Synthesis, Structure, and Chemical Vapor Deposition Studies of Molecular Precursors to NbP Films

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Treatment of niobium pentachloride with cyclohexylphosphine and phenylphosphine in dichloromethane afforded octachlorotetrakis(cyclohexylphosphine)diniobium(IV) (85%) and octachlorotetrakis(phenylphosphine)diniobium(IV) (88%), respectively, as brown-red and dark red crystalline solids. In addition, the phosphonium compound $[P(C_6H_{11})H_3]_2[NbCl_6]$ was isolated in 68% yield from the same preparation of octachlorotetrakis(cyclohexylphosphine)diniobium(IV). Studies are described which demonstrate that the primary phosphine serves as the hydrogen atom source for the formation of the phosphonium salts. Octachlorotetrakis(cyclohexylphosphine)diniobium(IV) can be prepared in 77% yield by addition of cyclohexylphosphine to $NbCl_4(THF)_2$ in toluene. The X-ray crystal structure determinations for two dimeric niobium(IV) complexes are described. Octachlorotetrakis(cyclohexylphosphine)diniobium(IV) crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.904(2)$ Å, $b = 10.243(2)$ Å, $c = 10.642(1)$ Å, $\alpha = 76.33(2)°$, $\beta = 67.231(8)°$, $\gamma = 73.76(2)°$, $V = 945.7(3)$ Å^3, and $Z = 1$. Octachlorotetrakis(phenylphosphine)diniobium(IV) crystallizes in the orthorhombic space group *Pbca* with $a = 8.873(2)$ Å, $b = 17.394(6)$ Å, $c = 21.778(3)$ Å, $V = 3361.1(9)$ Å^3, and $Z = 4$. Octachlorotetrakis(cyclohexylphosphine)diniobium(IV) and octachlorotetrakis(phenylphosphine)diniobium(IV) were evaluated as molecular precursors to niobium(III) phosphide (NbP) films in a chemical vapor deposition reactor. Octachlorotetrakis(phenylphosphine)diniobium(IV) was not volatile and was therefore not a useful precursor. However, octachlorotetrakis(cyclohexylphosphine)diniobium(IV) afforded specular, silver-colored films of NbP with substrate temperatures between 400 and 600 °C. The analysis of the films is presented.

Introduction

The fabrication of niobium(III) phosphide (NbP) films has received little attention, despite the useful properties of this material.[2−12] It is a metallic conductor, is as hard as high-carbon steel, and is resistant to attack by oxygen, sulfur dioxide, and hydrogen sulfide at temperatures as high as 600 °C.[2−13] The excellent chemical resistance of NbP has led to its application as a matrix electrolyte in phosphoric acid fuel cells.[11] An isostructural phosphide, tantalum(III) phosphide (TaP), has been used as a diffusion barrier layer in semiconductor devices.[12]

Bulk NbP can be prepared from the elements at high temperature,[2−5] by the reaction of niobium pentachloride with calcium phosphide[7] or sodium phosphide,[8] or through treatment of niobium(V) oxide with aluminum metal in the presence of red phosphorus.[9] Whiskers and pillars of crystalline NbP have been grown on quartz substrates coated with gold, platinum, palladium, or nickel layers.[13] These crystals were produced by chemical vapor deposition (CVD) using a three-precursor system consisting of niobium pentachloride, phosphorus trichloride, and hydrogen. The same precursors were later reported to yield thin films of NbP at a substrate temperature of 1050 °C.[10]

We previously reported that adducts of early transition metal halides with primary amines serve as single-source precursors for the fabrication of metal nitride phases using CVD techniques.[14−19] Additionally, we reported that a primary phosphine adduct of titanium tetrachloride affords TiP films when used as a single-source precursor in a CVD process.[20,21] In attempting to extend our studies to the phosphides of niobium,

