. All manipulations were carried out in a glovebox or by using Schlenk techniques. ZrI_4, $Zr(NEt_2)_4$, and $Zr(NMe_2)_4$ were prepared by following the literature procedures.[7,8] The compounds $Zr(NEt_2)_4$ and $Zr(NMe_2)_4$ were isolated, respectively, as a colorless liquid and a white solid. Solvents were purified by using standard methods and stored in the glovebox over 4-Å molecular sieves until they were needed. The pressure flasks used in the preparations described in the following paragraphs were thick-walled glass flasks equipped with high vacuum Teflon stopcocks. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, and Chemisar Laboratories, Inc., Guelph, Ontario, Canada.

$Zr(NMe_2)_3I$. A toluene (20 mL) solution of $Zr(NMe_2)_4$ (0.401 g, 1.50 mmol) was added to ZrI_4 (0.299 g, 0.500 mmol) in a pressure flask. Toluene was added (40 mL), and the flask was sealed and placed in an oil bath. The reaction mixture was stirred for 12 h at 110 °C (CAUTION: CLOSED FLASK HEATING). The light yellow solution was allowed to cool to room temperature, and the toluene was removed in vacuo. The residue, a dark yellow powder, was dissolved in toluene (7 mL). The solution was filtered through Celite, and the filtrate was concentrated in vacuo to about 2 mL. The flask was placed in the freezer (−35 °C), where light yellow crystalline blocks formed over 12 h (yield 0.302 g, 42%). Anal. Calcd for $C_6H_{18}IN_3Zr$: C, 20.57; H, 5.14; N, 12.00. Found: C, 20.68; H, 5.12; N, 11.68. ^1H NMR (C_6D_6): δ 2.77 (s, 12, $N(CH_3)_2$), 2.61 (s, 6, $\mu\text{-}N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 47.4 ($\mu\text{-}N(CH_3)_2$), 42.4 ($N(CH_3)_2$). IR (neat, KBr, cm^{-1}): 2957 m, 2856 s, 2820 s, 2773 s, 2361 w, 1452

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(1) Hoffman, D. M. *Polyhedron* **1994**, *13*, 1169.
(2) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 7833.
(3) Fix, R.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1991**, *3*, 1138.
(4) Atagi, L. M.; Samuels, J. A.; Smith, D. C.; Hoffman, D. M. *Mater. Res. Soc. Symp. Proc.* **1996**, *410*, 289.
(5) Lehn, J.-S.; Hoffman, D. M. Unpublished.
(6) Wendel, H.; Suhr, H. *Appl. Phys. A* **1992**, *54*, 389.
(7) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.
(8) Eberly, K. C. *Inorg. Synth.* **1963**, *7*, 52.

10.1021/ic025630b CCC: $22.00

s, 1437 s, 1398 m, 1292 m, 1246 s, 1211 m, 1178 m, 1140 s, 1105 w, 1095 m, 1070 w, 1057 m, 1030 m, 972 w, 956 w, 927 s, 889 m, 713 m, 594 m, 559 m, 459 m, 447 m, 430 s, 414 s, 407 s.

$Zr(NEt_2)_3I$. A toluene (20 mL) solution of $Zr(NEt_2)_4$ (1.14 g, 3.00 mmol) was added to ZrI_4 (0.599 g, 1.00 mmol) in a pressure flask. Toluene was added (40 mL), and the flask was sealed and placed in an oil bath. The reaction mixture was stirred for 15 h at 110 °C (CAUTION: CLOSED FLASK HEATING). The light yellow solution was allowed to cool to room temperature, and the toluene was removed under vacuum. The residue, a dark yellow liquid, was distilled under vacuum to give $Zr(NEt_2)_3I$ as a light yellow liquid (mp ≈21 °C; bp 110 °C/0.068 mmHg; yield 1.60 g, 92%). Anal. Calcd for $C_{12}H_{30}IN_3Zr$: C, 33.17; H, 6.91; N, 9.68. Found: C, 33.24; H, 6.93; N, 9.41.

