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Adducts of Titanium Tetrachloride with Alkylselenium Compounds: Molecular Precursors to Titanium Diselenide Films

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Treatment of titanium tetrachloride (2 equiv) with dimethyl diselenide or diethyl diselenide (1 equiv) in hexane at 0 °C, followed by crystallization at −20 °C, afforded $(TiCl_4)_2(Se_2(CH_3)_2)$ (78%) and $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$ (63%), respectively, as red and orange crystalline solids. $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$ is stable in solution and in the solid state at 23 °C, but $(TiCl_4)_2(Se_2(CH_3)_2)$ decomposes to $TiCl_4(Se(CH_3)_2)_2$, gray selenium, and other products upon standing in hexane solution, in the solid state, or upon sublimation at 250 °C. Treatment of titanium tetrachloride with 2 equiv of dimethyl selenide or diethyl selenide in hexane at ambient temperature afforded a spectroscopically pure brick red solid of $TiCl_4(Se(CH_3)_2)_2$ (96%) or $TiCl_4(Se(CH_2CH_3)_2)_2$ (96%), respectively. X-ray crystal structures of $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$, $TiCl_4(Se(CH_3)_2)_2$, and $TiCl_4(Se(CH_2CH_3)_2)_2$ were determined to establish solid state nuclearities. $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$ crystallizes in the hexagonal space group $P3_121$ with $a = 12.106(1)$ Å, $c = 10.786(1)$ Å, $V = 1368.8(4)$ Å^3, and $Z = 3$. $TiCl_4(Se(CH_3)_2)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.175(1)$ Å, $b = 13.051(1)$ Å, $c = 16.871(3)$ Å, $\beta = 102.675(8)°$, $V = 1756.3(2)$ Å^3, and $Z = 4$. $TiCl_4(Se(CH_2CH_3)_2)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.404(4)$ Å, $b = 16.376(7)$ Å, $c = 13.058(8)$ Å, $\beta = 101.45(4)°$, $V = 1342(1)$ Å^3, and $Z = 4$. $TiCl_4(Se(CH_3)_2)_2$ and $TiCl_4(Se(CH_2CH_3)_2)_2$ were evaluated as precursors to titanium diselenide films. $TiCl_4(Se(CH_3)_2)_2$ was not a good precursor, but $TiCl_4(Se(CH_2CH_3)_2)_2$ afforded rose-bronze colored titanium diselenide films at substrate temperatures of 500−600 °C. The films were characterized by X-ray powder diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. Surprisingly, titanium diselenide films prepared from $TiCl_4(Se(CH_2CH_3)_2)_2$ are moisture sensitive and are apparently hydrolyzed by ambient moisture to titanium dioxide and hydrogen selenide. The relevance of the coordination chemistry to the development of precursors to titanium diselenide films is discussed.

Introduction

Early transition metal dichalcogenides represent promising cathode materials for lithium batteries[2] and have been used as solid lubricants due to weak van der Waals interactions between adjacent layers in the lattice.[3] Recent emphasis on thin-film batteries has required that the cathodes be fabricated in thin-film form.[4] These issues have led to considerable interest in film deposition processes that lead to titanium disulfide[5−8] and molybdenum disulfide films.[9] We have reported that alkanethiol adducts of the formula $TiCl_4(HSR)_2$ function as single-source precursors to titanium disulfide (TiS_2) films[7] and that the films derived from these precursors are similar in high quality to films obtained from a two-component process employing titanium tetrachloride and an alkanethiol.[8] We reasoned that related

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[1] (a) Wayne State University. (b) University of Delaware.

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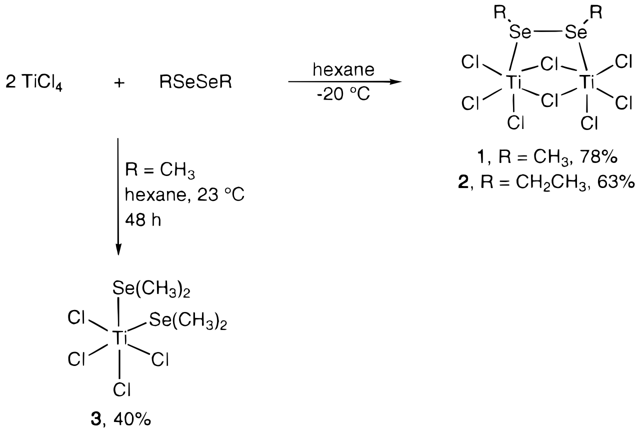
titanium tetrachloride adducts of organoselenium compounds might function as single-source precursors to titanium diselenide ($TiSe_2$) films. There has been very little study of reactions between titanium tetrachloride and organoselenium compounds.[10] Several reports have detailed the deposition of $TiSe_2$ films using physical deposition techniques,[11] but chemical vapor deposition (CVD) processes for fabrication of $TiSe_2$ films have not been described.

Herein we report a study of the coordination chemistry of titanium tetrachloride with dialkyl diselenides and dialkyl selenides and evaluation of the resultant complexes as single-source precursors to $TiSe_2$ films. Dialkyl diselenides form adducts of the formula $(TiCl_4)_2(Se_2R_2)$, and the dimethyl diselenide complex undergoes a complicated decomposition at ambient temperature to afford $TiCl_4(Se(CH_3)_2)_2$, elemental selenium, and other products. The complexes $TiCl_4(SeR_2)_2$ are more efficiently prepared by treating titanium tetrachloride with the alkyl diselenide. The crystal structures of $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$, $TiCl_4(Se(CH_3)_2)_2$, and $TiCl_4(Se(CH_2CH_3)_2)_2$ are reported and represent the first structure determinations of titanium complexes containing neutral organoselenium donors.[12] Finally, $TiCl_4(Se(CH_2CH_3)_2)_2$ functions as a single-source precursor for $TiSe_2$ films using CVD techniques and is the first such precursor to this phase. This is the first CVD route to $TiSe_2$ films.