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[1] (a) Wayne State University. (b) University of Delaware.
[2] Xu, J.; Greenblatt, M.; Emge, T.; Höhn, P.; Hughbanks, T.; Tian, Y. *Inorg. Chem.* **1996**, *35*, 845.
[3] Willerstrom, J.-O. *J. Less-Common Met.* **1984**, *99*, 273.
[4] Furuseth, S.; Kjekshus, A. *Acta Crystallogr.* **1964**, *17*, 1077.
[5] Boller, H.; Parthe, H. *Acta Crystallogr.* **1963**, *16*, 1095.
[6] Schönberg, N. *Acta Chem. Scand.* **1954**, *8*, 226.
[7] Ripley, R. L. *J. Less-Common Met.* **1962**, *4*, 496.
[8] Fitzmaurice, J. C.; Hector, A.; Parkin, I. P.; Keynes, M. *J. Mater. Sci. Lett.* **1994**, *13*, 1.
[9] Martin, J.; Gruehn, R. *Solid State Ionics* **1990**, *43*, 19.
[10] Motojima, S.; Wakamatsu, T.; Sugiyama, K. *J. Less-Common Met.* **1981,** *82*, 379.
[11] Takahashi, K.; Shimamoto, K.; Shunichi, M.; Watai, H.; Nakajo, H.; Ido, T. Japan Kokai Tokkyo Koho JP 63 29 457, 1986; *Chem. Abstr.* **1988**, *109*, 76602n.
[12] Komaki, K. Japan Kokai Tokkyo Koho JP 02 150 067, 1990; *Chem. Abstr.* **1990**, *113*, 182994j.
[13] Motojima, S.; Izushi, T.; Sugiyama, K.; Takahashi, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2122.
[14] Winter, C. H.; McKarns, P. J.; Scheper, J. T. *Mater. Res. Soc. Symp. Proc.* **1998**, *495*, 95.
[15] Jayaratne, K. C.; Yap, G. P. A.; Haggerty, B. S.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1996**, *35*, 4910.
[16] Lewkebandara, T. S.; Sheridan, P. H.; Heeg, M. J.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1994**, *33*, 5879.
[17] Winter, C. H.; Lewkebandara, T. S.; Proscia, J. W.; Rheingold, A. L. *Inorg. Chem.* **1994**, *33*, 1227.
[18] Winter, C. H.; Jayaratne, K. C.; Proscia, J. W. *Mater. Res. Soc. Symp. Proc.* **1994**, *327*, 103.
[19] Winter, C. H.; Viejo, V. C.; Proscia, J. W. *Mater. Res. Soc. Symp. Proc.* **1994**, *327*, 109.
[20] Lewkebandara, T. S.; Proscia, J. W.; Winter, C. H. *Chem. Mater.* **1995**, *7*, 1053.
[21] Lewkebandara, T. S.; Winter, C. H. *Adv. Mater. CVD* **1996**, *2*, 75.

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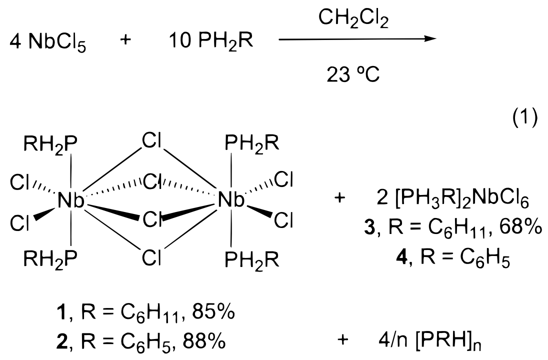
we envisioned that adducts of niobium(V) halides with phosphine ligands might be sufficiently volatile to serve as molecular precursors to thin films under CVD conditions. The coordination chemistry of niobium halides with tertiary phosphines has been extensively studied;[22−28] however, it is likely that the use of tertiary phosphines would lead to high levels of carbon in the resulting films.[29] Herein, we report a study of the reaction of niobium pentachloride with primary phosphines and subsequent evaluation of the resultant complexes as precursors for niobium phosphide phases. Treatment of niobium pentachloride with cyclohexylphosphine or phenylphosphine affords niobium(IV) adducts of the formula $Nb_2Cl_8(H_2PR)_4$, along with other products resulting from phosphine oxidation. The crystal structures of $Nb_2Cl_8(H_2PC_6H_{11})_4$ and $Nb_2Cl_8(H_2PC_6H_5)_4$ are reported. The cyclohexylphosphine adduct $Nb_2Cl_8(H_2PC_6H_{11})_4$ functions as a precursor to NbP films. This is the first report of a molecular precursor for NbP films and is the first low-temperature deposition of NbP by CVD techniques.

Results

Reaction of Niobium Pentachloride with Primary Phosphines. Treatment of niobium pentachloride with excess cyclohexylphosphine or phenylphosphine in dichloromethane resulted in the formation of a brown-red or dark red solution with concomitant production of a purple precipitate. Workup as described in the Experimental Section afforded octachlorotetrakis(cyclohexylphosphine)diniobium(IV) (**1**, 85%) and octachlorotetrakis(phenylphosphine)diniobium(IV) (**2**, 88%), respectively, as brown-red and dark red crystalline solids (eq 1). Complex **1** was fully characterized by spectroscopic and analytical techniques. X-ray crystal structures of **1** and **2** were determined as described below and showed them to possess dimeric, chloride-bridged structures. NMR spectra of **2** could not be obtained, since the complex was completely insoluble in unreactive solvents after filtration and removal of the dichloromethane solvent.