^{1}H NMR (C_6D_6): δ 1.08 (t, 18, $J = 6.6$ Hz, $\mathrm{N(CH_2C}H_3\mathrm{)_2}$), 3.21 (q, 12, $J = 6.6$ Hz, $\mathrm{N(C}H_2\mathrm{CH_3)_2}$). ^{13}C{^{1}H} NMR ($C_6D_6$): δ 43.1 (s, $\mathrm{N(}C\mathrm{H_2CH_3)_2}$), 16.4 (s, $\mathrm{N(CH_2}C\mathrm{H_3)_2}$). IR (neat, KBr, cm^{-1}): 2964 s, 2928 s, 2850 s, 2702 w, 2677 w, 1460 s, 1446 s, 1371 s, 1354 s, 1296 w, 1276 w, 1248 w, 1188 s, 1151 s, 1113 s, 1064 w, 1053 w, 1022 w, 1001 s, 947 w, 910 w, 871 s, 829 w, 787 s, 742 w, 588 s, 428 s, 411 s.

$Zr(NMe_2)_2I_2$. A toluene (20 mL) solution of $Zr(NMe_2)_4$ (0.133 g, 0.500 mmol) was added to ZrI_4 (0.299 g, 0.500 mmol) in a pressure flask. Toluene was added (40 mL), and the flask was sealed and placed in an oil bath. The mixture was stirred at 110 °C for 12 h, and then at 125 °C for another 12 h to ensure complete dissolution of the reactants and products (CAUTION: CLOSED FLASK HEATING). The light yellow solution was allowed to cool to room temperature, which caused a precipitate to appear. The toluene was removed under vacuum. The residue, a yellow powder, was washed with hexanes (2 × 7 mL) and then dried for 24 h under vacuum (yield 0.351 g, 81%). $Zr(NMe_2)_2I_2$ slowly decomposes as a solid at 100 °C, and more quickly at 120 °C. Anal. Calcd for $C_4H_{12}I_2N_2Zr$: C, 11.09; H, 2.78; N, 6.47. Found: C, 11.38; H, 2.97; N, 6.30.

^{1}H NMR (CD_2Cl_2): δ 3.24 (s, $\mathrm{N(C}H_3\mathrm{)_2}$). ^{13}C{^{1}H} NMR ($CD_2Cl_2$): δ 42.1 (s, $\mathrm{N(}C\mathrm{H_3)_2}$). IR (neat, KBr, cm^{-1}): 2924 s, 2874 m, 2854 m, 2781 m, 1452 s, 1433 s, 1400 s, 1251 s, 1209 m, 1122 s, 1093 m, 1047 w, 1031 s, 922 s, 871 s.

$Zr(NEt_2)_2I_2$. A toluene (20 mL) solution of $Zr(NEt_2)_4$ (0.190 g, 0.500 mmol) was added to ZrI_4 (0.299 g, 0.500 mmol) in a pressure flask. Toluene was added (40 mL), and the flask was sealed and placed in an oil bath. The mixture was stirred for 12 h at 110 °C, and then at 125 °C for another 12 h to ensure complete dissolution of the reactants and products (CAUTION: CLOSED FLASK HEATING). The light yellow solution was allowed to cool to room temperature, and the toluene was removed under vacuum. The residue, a yellow powder, was washed with hexanes (2 × 7 mL) and dried under vacuum for 24 h (yield 0.419 g, 86%). Yellow crystalline blocks can be grown from a saturated dichloromethane solution at −65 °C. Anal. Calcd for $C_8H_{20}I_2N_2Zr$: C, 19.63; H, 4.09; N, 5.73. Found: C, 19.59; H, 4.09; N, 5.48.