Results

Reaction of Titanium Tetrachloride with Alkyl Diselenides. Treatment of titanium tetrachloride (2 equiv) with dimethyl diselenide and diethyl diselenide in hexane at 0 °C, followed by crystallization at −20 °C, afforded $(TiCl_4)_2(Se_2(CH_3)_2)$ (**1**, 78%) and $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$ (**2**, 63%), respectively, as red and orange crystalline solids (Scheme 1). Complexes **1** and **2** were fully characterized by spectroscopic and analytical techniques. The ^1H and $^{13}C\{^1H\}$ NMR spectra were diagnostic of the adduct structures and showed downfield shifts relative to the free ligands. For example, **1** revealed resonances at δ 2.62 in the ^1H NMR spectrum and at 10.95 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The analogous values for free dimethyl diselenide are δ 2.55 and 10.36 ppm. The molecular geometry of **2** was established by an X-ray structure determination (vide infra). The microanalysis for **1** indicated a composition similar to that of **2**. In the synthesis of **1**, it was necessary to keep the reaction temperature below 0 °C, since **1** readily decomposed at higher temperatures, as outlined below. By contrast, **2** was stable at 23 °C.

Scheme 1



1, R = CH_3, 78%
2, R = CH_2CH_3, 63%

3, 40%

Decomposition of 1. Treatment of titanium tetrachloride with 2 equiv of dimethyl diselenide in hexane at ambient temperature for 48 h, followed by crystallization at −20 °C, afforded $TiCl_4(Se(CH_3)_2)_2$ (**3**, 40%) as a deep red crystalline solid. Compound **3** was fully characterized by spectroscopic and analytical techniques. The melting point and ^1H and $^{13}C\{^1H\}$ NMR spectra were identical to those of **3** that was prepared independently (vide infra). Complex **3** was further characterized by an X-ray crystal structure determination (vide infra).

In order to gain insight into the formation of **3**, its formation was monitored by NMR spectroscopy. Treatment of titanium tetrachloride (2 equiv) with dimethyl diselenide (1 equiv) in chloroform-*d* at 23 °C immediately afforded a dark red solution. After about 5 min, the ^1H NMR spectrum showed a singlet at δ 2.84 with $J_{H-Se} = 11.4$ Hz. The $^{13}C\{^1H\}$ NMR spectrum revealed only a singlet at 14.11 ppm (J_{C-Se} not resolved). For comparison, the analogous chemical shifts for free dimethyl diselenide were δ 2.55 ($J_{H-Se} = 7.2$ Hz) and 10.36 ($J_{C-Se} = 43.7$ Hz) and for pure **1** the chemical shifts were δ 2.62 ($J_{H-Se} = 11.4$ Hz) and 10.95 (J_{C-Se} not resolved), while for pure **3** these values were δ 2.48 ($J_{H-Se} = 8.1$ Hz) and 17.68 (J_{C-Se} not resolved). Clearly a new species is formed upon treatment of titanium tetrachloride with dimethyl diselenide, since the chemical shifts in the NMR tube experiment do not correspond to those of free dimethyl diselenide, **1**, or **3**. After 6 h, the ^1H and $^{13}C\{^1H\}$ NMR spectra displayed new resonances corresponding to **3**. The resonances for **3** continued to grow for 8 days until the integration of the ^1H NMR spectrum indicated a 55:45 mixture of the new species (δ 2.84 in ^1H NMR) and **3**. After 8 days, the 55:45 mixture of the new species and **3** was constant within experimental error.

To understand the reaction further, **1** was placed at the end of a 2 cm × 35 cm glass sublimation tube. The tube was evacuated to ca. 0.01 mmHg and then was placed in a horizontal sublimation oven held at 250 °C with about 12 cm of the tube protruding from the furnace. In this way, the volatile components sublimed from the hot part of the tube to the cold end. After 18 h, red crystals were observed furthest from the furnace, while a silver-colored compound had collected just outside where the tube projected from the furnace. The two components were isolated by scraping them from the tube in a drybox. The red crystals were identified by ^1H and $^{13}C\{^1H\}$ NMR as **3**, with a yield of 65%. The silver-colored solid was identified as gray selenium by X-ray power diffraction and melting point, in a yield of 65%. In a sublimation starting with 1.054 g of **1**, there was a residue of 0.023 g left at the end of the sublimation. Because the experiment was run under dynamic vacuum, and

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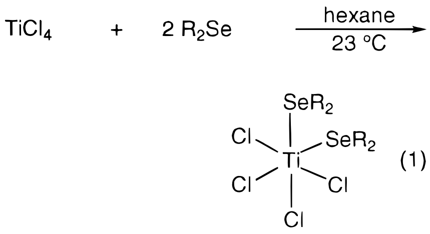
3 is extremely volatile, some of the **3** could have been lost from the tube and this would account for the 65% yield. The cold trap was bright red after the sublimation, supporting some loss of **3**. The gray selenium was difficult to scrape from the tube, and some was lost in the manipulation. If the sublimation was run at 48 °C, gray selenium did not sublime and the medium red titanium−containing sublimate was a 52:48 mixture of **1** and **3** as determined by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Interestingly, **1** decomposes slowly to **3** upon standing at ambient temperature in a drybox under an argon atmosphere. The decomposition is characterized by the slow appearance of deep red crystals of **3** in the orange powder of **1**. The qualitative rate of the solid state reaction was highly variable, with some samples of **1** decomposing completely to **3** in as little as 6 days, while other samples decomposed only slightly (as judged visually and by ^{1}H and ^{13}C{^{1}H} NMR) over 1 month. While this conversion was not pursued in detail due to its variability, it may be sensitive to trace impurities in **1**.

Independent Syntheses of TiCl$_4$(SeR$_2$)$_2$. Identification of **3** as a decomposition product of **1** required its independent synthesis. Treatment of titanium tetrachloride with 2 equiv of methyl selenide and ethyl selenide in hexane at ambient temperature, followed by workup afforded spectroscopically pure brick red solids of TiCl$_4$(Se(CH$_3$)$_2$)$_2$ (**3**, 96%) and TiCl$_4$(Se(CH$_2$CH$_3$)$_2$)$_2$ (**4**, 96%), respectively (eq 1). Sublimation of these crude products (30−40 °C/0.01 mmHg) yielded analytically pure deep red crystals of **3** and **4**. Complexes **3** and **4** were fully characterized by spectroscopic and analytical techniques. The ^{1}H and ^{13}C{^{1}H} NMR spectra revealed intact alkyl groups with downfield shifts relative to the free ligands, which confirmed adduct structures. X-ray structure determinations (vide infra) established the molecular geometries of **3** and **4**. Complexes **3** and **4** were thermally stable in hexane at 23 °C for weeks in the absence of air, and no precipitates were observed during this time. Complexes **3** and **4** have been previously reported.[10] The reported melting points and ^{1}H NMR chemical shifts are similar to those given herein.