(1)

During the preparation of **1** and **2**, purple precipitates formed. Since the formation of **1** and **2** involves one-electron reduction of niobium(V) to niobium(IV), it was likely that these precipitates contained phosphonium ions resulting from the oxidation of the respective phosphines. The precipitates were air sensitive and intensely purple, suggesting the presence of niobium(IV) in the compound. A C, H, Cl microanalysis of the precipitate resulting from the formation of **1** was consistent with a formulation of $[C_6H_{11}PH_3]_2[NbCl_6]$ (**3**, 68%). The presence of cyclohexylphosphonium ions in **3** was supported by the infrared spectrum, which showed P−H stretches at 2443 and 2404 cm^{-1}. For comparison, neat cyclohexylphosphine has a P−H stretch at 2285 cm^{-1}. Furthermore, the infrared spectrum of **3** was virtually identical to that of $[C_6H_{11}PH_3]_2[Cl_5TaOTaCl_5]$, which we have characterized by X-ray crystallography and which contains cyclohexylphosphonium ions.[30] The presumed phenylphosphonium salt **4** was not submitted for elemental analysis, since the infrared spectrum showed a mixture of **4** and **2**. The insolubility of **2** and **4** precluded further separation.

A significant question is the origin of the hydrogen atom in **3**. Poli and co-workers have reported a study of the reaction of $CpNbCl_4$ with tertiary phosphines to afford $CpNbCl_3(PR_3)_2$ and phosphonium salts.[31] It was proposed in Poli's study that the hydrogen atom in the phosphonium ion product originated from the toluene solvent. To test for a solvent-derived hydrogen atom in **3**, we repeated the reaction of niobium pentachloride with cyclohexylphosphine (2 equiv) in dichloromethane-d_2. Workup afforded **1** (28%) and **3** (40%). Inspection of the infrared spectra of both **1** and **3** did not show any new stretches that could be assigned to phosphorus−deuterium bonds (expected ν_{P-D} ca. 1700 cm^{-1}). Accordingly, the hydrogen atoms in **3** are not derived from dichloromethane solvent. The fact that the yields of **1** and **3** were substantially lower with a 1:2 molar ratio of niobium pentachloride to cyclohexylphosphine than with excess cyclohexylphosphine supported the idea that the hydrogen atom in **3** originated from cyclohexylphosphine. To test for this possibility, the reaction of niobium pentachloride with cyclohexylphosphine in dichloromethane-d_2 was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at ambient temperature. After filtration to remove insoluble **3**, the $^{31}P\{^1H\}$ NMR spectrum revealed a resonance due to **1** at −2.6 ppm, as well as new broad, roughly equal-intensity resonances at 23.5, −69.0, and −87.8 ppm. The resonance at −87.8 ppm is close to the chemical shifts reported for *meso*- and D,L-$(C_6H_{11})_2P_2H_2$ (−86.3 and −89.7 ppm in THF[32]). The broad resonance at 23.5 ppm is similar to the chemical shifts found for oligophosphanes derived from phenylphospine (ca. 20 ppm), which were obtained by a catalytic coupling reaction of phenylphosphine.[33] We were unable to assign the resonance at −69.0 ppm, but it may correspond to a low oligomer derived from cyclohexylphosphine, since the chemical shifts of low molecular weight oligomers of phenylphosphine were intermediate between those of phenylphosphine and the high oligomers derived therefrom.[33] Hence, the hydrogen atom in **3** appears to originate from the cyclohexylphosphine. Such a hydrogen source is not surprising, in view of the relatively low phosphorus−hydrogen bond strength (76.4 kcal/mol in PH_3[34]). Clearly, more than 2 equiv amounts of primary phosphine are required to achieve maximum yields of **1** and **3**. The stoichiometry in eq 1 is suggested to reflect the hydrogen abstraction step.