^{1}H NMR (CD_2Cl_2): δ 1.24 (t, 18, $J = 6.9$ Hz, $\mathrm{N(CH_2C}H_3\mathrm{)_2}$), 3.52 (q, 12, $J = 6.6$ Hz, $\mathrm{N(C}H_2\mathrm{CH_3)_2}$). ^{13}C{^{1}H} NMR ($CD_2Cl_2$): δ 40.6 ($\mathrm{N(}C\mathrm{H_2CH_3)_2}$), 14.0 ($\mathrm{N(CH_2}C\mathrm{H_3)_2}$). IR (Nujol, KBr, cm^{-1}): 2960 s, 2924 s, 2862 s, 2758 w, 2673 w, 1462 s, 1446 s, 1371 s, 1352 s, 1334 w, 1315 w, 1271 m, 1244 w, 1184 s, 1143 s, 1099 s, 1066 m, 1051 s, 995 s, 912 w, 871 s, 787 s, 723 w, 596 m, 505 w.

$Zr(NMe_2)I_3$. A toluene (20 mL) solution of $Zr(NMe_2)_4$ (0.027 g, 0.10 mmol) was added to ZrI_4 (0.18 g, 0.30 mmol) in a pressure flask. Toluene was added (80 mL), and the flask was sealed and placed in an oil bath. The mixture was stirred for 12 h at 110 °C, and then at 125 °C for another 12 h to ensure complete dissolution of the reactants and products (CAUTION: CLOSED FLASK HEATING). The reaction mixture, a light yellow solution and a precipitate, was allowed to cool to room temperature. More precipitate appeared upon cooling. The toluene was removed under vacuum. The residue, a dark yellow powder, was dissolved in CH_2Cl_2 (100 mL) by stirring the powder for 24 h in the solvent. The solution was filtered to remove a small amount of insoluble material. A large volume (80 mL) of pentane was added to the filtrate, which caused a yellow solid to precipitate. After the solid had settled for 5 h, the supernatant liquid was removed with a pipet, and the solid was washed with pentane (4 × 10 mL) and then dried for 12 h under vacuum (yield 0.090 g, 43%). A satisfactory carbon analysis was not obtained. Anal. Calcd for $C_2H_6I_3NZr$: C, 4.65; H, 1.16; N, 2.71. Found: C, 5.42; H, 1.38; N, 2.82.

IR (Nujol, KBr, cm^{-1}): 2953 s, 2922 s, 2862 s, 2750 w, 2361 w, 2343 w, 1580 m, 1502 w, 1454 s, 1406 w, 1377 m, 1303 w, 1242 s, 1151 w, 1099 m, 1074 m, 1016 s, 922 w, 875 w, 862 w, 806 w, 738 w, 619 s.

$Zr(NEt_2)I_3$. A toluene (20 mL) solution of $Zr(NEt_2)_4$ (0.027 g, 0.066 mmol) was added to ZrI_4 (0.12 g, 0.20 mmol) in a pressure flask. Toluene was added (80 mL), and the flask was sealed and placed in an oil bath. The mixture was stirred for 12 h at 110 °C, and then at 125 °C for another 12 h to ensure complete dissolution of the reactants and products (CAUTION: CLOSED FLASK HEATING). The light yellow solution was allowed to cool to room temperature, and the toluene was removed under vacuum. The residue, a yellow powder, was dissolved in CH_2Cl_2 (100 mL) by stirring the powder for 24 h in the solvent. The solution was filtered to remove a small amount of insoluble material. Pentane (80 mL) was added to the filtrate whereupon a yellow solid precipitated. The solid was allowed to settle for 12 h. The supernatant liquid was then removed with a pipet, and the remaining solid was washed with pentane (3 × 20 mL) and then dried under vacuum for 10 h (yield 0.090 g, 61%). Yellow crystalline blocks of the compound were grown by cooling slowly to room temperature a superheated (135 °C) saturated toluene solution. Anal. Calcd for $C_4H_{10}I_3NZr$: C, 8.83; H, 1.84; N, 2.57. Found: C, 8.85; H, 1.90; N, 2.64.