(1)

3, R = CH$_3$, 96%
4, R = CH$_2$CH$_3$, 96%

Crystal Structures of 2−4. The X-ray crystal structures of **2**−**4** were determined to establish their molecular geometries. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2−4, and perspective views are presented in Figures 1−3. Further data are available in the Supporting Information.

Complex **2** crystallized as a Ti$_2$Cl$_8$ unit with each selenium of the diethyl diselenide ligand bonded to a titanium atom. There are three distinct types of titanium−chlorine bonds present in **2**. The bridging chlorine atoms (Cl(4), Cl(4A)) are symmetrically bonded and show titanium−chlorine distances of 2.459(3) and 2.471(4) Å. The equatorial chlorine atoms (Cl(1), Cl(2)) (all trans to bridging chlorine atoms) exhibit titanium−chlorine bond lengths of 2.200(5) and 2.195(3) Å. The third type of titanium−chlorine bond (Cl(3)) is trans to the diethyl diselenide selenium donor and shows a bond length of 2.195(3) Å. Cl(1), Cl(2), and Cl(3) show titanium−chlorine bond lengths that are 0.259−0.276 Å shorter than the related distances with the bridging ligands Cl(4) and Cl(4A). The titanium−selenium bond length is 2.796(2) Å. The geometry about each titanium exhibits substantial deviations from idealized octahedral geometry. The cis chlorine−titanium−chlorine angles range from 81.41 to 101.7°, with an average value of 94.8°. The trans chlorine−titanium−chlorine angles are 161.77(13) and

Table 1. Experimental Crystallographic Data for **2**−**4**

	2	**3**	**4**
empirical formula	$C_4H_{10}Cl_8Se_2Ti_2$	$C_4H_{12}Cl_4Se_2Ti$	$C_8H_{20}Cl_4Se_2Ti$
fw	595.44	407.77	463.86
space group	$P3_121$	$P2_1/n$	$P2_1/n$
a (Å)	12.106(1)	6.404(4)	8.175(1)
b (Å)		16.376(7)	13.051(1)
c (Å)	10.786(1)	13.058(8)	16.871(3)
β (deg)		101.45(4)	102.675(8)
V (Å^3)	1368.8(4)	1342(1)	1756.3(2)
Z	3	4	4
T (K)	238(2)	296(2)	298(2)
$\lambda_{\text{Mo K}\alpha}$ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	2.167	2.022	1.754
μ (cm^{-1})	60.08	68.24	52.15
R^a (%)	3.78	4.12	4.44
$R_w{}^a$ (%)	8.85	5.02	8.77

[a] $R = (\sum|\Delta F|)/\sum|F_o|$; $R_w = [(\sum w|\Delta F|^2)/\sum wF_o{}^2]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **2**

Ti−Se	2.796(2)	Ti−Cl(4A)	2.471(4)
Ti−Cl(1)	2.200(5)	Se−Se(A)	2.344(2)
Ti−Cl(2)	2.195(3)	Se−C(1)	1.973(8)
Ti−Cl(3)	2.195(3)	C(1)−C(2)	1.524(13)
Ti−Cl(4)	2.459(3)		
Cl(1)−Ti−Cl(2)	98.91(14)	Ti−Cl(4)−Ti(A)	100.35(12)
Cl(1)−Ti−Cl(3)	101.0(2)	Ti−Se−Se(A)	104.38(5)
Cl(1)−Ti−Cl(4)	89.41(13)	Cl(1)−Ti−Se	85.25(11)
Cl(2)−Ti−Cl(3)	101.7(2)	Cl(2)−Ti−Se	88.96(9)
Cl(2)−Ti−Cl(4)	161.77(13)	Cl(3)−Ti−Se	166.57(14)
Cl(3)−Ti−Cl(4)	92.53(13)	Cl(4)−Ti−Se	75.51(7)
Cl(1)−Ti−Cl(4A)	163.91(12)	C(1)−Se−Se(A)	97.4(3)
Cl(2)−Ti−Cl(4A)	88.59(13)	Se−C(1)−C(2)	112.5(7)
Cl(3)−Ti−Cl(4A)	91.3(2)	C(1)−Se−Ti	106.2(3)
Cl(4)−Ti−Cl(4A)	79.65(12)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ti−Cl(1)	2.304(4)	Ti−Cl(4)	2.262(4)
Ti−Cl(2)	2.252(4)	Ti−Se(1)	2.777(4)
Ti−Cl(3)	2.248(4)	Ti−Se(2)	2.743(4)
Cl(1)−Ti−Cl(2)	95.2(1)	Cl(2)−Ti−Se(1)	88.6(1)
Cl(1)−Ti−Cl(3)	96.5(1)	Cl(2)−Ti−Se(2)	166.5(1)
Cl(1)−Ti−Cl(4)	160.3(1)	Cl(3)−Ti−Se(1)	169.2(1)
Cl(2)−Ti−Cl(3)	102.2(1)	Cl(3)−Ti−Se(2)	90.8(1)
Cl(2)−Ti−Cl(4)	96.9(1)	Cl(4)−Ti−Se(1)	83.6(1)
Cl(3)−Ti−Cl(4)	96.1(1)	Cl(4)−Ti−Se(2)	85.3(1)
Cl(1)−Ti−Se(1)	81.2(1)	Se(1)−Ti−Se(2)	78.4(1)
Cl(1)−Ti−Se(2)	79.4(1)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ti−Cl(1)	2.230(3)	Ti−Cl(4)	2.229(3)
Ti−Cl(2)	2.271(3)	Ti−Se(1)	2.740(2)
Ti−Cl(3)	2.272(3)	Ti−Se(2)	2.763(2)
Cl(1)−Ti−Cl(2)	82.68(8)	Cl(2)−Ti−Se(1)	82.68(8)
Cl(1)−Ti−Cl(3)	97.01(12)	Cl(2)−Ti−Se(2)	81.47(8)
Cl(1)−Ti−Cl(4)	100.89(12)	Cl(3)−Ti−Se(1)	81.66(9)
Cl(2)−Ti−Cl(3)	158.47(13)	Cl(3)−Ti−Se(2)	81.38(9)
Cl(2)−Ti−Cl(4)	95.98(12)	Cl(4)−Ti−Se(1)	170.21(10)
Cl(3)−Ti−Cl(4)	96.94(11)	Cl(4)−Ti−Se(2)	89.99(9)
Cl(1)−Ti−Se(1)	88.90(8)	Se(1)−Ti−Se(2)	80.22(5)
Cl(1)−Ti−Se(2)	169.12(10)		

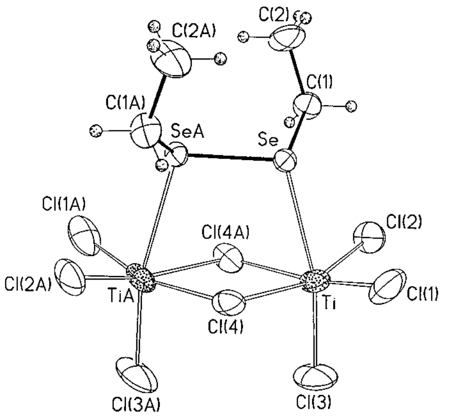


Figure 1. Perspective view of $(TiCl_4)_2(Se_2(CH_2CH_3)_2)$ (**2**) with thermal ellipsoids at the 30% probability level.

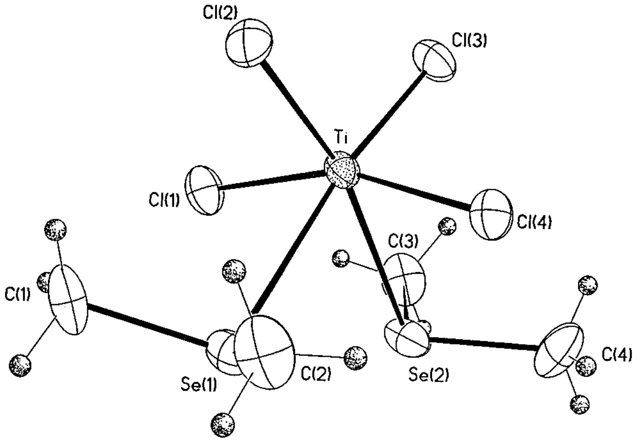


Figure 2. Perspective view of $TiCl_4(Se(CH_3)_2)_2$ (**3**) with thermal ellipsoids at the 30% probability level.

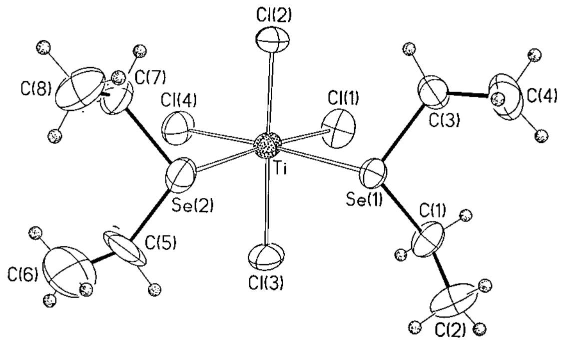


Figure 3. Perspective view of $TiCl_4(Se(CH_2CH_3)_2$ (**4**) with thermal ellipsoids at the 30% probability level.

163.97(12)°. The Cl(4)−Ti−Cl(4A) angle (79.65°) is constrained to be less than 90° by the Ti_2Cl_2 ring. The Se−Se(A) distance is 2.344(2) Å, which is shorter than the titanium−titanium nonbonded distance, as judged by the deviation of angles associated with Se from idealized octahedral values (cis angles 75.51−88.96°; Cl(3)−Ti−Se 166.57°). The sum of the angles about selenium (307.98°) is less than the expected value for pyramidal, trisubstituted selenium with one lone pair (ca. 328.5°).

Complex **3** crystallizes as a monomeric cis-adduct with distorted octahedral geometry about titanium. The chlorine atoms that are trans to selenium atoms (Ti−Cl(2) 2.252(4), Ti−Cl(3) 2.248(4) Å) have bond lengths, within experimental error, similar to those of the mutually trans chlorine atoms (Ti−Cl(1) 2.304(4), Ti−Cl(4) 2.262(4) Å). The titanium−selenium bond lengths (Ti−Se(1) 2.777(4), Ti−Se(2) 2.743(4) Å) are slightly shorter than the related value in **2**. This difference, albeit at the edge of experimental uncertainty, may reflect the inability of the diethyl diselenide ligand in **2** to achieve optimum bonding with the titanium centers due to the fixed selenium−selenium distance. The cis chlorine−titanium−chlorine angles are all larger than 90° and range from 95.2(1) to 102.2(1)°. The trans chlorine−titanium−chlorine angle is 160.3(1)°. The larger cis angles associated with the chlorine−titanium−chlorine angles are reflected in chlorine−titanium−selenium angles that are largely less than 90° (range 79.4(1)-90.8(1)°; average = 84.8°). The trans chlorine−titanium−selenium angles are 166.5(1)° (Cl(2)−Ti−Se(2)) and 169.2(1)° (Cl(3)−Ti−Se(1)). The selenium−titanium−selenium angle is 78.4(1)°. The deviations from ideal octahedral geometry can be rationalized by the presence of two very long titanium−selenium bonds, which allows the angles associated with the chlorines to increase slightly to relieve lone pair−lone pair repulsions. The sums of the angles about Se(1) (306.4°) and Se(2) (308.5°) are similar to the related value in **2** and are less than the expected value for pyramidal, trisubstituted selenium with one lone pair (ca. 328.5°).