IR (Nujol, KBr, cm^{-1}): 2953 m, 2924 s, 2862 s, 1639 m, 1554 m, 1462 s, 1452 s, 1416 w, 1384 s, 1246 m, 1155 m, 1113 w, 1097 w, 1031 m, 756 m.

X-ray Crystallography. Crystal data are presented in Table 1. Crystals of $[Zr(NMe_2)_3I]_2$, $[Zr(NEt_2)_2I_2]_2$, and $[Zr(NEt_2)I_3]_2$ are colorless flat plates, pale yellow columns, and orange thin plates, respectively. The complexes $[Zr(NMe_2)_3I]_2$ and $[Zr(NEt_2)_2I_2]_2$ were crystallized from cold toluene (−35 °C, 12 h) and dichloromethane (−65 °C, 20 h) solutions, respectively. The complex $[Zr(NEt_2)I_3]_2$ was crystallized by cooling slowly a superheated (≈135 °C) toluene solution (≈0.1 g/0.1 L at 135 °C) to room temperature. In all cases, the crystals were handled under mineral oil during the mounting procedure. Data were collected on a Siemens SMART CCD instrument. No experimental difficulties were encountered. Full details can be found in the Supporting Information.

Results and Discussion

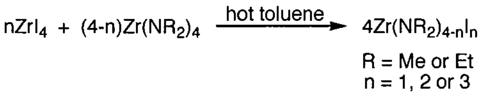
Synthesis. The complexes $Zr(NR_2)_{4-n}I_n$ (R = Me or Et; $n = 1-3$) were prepared by reacting ZrI_4 and $Zr(NR_2)_4$ in hot toluene (Scheme 1). The complex $Zr(NEt_2)_3I$ is a distillable liquid (110 °C/0.07 mmHg), and $Zr(NMe_2)_3I$ is a sublimable solid (90 °C/0.04 mmHg with slight decomposition). The di- and tri-iodides are nonvolatile solids that decomposed during attempted sublimations. The $Zr(NR_2)_3I$ compounds are soluble in hexane, benzene, and methylene chloride, but for the other compounds, the solubility becomes

Table 1. Crystal Data for $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$, $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$, and $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$

	$[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$	$[Zr(NEt_2)_2I(\mu\text{-}I)]_2$	$\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$
formula	$C_{12}H_{36}N_6I_2Zr_2$	$C_{16}H_{40}N_4I_4Zr_2$	$C_8H_{20}N_2I_6Zr_2$
fw	700.71	978.56	1088.10
cryst dim. (mm^3)	0.36 × 0.26 × 0.08	0.30 × 0.10 × 0.08	0.30 × 0.18 × 0.06
space group	$P\bar{1}$ (triclinic)	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)
a, Å	8.5884(6)	8.149(2)	7.1219(8)
b, Å	8.7949(6)	13.480(3)	7.6193(8)
c, Å	18.1676(12)	14.420(3)	11.7175(12)
α, deg	92.487(1)	90.00	90.323(2)
β, deg	99.479(1)	100.440(10)	106.820(2)
γ, deg	117.836(1)	90.00	108.206(2)
temp, °C	−50(2)	−50(2)	−50(2)
Z	2	2	1
V, $Å^3$	1185.48(14)	1557.8(6)	574.93(11)
D_{calcd}, g/cm^3	1.963	2.086	3.143
μ, mm^{-1}	3.489	4.641	8.951
R, R_w[a]	0.0258, 0.0732[b]	0.0268, 0.0694[c]	0.0273, 0.0743[d]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (0.0353P)^2 + (1.8055P)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = [\sigma^2(F_o^2) + (0.0237P)^2 + (7.6700P)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = [\sigma^2(F_o^2) + (0.0382P)^2 + (2.8208P)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1



$$nZrI_4 + (4\text{-}n)Zr(NR_2)_4 \xrightarrow{\text{hot toluene}} 4Zr(NR_2)_{4\text{-}n}I_n$$

R = Me or Et
n = 1, 2 or 3

progressively poorer as the amide ligands are replaced by iodide. The complex $Zr(NEt_2)I_3$, for example, is insoluble in toluene at room temperature and only slightly in methylene chloride (≈2−3 g/L), and $Zr(NMe_2)I_3$ is virtually insoluble in methylene chloride (<1 g/L at 23 °C).