Complex **4** crystallizes as a monomeric cis-adduct with distorted octahedral geometry about titanium. Bonds involving the chlorine atoms that are trans to selenium atoms (Ti−Cl(1) 2.230(3), Ti−Cl(4) 2.229(3) Å) are slightly shorter than bonds involving the mutually trans chlorine atoms (Ti−Cl(2) 2.271(3), Ti−Cl(3) 2.272(3) Å), although the differences are at the edge of experimental uncertainty. The titanium−selenium bond lengths (Ti−Se(1) 2.740(2), Ti−Se(2) 2.763(2) Å) are slightly shorter than the related value in **2** and are similar to those in **3**. The cis chlorine−titanium−chlorine angles are all larger than 90° and range from 95.98(12) to 100.89(12)°. The trans chlorine−titanium−chlorine angle is 158.47(13)°. The larger cis angles associated with the chlorine−titanium−chlorine angles are reflected in chlorine−titanium−selenium angles that are less than 90° (range 81.38(9)-89.99(9)°; average = 84.35°). The trans chlorine−titanium−selenium angles are 169.12(10)° (Cl(1)−Ti−Se(2)) and 170.21(10)° (Cl(4)−Ti−Se(1)). The selenium−titanium−selenium angle is 80.22(5)°. The sums of the angles about Se(1) (309.1°) and Se(2) (308.8°) are similar to the related values in **2** and **3** and are less than the expected value for pyramidal, trisubstituted selenium with one lone pair (ca. 328.5°). The structural features of **4** are nearly identical to those of **3**.

There are very few crystallographically characterized complexes that contain titanium−selenium bonds.[12] The majority have contained titanium−selenium σ-bonds, with bond lengths that range between 2.383 and 2.729 Å. The titanium−selenium coordinate covalent bonds in **2**−**4** are longer, consistent with the difference in bonding. The complex $Cp_2Ti(Se_2PPh_2)$, which formally contains one titanium−selenium σ-bond and one coordinate covalent bond, has titanium−selenium bond lengths (2.754(3), 2.764(3) Å) which are similar to the analogous values in **2**−**4**.[12a] The selenium−selenium bond length in **2** (2.344(2) Å) is slightly longer than analogous bonds in diorgano diselenides (Se−Se 2.285−2.328 Å).[13] Formation of a dinuclear structure with **2** appears to be the lowest energy formulation (or perhaps the most crystalline) available to the system. A mononuclear structure with an η^2-diethyl diselenide ligand is

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(13) For selected X-ray crystal structures of diorgano diselenides, see: Palmer, H. T.; Palmer, R. A. *Acta Crystallogr.* **1969**, *B25*, 1090. Marsh, R. E. *Acta Crystallogr.* **1952**, *5*, 458. Back, T. G.; Codding, P. W. *Can. J. Chem.* **1983**, *61*, 2749. Morris, G. D.; Einstein, F. W. B. *Acta Crystallogr.* **1986**, *C42*, 1433.

apparently not sterically accessible, due to either steric interactions between titanium−chlorine bonds and the diethyl diselenide ligand or poor overlap between titanium orbitals and the lone pairs of the diethyl diselenide ligand. We previously reported that titanium tetrachloride reacts with methyl disulfide to afford the complex $(TiCl_4)_2(CH_3SSCH_3)$, which has a structure similar to that of **2**.[14] The formation of the bis(dialkyl selenide) complexes **3** and **4** is similar to that of complexes that form upon treatment of titanium tetrachloride with alkanethiols[7] and dialkyl sulfides.[14]

Deposition of Titanium Diselenide Films from 4. A major goal of this work was to develop single-source precursors to $TiSe_2$ films. Dialkyl diselenides were not chosen as selenium partners, since **1** decomposed to a range of products. Attention was therefore focused on the dialkyl selenide adducts **3** and **4**. Initial evaluation of **3** as a single-source precursor did produce $TiSe_2$ films, but the depositions were not reproducible and the film morphology was generally poor. Films deposited using **4** were of much higher quality, and the film fabrication and analysis are described in this section.

Depositions were conducted at 500 and 600 °C using **4** as a single-source precursor in an apparatus that was previously described.[15] Compound **4** sublimes at about the same temperature and pressure as $TiCl_4(HSC_6H_{11})_2$, which has a vapor pressure of ca. 2 Torr at 23 °C.[7] Samples of **4** that were used for film depositions showed no resonances ($\leq 0.5\%$) in the ^1H NMR spectrum beyond those expected for a diethyl selenide ligand. Films were deposited on Corning 7059 glass, which was prepared by wiping with a Kimwipe until visually clean. To conduct the deposition, **4** (ca. 1 g) was sublimed at ca. 0.01 mmHg into the deposition furnace. Compound **4** was volatilized by pulling the deposition tube so that the end of the tube was just at the edge of the furnace. In this fashion, **4** sublimed quantitatively over the substrate in about 15 min. Since a hot-walled reactor was employed, both the tube and substrate were coated with titanium diselenide. Films deposited at 500 and 600 °C were rose-bronze colored with matte finishes.

The films prepared at 500 and 600 °C were analyzed by X-ray powder diffraction immediately after deposition. The 600 °C film displayed reflections that matched the reference spectrum for $TiSe_2$ (JCPDS File No. 30-1383) almost exactly, indicating a random orientation of crystallites.[16] By contrast, the 500 °C film showed preferential growth along the (002) direction.[11b,16] A scanning electron micrograph of a film deposited at 500 °C showed flat plates with diameters of ca. 5−8 μm and thicknesses of about 1 μm. The plates were oriented with the plane of the plates being approximately perpendicular to the plane of the substrate. The 600 °C film revealed more irregular-shaped plates of sizes similar to those observed in the 500 °C film. The plates were randomly oriented, accounting for the X-ray diffraction spectrum obtained on this film.

Upon exposure of the deposited films to ambient atmosphere, their metallic sheen gradually disappeared. After 30 days, the films had become translucent with a very pale orange coloration. The X-ray powder diffraction spectra of these films showed no reflections, indicating that the films were amorphous. A scanning electron micrograph of a film after 47 days of exposure to the laboratory atmosphere showed fibers and fibrous plates with lengths of 5−10 μm and thicknesses of about 0.5 μm. An X-ray photoelectron spectrum of a film deposited at 600 °C analyzed after 7 days of exposure to laboratory ambient conditions revealed the presence of titanium (Ti $2p_{3/2} = 458.85$ eV), selenium (Se 3d = 55.22 eV), and oxygen (O 1s = 531.2 eV), relative to residual carbon present in the vacuum chamber (C 1s = 284.6 eV; from pump oil). The surface Ti $2p_{3/2}$ binding energy is similar to the value reported for titanium dioxide (Ti $2p_{3/2} = 458.5$ eV).[17] The data suggest a surface that is partially oxidized. Therefore, it appears that our $TiSe_2$ films are not stable to ambient moisture and slowly degrade to give amorphous Ti−O−Se materials.

Discussion

The goal of this project was to identify stable, volatile complexes containing titanium and selenium that might serve as CVD precursors to $TiSe_2$ films. On the basis of upon our earlier experiences with precursors to TiS_2 films,[7,8,14] adducts derived from reaction of titanium tetrachloride and alkyl diselenides or dialkyl selenides might be stable and volatile enough to serve as source compounds. The initial focus was on adducts of alkyl diselenides, since dimethyl diselenide and diethyl diselenide are commercially available, relatively inexpensive, and much less volatile than the analogous dialkyl selenides (i.e., less odiferous). Treatment of titanium tetrachloride with dimethyl diselenide and diethyl diselenide led to the adducts **1** and **2**, which adopt a dinuclear structure with a Ti_2Cl_8 core with the alkyl diselenide bonded to one coordination site per titanium. Complex **2** is thermally stable in solution and the solid state at 23 °C and sublimes at ca. 70 °C (0.01 mmHg) without visible decomposition. By contrast, **1** is not thermally stable and decomposes in the solid state, in solution, and upon attempted sublimation. The decomposition of **1** was investigated in detail, since it is highly relevant to the use of **1** and **2** as source compounds. In hexane solution at ambient temperature, **1** decomposed over 48 h to afford the dimethyl selenide adduct **3** in 40% yield. In the NMR tube reaction in chloroform-*d*, treatment of titanium tetrachloride with dimethyl diselenide initially forms a new species that does not correspond to any of the complexes isolated in this study. This new species slowly decomposes to **3**. While the identity of this complex remains unknown, a reasonable formulation would be the 1:1 adduct $TiCl_4(Se_2(CH_3)_2)$. $TiCl_4(Se_2(CH_3)_2)$ must be less stable or less crystalline than **1**, since only **1** could be isolated. Upon sublimation at 250 °C, **1** decomposed to **3** (65%) and gray selenium (65%). The latter decomposition pathway is strikingly similar to the thermal decomposition of free dialkyl diselenides. Dialkyl diselenides decompose to the dialkyl selenides and elemental selenium upon thermolysis at 140−550 °C, depending upon the radical stabilizing ability of the alkyl group.[18] The decomposition of **1** upon sublimation is consistent with the stoichiometry outlined in eq 2. Titanium tetrachloride was not specifically identified in the decomposition of **1**, but a colorless liquid with no resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra was collected from the end of the tube when the sublimation was conducted at 48 °C. In the decomposition of **1**, titanium tetrachloride acts as a trap for methyl selenide to form **3**. The fact that **1** decomposes at 23 °C in hexane whereas hexane solutions of dimethyl diselenide are totally stable under these

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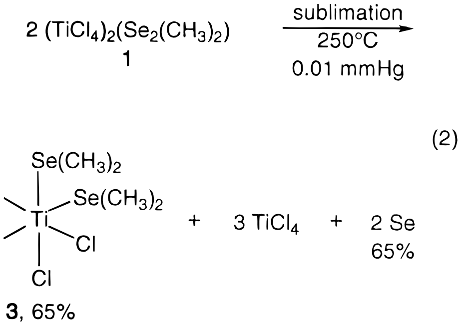
(14) Lewkebandara, T. S.; McKarns, P. J.; Haggerty, B. S.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Polyhedron* **1998**, *17*, 1.

(15) Winter, C. H.; Lewkebandara, T. S.; Sheridan, P. H.; Proscia, J. W. *Mater. Res. Soc. Symp. Proc.* **1993**, *282*, 293.

(16) *Inorganic Phases*; JCPDS-International Centre for Diffraction Data: Swarthmore, PA, 1988.

(17) *Handbook of X-Ray Photoelectron Spectroscopy*; Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., Murlenberg, G. E., Eds.; Perkin-Elmer Corp., Physical Electronics Division: Eden Prairie, MN, 1979; p 68.

(18) For selected leading references, see: (a) Chu, J. Y. C.; Lewicki, J. W. *J. Org. Chem.* **1977**, *42*, 2491. (b) Hirabayashi, T.; Mohmand, S.; Bock, H. *Chem. Ber.* **1982**, *115*, 2491.



(2)

conditions implies that titanium tetrachloride plays an intimate role in the decomposition under these conditions.

The use of **3** and **4** as single-source precursors for the fabrication of $TiSe_2$ films was investigated. It was very difficult to obtain good-quality $TiSe_2$ films from **3**, so effort was concentrated on the use of **4**. As described above, **4** functions as a good precursor to rose-bronze colored $TiSe_2$ films. The identity of the films was established by X-ray powder diffraction and was further probed by scanning electron microscopy. The $TiSe_2$ films were moisture sensitive and slowly decomposed over ca. 30 days at 23 °C. Such instability is surprising because TiS_2 films that we have prepared are stable for ≥ 5 years under similar conditions.[7,8] Moreover, previous reports of $TiSe_2$ films have not indicated any sensitivity toward water.[11] We propose that $TiSe_2$ is intrinsically unstable toward hydrolysis to afford TiO_2 and H_2Se. Scanning electron micrographs of films prepared from **4** revealed porous assemblies of 5−10 μm diameter plates. The porous nature of our films may facilitate hydrolysis by allowing water to diffuse rapidly into the coating. The hydrolyzed films were amorphous by X-ray diffraction, and the presence of oxygen in the film was demonstrated by X-ray photoelectron spectroscopy. Scanning electron micrographs of the oxidized films showed interpenetrating fibers and fibrous plates. The film remained porous, so hydrolysis of the surface did not "seal" the interior of the film from atmospheric intrusion.