X-ray Structure Determinations. The X-ray crystal structures of $Zr(NMe_2)_3I$ (Figure 1), $Zr(NEt_2)_2I_2$ (Figure 2), and $Zr(NEt_2)I_3$ (Figure 3) were determined. Selected bond distances and angles are presented in Tables 2−4.

In the solid state, the compounds $Zr(NMe_2)_3I$ and $Zr(NEt_2)_2I_2$ are the discrete dimers $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ and $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$, and $Zr(NEt_2)I_3$ is the polymer of dimers $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$. The zirconium coordination geometry in $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ and $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$ is trigonal bipyramidal. In the former, the axial positions are occupied by terminal iodide and bridging amide ligands (av I−Zr−N_{bridge} = 164°) and in the latter by terminal and bridging iodide ligands (I1′−Zr−I2 = 159°). For both complexes, the angles between the ligands that define the trigonal planes of the trigonal bipyramids sum to within 2° of 360°. The four-member $Zr(\mu\text{-}NMe_2)_2Zr$ ring in $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ has a slight fold along the N···N vector (20.4°), giving the ring a butterfly configuration, while the $Zr(\mu\text{-}I)_2Zr$ rings in $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$ and $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$ are planar (crystallographically imposed). The structure of $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ resembles closely the structure of $[Zr(NMe_2)_2Cl(\mu\text{-}NMe_2)]_2$.[9]

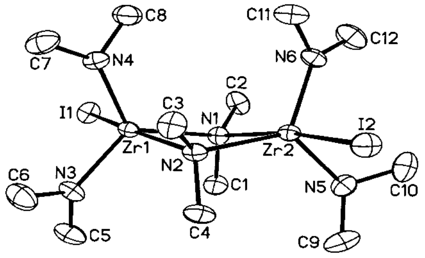


Figure 1. View of the $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ molecule showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogens omitted.

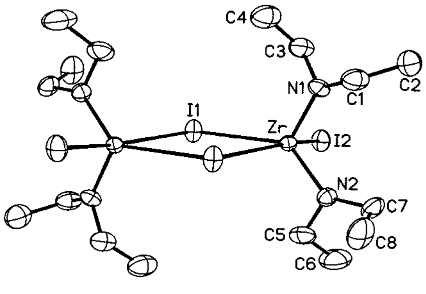


Figure 2. View of the $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$ molecule showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogens omitted.

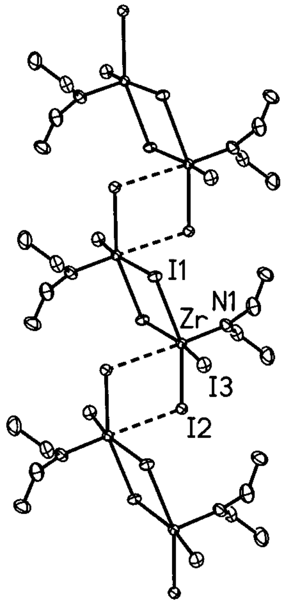


Figure 3. View of $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$ showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogens omitted.