We did not pursue the study of $TiSe_2$ films further, due to their hydrolytic instability. Presumably, oxidation of the film liberates highly toxic H_2Se. Interestingly, the films gave off a very slight bad odor until they became translucent (requiring ca. 30 days), which is consistent with hydrolysis. If $TiSe_2$ is desired in thin-film form, **4** is a good precursor but the films would have to be protected from exposure to air (e.g., overcoat with protective layer, and handle only in a drybox). We note that $TiSe_2$ films would probably be useless as lubricating coatings, at least as produced from **4**.

The observation that **4** is a much better precursor than **3** is important. We propose that this difference is due to the ability of diethyl selenide to lose ethylene to form ethaneselenol, hydrogen selenide, or some other selenium compound that is more reactive than diethyl selenide. An analogous decomposition of dimethyl selenide would require the elimination of methylene, which is a high-energy species. It is likely that **3** and **4** vaporize by reversion to titanium tetrachloride and 2 equiv of the dialkyl selenide, since they sublime at such low temperatures without decomposition. Thus, **4** may not be a "true" single-source precursor in the sense that the titanium−selenium bond does not remain intact in the vapor phase. Rather, **4** contains the elements necessary to form $TiSe_2$ in a volatile and easily prepared form. The use of **4** therefore minimizes selenium waste, which is important considering the bad smell and toxicity of volatile selenium compounds. It is very likely that a two-component CVD process, analogous to what we have previously used to prepare TiS_2 films,[8] would afford $TiSe_2$ films. However, we specifically excluded this approach from consideration in favor of the methodology described herein, to avoid using large amounts of organoselenium compounds and concomitant generation of selenium waste.

Experimental Section

General Considerations. All manipulations were performed under argon using either drybox or Schlenk line techniques. Hexane was distilled over sodium. Chloroform-*d* was dried over 4-Å molecular sieves. Titanium tetrachloride, dimethyl selenide, dimethyl diselenide, diethyl selenide, and diethyl diselenide were purchased (Aldrich Chemical Co. or Strem Chemicals, Inc.) and used as received.

^1H, $^{13}C\{^1H\}$, and ^{77}Se NMR spectra were obtained at 300, 75, and 57 MHz, respectively, in chloroform-*d*. Infrared spectra were recorded using Nujol mulls. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points are uncorrected. X-ray diffraction spectra were run on a Rigaku Rotaflex diffractometer equipped with a rotating-anode source. Electron microscopy was conducted on a Hitachi Model S-2400 scanning electron microscope. X-ray photoelectron spectroscopy was performed on a Surface Science Model SSX-100 spectrometer using Al Kα radiation. Samples were calibrated against the C 1s binding energy (284.6 eV) of residual pump oil in the analysis chamber.

Preparation of $(TiCl_4)_2(Se_2(CH_3)_2)$ (1). A 150-mL Schlenk flask was charged with dimethyl diselenide (0.18 g, 0.95 mmol), hexane (25 mL), and a stir bar and was fitted with a rubber septum. This solution was cooled to 0 °C, and titanium tetrachloride (0.2 mL, 1.9 mmol) was added via syringe to form a turbid orange-red solution. The mixture was stirred for 0.25 h at 0 °C and then cooled to −20 °C. After 18 h, the solvent was decanted to afford **1** as red crystals (0.42 g, 78% based on titanium tetrachloride): mp 67−70 °C dec; IR (Nujol, cm^{-1}) 3022 (w), 1455 (s), 1408 (s), 1401 (s), 1311 (w, br), 1273 (m), 1268 (s), 975 (w, br), 921 (vs), 901 (s), 723 (m, br); ^1H NMR ($CDCl_3$, 21 °C, δ) 2.62 (s, $J_{H-Se} = 11.4$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 10.95 (s); ^{77}Se NMR ($CDCl_3$, 21 °C, ppm) 293.9 (s).

Anal. Calcd for $C_2H_6Cl_8Se_2Ti_2$: C, 4.23; H, 1.07; Cl, 49.99. Found: C, 4.30; H, 1.17; Cl, 50.08.

Preparation of $(TiCl_4)_2(Se_2(CH_3CH_2)_2)$ (2). In a fashion similar to the preparation of **1**, titanium tetrachloride (0.21 mL, 1.91 mmol) and diethyl diselenide (0.206 g, 0.954 mmol) were reacted to afford **2** as orange crystalline plates (0.356 g, 63% based on titanium tetrachloride): mp 67−70 °C dec; IR (Nujol, cm^{-1}) 1446 (s), 1414 (m), 1310 (w, br), 1263 (w), 1228 (s), 1220 (vs), 1045 (m, br), 1006 (m), 959 (s), 749 (s), 726 (m, br); ^1H NMR ($CDCl_3$, 21 °C, δ) 3.07 (q, $J = 7.5$ Hz, $SeC\boldsymbol{H}_2CH_3$), 1.52 (t, $J = 7.5$ Hz, $SeCH_2C\boldsymbol{H}_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 25.73 (s, $Se\boldsymbol{C}H_2CH_3$), 16.28 (s, $SeCH_2\boldsymbol{C}H_3$).

Anal. Calcd for $C_4H_{10}Cl_8Se_2Ti_2$: C, 8.07; H, 1.69; Cl, 47.63. Found: C, 8.14; H, 1.80; Cl, 47.87.

Preparation of $TiCl_4(Se(CH_3)_2)_2$ (3) by Decomposition. A 150-mL Schlenk flask was charged with dimethyl diselenide (0.204 g, 1.09 mmol), hexane (35 mL), and a stir bar and was fitted with a rubber septum. Titanium tetrachloride (0.120 mL, 1.09 mmol) was added via syringe to form a turbid orange-red solution. After 48 h, the red solution was decanted from a brown insoluble powder (0.025 g), and the solution was filtered through a 2-cm pad of Celite. The filtrate was then cooled to −20 °C. After 72 h, the solvent was decanted to afford **3** as dark red crystals (0.089 g, 40% based on dimethyl diselenide). The melting point and ^1H and $^{13}C\{^1H\}$ NMR spectra were identical to those of **3** prepared independently.