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(9) Kempe, R.; Hillebrand, G.; Spannenberg, A. *Z. Kristallogr.-New Cryst. Struct.* **1997**, *212*, 490.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$

	Distances		
Zr1−N1	2.216(3)	Zr2−N1	2.336(3)
Zr1−N2	2.336(3)	Zr2−N2	2.237(3)
Zr1−N3	2.012(3)	Zr2−N5	2.008(3)
Zr1−N4	2.007(3)	Zr2−N6	2.007(3)
Zr1−I1	2.9357(4)	Zr2−I2	2.9193(4)
	Angles		
N1−Zr1−N2	76.81(11)	N1−Zr2−N2	76.42(10)
N1−Zr1−N3	122.60(13)	N2−Zr2−N5	124.83(13)
N1−Zr1−N4	121.62(13)	N2−Zr2−N6	119.99(13)
N3−Zr1−N4	115.58(14)	N5−Zr2−N6	114.76(15)
N2−Zr1−N3	94.42(12)	N1−Zr2−N6	94.82(12)
N2−Zr1−N4	95.11(12)	N1−Zr2−N5	93.25(13)
N1−Zr1−I1	86.75(8)	N2−Zr2−I2	88.63(8)
N2−Zr1−I1	163.25(7)	N1−Zr2−I2	164.50(7)
N3−Zr1−I1	91.73(10)	N5−Zr2−I2	91.96(10)
N4−Zr1−I1	96.25(10)	N6−Zr2−I2	96.23(9)
Zr1−N1−Zr2	101.44(11)	Zr2−N2−Zr1	100.79(11)
av term. C−N−C (range)	110.7 (110.1(4)−111.2(4))	av term. Zr−N−C (range)	124.3 (113.7(3)−134.3(3))
C1−N1−Zr1	102.5(2)	C1−N1−Zr2	111.7(2)
C2−N1−Zr1	124.3(3)	C2−N1−Zr2	109.6(2)
C3−N2−Zr1	111.2(2)	C3−N2−Zr2	121.4(2)
C4−N2−Zr1	112.8(2)	C4−N2−Zr2	102.8(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$

	Distances		
Zr−I1	2.9907(10)	Zr−N1	1.974(6)
Zr−I1′	2.9854(9)	Zr−N2	1.972(6)
Zr−I2	2.8544(9)		
	Angles		
N1−Zr−I1	115.00(18)	N1−Zr−I2	102.64(17)
N2−Zr−I1	133.62(18)	N2−Zr−I2	98.07(18)
I2−Zr−I1	83.77(2)	N2−Zr−N1	109.8(2)
I1′-Zr-I1	77.69(2)	N2−Zr−I1′	88.15(18)
I2−Zr−I1′	159.22(3)	N1−Zr−I1′	93.74(17)
C1−N1−C3	115.5(6)	C7−N2−C5	115.3(6)
C1−N1−Zr	130.3(5)	C7−N2−Zr	135.7(5)
C3−N1−Zr	113.9(5)	C5−N2−Zr	108.8(5)
Zr′−I1−Zr	102.31(2)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$

	Distances		
Zr−I1	2.9363(7)	Zr−I1′	2.9993(8)
Zr−I2	2.8507(8)	Zr−I2′	3.2029(8)
Zr−I3	2.7736(7)	Zr−N1	1.967(6)
	Angles		
N1−Zr−I1	95.47(18)	I3−Zr−I2′	83.52(2)
N1−Zr−I1′	97.99(17)	I2−Zr−I2′	82.45(2)
N1−Zr−I2	101.19(19)	I1−Zr−I2′	81.25(2)
N1−Zr−I3	94.35(17)	I1′-Zr-I2′	83.74(2)
I2−Zr−I3	98.51(2)	Zr−I1−Zr′	98.98(2)
I1−Zr−I3	90.93(2)	Zr−I2−Zr′	97.55(2)
I1−Zr−I2	160.10(3)	N1−Zr−I2′	176.04(19)
I3−Zr−I1′	165.84(3)	C1−N1−C3	113.9(6)
I2−Zr−I1′	85.92(2)	C1−N1−Zr	117.0(5)
I1−Zr−I1′	81.02(2)	C3−N1−Zr	128.9(5)

The Zr coordination geometry in $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$ is approximately octahedral. An iodide on an adjacent dimer in the polymer chain is weakly coordinated trans to the amide ligand (I2′−Zr−N1 = 176°).

In the $Zr(\mu\text{-}NMe_2)_2Zr$ ring of $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$, the Zr−N distances differ by 0.1 Å with the bond trans to I2 being the longer of the two. The two unique $Zr-I_{bridge}$ distances in $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$ are the same by the 3σ criterion, and in $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$, they differ only slightly (<0.1 Å). The $Zr-I_{terminal}$ distances in the complexes range from 2.7736(7) to 2.9357(4) Å, with the shortest distance in $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$ and the longest in $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$. The lengthening of the $Zr-I_{terminal}$ distances as the number of nitrogens in the Zr coordination sphere increases may be a consequence of the strong π donor ability of the amides, which compete with iodide for pπ donation to zirconium, or it may be a consequence of increasing steric congestion as amide is substituted for iodide. The Zr−I2 distance in $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$ is slightly longer than the Zr−I3 distance because I2 is involved in the weak interdimer interaction (Zr−I2′ = 3.2029(8) Å). In general, the terminal and bridging Zr−I distances are within the range of distances reported previously ($Zr-I_{terminal}$ = 2.692(1)−3.003(1) Å and $Zr-I_{bridge}$ = 2.868(1)−3.029(1) Å).[10−24] The $Zr-N_{terminal}$ distances in $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ (av 2.009(3) Å) are slightly longer than those in the diethylamide derivatives (av 1.971(6) Å). As a more general comparison, the Zr−N distances[25] in $Zr(NEt_2)_2Cl_2(THF)_2$ average 2.023(7) Å, and the terminal $Zr-NMe_2$ distances in $Zr(NMe_2)_2Cl_2(THF)_2$,[25] $[Zr(NMe_2)_3(\mu\text{-}NMe_2)]_2$,[26] $(Me_2N)_2(THF)Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_3$, $(Me_2N)_2(THF)Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2Cl$, and $(Me_2N)(THF)Cl_2Zr(\mu\text{-}Cl)_2Li(THF)_2$ range from 1.990(5) to 2.108(3) Å.[27] The $Zr-N_{bridge}$ distances in $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ are within the range of distances observed previously.[26,27]

The C−N−C angles of the terminal amide ligands in the three structures fall in the narrow range 110−116°, but the Zr−N−C angles vary widely (109−136°), indicating that the energy cost to bend Zr−N−C must be small and that the angle is set by steric interactions.

Solution Characterization. Consistent with the solid state structure, room temperature ^1H and $^{13}C\{^1H\}$ NMR spectra

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(10) Krebs, V. B.; Henkel, G.; Dartmann, M. *Acta Crystallogr. B* **1979**, *35*, 274.
(11) Troyanov, S. I.; Meetsma, A.; Teuben, J. H. *Inorg. Chim. Acta* **1998**, *271*, 180.
(12) Kubiak, R.; Ejsmont, K. *Acta Crystallogr. C* **1998**, *54*, 572.
(13) Cotton, F. A.; Wojtczak, W. A. *Acta Crystallogr. C* **1994**, *50*, 1662.
(14) Cotton, F. A.; Kibala, P. A.; Shang, M.; Wojtczak, W. A. *Organometallics* **1991**, *10*, 2626.
(15) Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 908.
(16) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1971**, 2225.
(17) Cotton, F. A.; Shang, M.; Wojtczak, W. A. *Inorg. Chem.* **1991**, *30*, 3670.
(18) Walther, D.; Fischer, R.; Görls, H.; Koch, J.; Schweder, B. *J. Organomet. Chem.* **1996**, *508*, 13.
(19) King, W. A.; DiBella, S.; Gulino, A.; Lanza, G.; Fragalà, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 355.
(20) Antiñolo, A.; Lappert, M. F.; Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1463.
(21) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L. *Organometallics* **1989**, *8*, 250.
(22) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; Spek, A. L. *Organometallics* **1989**, *8*, 2948.
(23) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178.
(24) Lachgar, A.; Dudis, D. S.; Corbett, J. D. *Inorg. Chem.* **1990**, *29*, 2242.
(25) Brenner, S.; Kempe, R.; Arndt, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2021.
(26) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Polyhedron*, **1988**, *7*, 2515.
(27) Wu, Z.; Diminnie, J. B.; Xue, Z. *Inorg. Chem.* **1998**, *37*, 2570.