NMR Tube Experiment. A 5-mm NMR tube was charged with dimethyl diselenide (0.010 mL, 0.106 mmol) and chloroform-*d* (0.8 mL) and was fitted with a rubber septum. Titanium tetrachloride (0.012 mL, 0.109 mmol) was added to afford a dark red solution. NMR spectra were taken immediately: ^1H NMR ($CDCl_3$, 21 °C, δ) 2.70 (s, $J_{H-Se} = 11.5$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 12.79 (s). Subsequent spectra were recorded over a period of 10 days: ^1H NMR ($CDCl_3$, 21 °C, δ, 10 d) 2.70 (s, $J_{H-Se} = 11.5$ Hz, integration = 36 mm), 2.50 (s, $J_{H-Se} = 11.4$ Hz, $TiCl_4((C\boldsymbol{H}_3)_2Se)_2$, integration = 29 mm); $^{13}C\{^1H\}$

NMR ($CDCl_3$, 21 °C, ppm, 10 d) 18.27 (s, $TiCl_4((\boldsymbol{C}H_3)_2Se)_2$), 12.76 (s, $J_{C-Se} = 42.7$ Hz).

Sublimation of $(TiCl_4)_2(Se_2(CH_3)_2)$ (1). A 1-dram vial was charged with **1** (1.05 g, 1.86 mmol), and a plug of glass wool was fitted over the end of the vial. The vial was inserted into a 2 cm × 35 cm glass tube, which was equipped with a vacuum adapter. The tube was evacuated to ca. 0.01 mmHg and was placed in a horizontal sublimation oven held at 250 °C with about 12 cm of the tube protruding from the furnace. After 18 h, red crystals of **3** were observed in the cool part of the tube furthest from the furnace (0.248 g, 65%). Silver-colored gray selenium sublimed to the cool part of the tube nearest the furnace (0.095 g, 65%). Red crystals: mp 95−96 °C dec; ^1H NMR ($CDCl_3$, 21 °C, δ) 2.48 (s, $J_{H-Se} = 8.1$ Hz, $TiCl_4((C\boldsymbol{H}_3)_2Se)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 17.68 (s, $TiCl_4((\boldsymbol{C}H_3)_2Se)_2$). Silver solid: mp 218−219 °C; the X-ray powder diffraction spectrum was identical to the reference spectrum for gray selenium (JCPDS No. 6-362).[16]

Independent Preparation of $TiCl_4(Se(CH_3)_2)_2$ (3). A 150-mL Schlenk flask was charged with titanium tetrachloride (5.00 mL, 45.8 mmol), hexane (50 mL), and a stir bar and was fitted with a rubber septum. This solution was cooled to 0 °C, and dimethyl selenide (10.0 g, 91.5 mmol) was added by syringe. A brick red color formed, and the solution was stirred for 1.5 h. The volatile components were pumped off to afford **3** as a brick red solid (17.90 g, 96% based on titanium tetrachloride). Deep red crystals were obtained by sublimation of the crude powder at 40 °C/0.01 mmHg: mp 95−96 °C (dec with sublimation); IR (Nujol, cm^{-1}) 3023 (w), 3010 (w), 1412 (s), 1360 (m), 1280 (m), 1261 (m), 1162 (w), 1091 (w), 1015 (w), 963 (m), 921 (s), 911 (s), 878 (w), 793 (w), 718 (w); ^1H NMR ($CDCl_3$, 21 °C, δ) 2.48 (s, $J_{H-Se} = 8.1$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 17.68 (s); ^{77}Se NMR ($CDCl_3$, 21 °C, ppm) 174.8 (s).

Anal. Calcd for $C_4H_{12}Cl_4Se_2Ti$: C, 11.78; H, 2.97. Found: C, 11.42; H, 2.93.

Preparation of $TiCl_4(Se(CH_2CH_3)_2)_2$ (4). In a fashion similar to the preparation of **3**, titanium tetrachloride (0.085 mL, 0.775 mmol) and diethyl selenide (0.209 g, 1.53 mmol) were reacted to afford **4** as a brick red solid (0.346 g, 96% based on titanium tetrachloride): mp 41−44 °C; IR (Nujol, cm^{-1}) 3019 (w), 1464 (vs), 1408 (s), 1401 (s), 1274 (m), 1268 (m), 921 (s), 902 (m), 723 (m, br); ^1H NMR ($CDCl_3$, 21 °C, δ) 3.10 (q, $J = 7.5$ Hz, $SeC\boldsymbol{H}_2CH_3$), 1.54 (t, $J = 7.5$ Hz, $SeCH_2C\boldsymbol{H}_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 28.53 (s, $Se\boldsymbol{C}H_2CH_3$), 14.70 (s, $SeCH_2\boldsymbol{C}H_3$).

Anal. Calcd for $C_8H_{20}Cl_4Se_2Ti$: C, 20.71; H, 4.35; Cl, 30.57. Found: C, 20.60; H, 4.38; Cl, 30.68.

Crystal Structure Determinations of 2−4. Parameters associated with the data collections and refinements are given in Table 1. Crystals were obtained by sublimation at 30−40 °C/0.01 mmHg (**3**, **4**) or crystallization from hexane at −20 °C (**2**). Suitable crystals were selected and mounted in thin-walled, nitrogen-flushed glass capillaries. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \le 2\theta \le 25°$).

Preliminary photographic data indicated a hexagonal crystal system with $\bar{3}m$ Laue symmetry for **2** and monoclinic crystal systems for **3** and **4**. The systematic absences in the diffraction data are consistent with $P3_121$ or $P3_221$ for **1** and uniquely consistent with $P2_1/n$ for **3** and **4**. Solution of **2** in $P3_121$ resulted in computationally stable and chemically reasonable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were not applied because there was less than 10% variation in the integrated ψ-scan intensities. The Flack parameter for **2** refined to 0.02(3), indicating that the correct absolute hand of the structure was determined. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library.[19]

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9510712) for support of this research.

Supporting Information Available: Scanning electron micrographs and the X-ray powder diffraction spectrum of the deposited film (3 pages). X-ray crystallographic files, in CIF format, for complexes **2**−**4** are available on the Internet only. Ordering and access information is given on any current masthead page.

IC970945Q

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(19) Sheldrick, G. *SHELXTL*, Version 5.3; Siemens XRD: Madison, WI.