for $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ had two peaks in a 2:1 ratio corresponding to the terminal and bridging amide ligands, respectively. Room temperature spectra for the tris(diethylamide) analogue, however, displayed resonances for only one kind of amide ligand. The ^1H NMR spectrum (toluene-d_8 solution) did not change significantly when the probe temperature was lowered to −55 °C. Cryoscopic molecular weight determinations[28−30] for $Zr(NEt_2)_3I$ (cyclohexane solvent,[31] average of three determinations) gave a molecular weight of 388 ± 9 g/mol (monomer theoretical MW = 434 g/mol). The NMR and molecular weight data suggest that $Zr(NEt_2)_3I$ is a monomer in solution.

In ^1H NMR spectra for $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$, which has virtual C_{2h} symmetry in the solid state, the methylene protons should appear as an AB quartet coupled to three protons. Room and low temperature spectra (to −55 °C, $CDCl_3$), however, showed only a simple quartet for the methylene protons. A monomer−dimer equilibrium could explain this discrepancy. A cryoscopic molecular weight determination was not attempted for $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$ or its dimethylamide analogue because suitable solvents for the experiments could not be identified. The triiodide complexes were not characterized in solution because of their very low solubility in noncoordinating solvents.

Conclusion

Six $Zr(NR_2)_{4-n}I_n$ (R = Me or Et; $n = 1$, 2 or 3) compounds were prepared in moderate yields by ligand scrambling reactions involving ZrI_4 and $Zr(NR_2)_4$ in hot toluene solutions. In the solid state, $Zr(NMe_2)_3I$ and $Zr(NEt_2)_2I_2$ are the discrete dimers $[Zr(NMe_2)_2I(\mu\text{-}NMe_2)]_2$ and $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$, and $Zr(NEt_2)I_3$ is the polymer of dimers $\{[Zr(NEt_2)I_2(\mu\text{-}I)]_2\}_n$. In solution, $Zr(NEt_2)_3I$ is proposed to be monomeric on the basis of NMR data and a molecular weight determination. NMR data for $[Zr(NEt_2)_2I(\mu\text{-}I)]_2$ suggest that it does not retain the dimer structure in solution.

Our purpose in preparing the $Zr(NR_2)_{4-n}I_n$ compounds was to assess their suitability as CVD precursors to zirconium(III) nitride films. $Zr(NEt_2)_3I$ is the most promising precursor candidate among the new compounds because it is a thermally stable, volatile liquid. Volatile liquids are preferred as precursors because they can be transported easily and at a consistent rate from the precursor container to the CVD reactor.

Acknowledgment. We thank Dr. James Korp for technical assistance with the crystal structure determinations. This work was supported in part by the MRSEC Program of the National Science Foundation, the State of Texas Advanced Research Program, Saint-Gobain Recherche, and the Robert A. Welch Foundation.

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025630B

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(28) Moulin, M. *J. Chim. Phys.* **1910**, *8*, 21.
(29) Hofsommer, R. *Naturwiss. Unterr., Phys./Chem./Biol.* **1974**, *22*, 68.
(30) Gillespie, R. J.; Milne, J. B.; Thompson, R. C. *Inorg. Chem.* **1966**, *5*, 468.
(31) *CRC Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press LLC: Boca Raton, FL, 1999; p 15−21.