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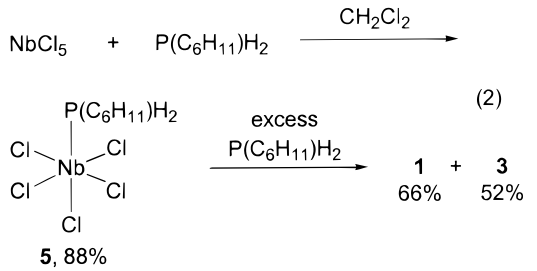
(22) Manzer, L. E. *Inorg. Chem.* **1977**, *16*, 525.
(23) Samuel, E.; Labauze, G.; Livage, J. *Nouv. J. Chim.* **1977**, *1*, 93.
(24) Labauze, G.; Samuel, E.; Livage, J. *Inorg. Chem.* **1980**, *19*, 1384.
(25) Boyd, P. D.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1987**, 307.
(26) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 945.
(27) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592.
(28) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Polyhedron* **1985**, *4*, 1103.
(29) Williams, K. B.; Stewart, O.; Reck, G. P.; Proscia, J. W. *Mater. Res. Soc. Symp. Proc.* **1994**, *327*, 121.
(30) Scheper, J. T.; Liable-Sands, L. M.; Rheingold, A. L.; Heeg, M. J.; Winter, C. H. Manuscript in preparation.
(31) Fettinger, J. C.; Keogh, D. W.; Poli, R. *Inorg. Chem.* **1995**, *34*, 2343.
(32) Albrand, J. P.; Taieb, C. In *Phosphorus Chemistry: Proceedings of the 1981 International Conference*; Quin, L. D., Verkade, J. D., Eds.; ACS Symposium Series 171; American Chemical Society: Washington, DC, 1981; pp 577−580.
(33) Xin, S.; Woo, H. G.; Harrod, J. F.; Samuel, E.; Lebuis, A.-M. *J. Am. Chem. Soc.* **1997**, *119*, 5307.
(34) Toy, A. D. F. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, U.K., 1973; Vol. 2, p 415.

Poli isolated adducts of the formula $CpNbCl_4(PR_3)$ upon treatment of $CpNbCl_4$ with 1 equiv of PR_3 and found that reduction to niobium(IV) occurred only upon addition of excess PR_3.[31] To test for a similar situation in our reactions, niobium pentachloride was treated with 1 equiv of cyclohexylphosphine at −78 °C in dichloromethane. Workup afforded $NbCl_5(P(C_6H_{11})H_2)$ (**5**, 88%) as a light orange solid (eq 2). Complex **5** was characterized by spectroscopic and analytical techniques. While it was not possible to grow crystals of **5** of sufficient quality for X-ray crystallography, we have determined the crystal structure of the analogous tantalum complex and found it to be an octahedral monomer.[30] It is very likely that **5** has a similar structure. While **5** showed no evidence for decomposition to **1** and **3** in dichloromethane at ambient temperature over 24 h, addition of excess cyclohexylphosphine to **5** under the conditions described in eq 1 resulted in the formation of **1** (66%) and **3** (52%). These experiments are consistent with **5** being an intermediate in the formation of **1** and **3**.



The formation of **1** and **2** described above wasted some of the starting reagents through formation of **3** and **4**. We envisioned that it might be possible to prepare **1** and **2** from a niobium(IV) chloride precursor and thereby avoid use of extra phosphine ligands. Accordingly, treatment of $NbCl_4(THF)_2$[22] with cyclohexylphosphine (2 equiv) in toluene at ambient temperature led to displacement of the THF ligands and formation of **1** in 77% yield (eq 3). The spectroscopic properties of **1** so produced were identical to those of **1** prepared as described above.

$$NbCl_4(THF)_2 + 2\ P(C_6H_{11})H_2 \xrightarrow[23\ ^\circ C]{toluene} \mathbf{1},\ 77\% \qquad (3)$$

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

Complexes **1** and **2** crystallize as dimers that are held together by four bridging chloride ions. Additionally, each niobium atom bears two terminal chloride ions and two phosphine ligands, and there are short niobium−niobium distances suggesting metal−metal bonds. The geometry about each niobium atom in **1** and **2** is square antiprismatic, with one face consisting of mutually trans phosphine and chloride ligands and the other face consisting of four bridging chloride ligands. The terminal niobium−chlorine bond lengths in **1** and **2** range between 2.49 and 2.51 Å, while the bridging niobium−chlorine bond lengths range between 2.52 and 2.57 Å. The niobium−phosphorus bond lengths range between 2.61 and 2.63 Å. The niobium−niobium distance in **1** is 2.809(1) Å, and in **2** it is 2.7949(10) Å. Cotton has suggested that the structurally similar dimeric molecule $Nb_2Cl_8(PMe_2Ph)_4$ has a niobium−niobium bond, on the basis of a metal−metal distance of 2.838(1) Å.[27] The similar bond lengths in **1** and **2** imply that they also contain metal−metal bonds. The angles about each niobium center reflect the expected values for square antiprismatic geometry. For example, the cis chlorine−niobium−chlorine angles for **1** range between 71.8 and 106.1°, while cis chlorine−niobium−phosphorus angles encompass 69.6−80.1°. For **1**, the trans chlorine−niobium−chlorine angles are 144.0(1) and 143.3(1)°, while the trans chlorine−niobium−phosphorus angles are 143.3(1) and 143.7(1)°. The phosphorus−niobium−phosphorus angle in **1** is 113.0(1)°. The small values of the niobium−chlorine−niobium angles in **1** associated with the bridging chloride ligands (67.1(1), 67.2(1)°) reflect the distortions required for the formation of the niobium−niobium bond. The related angles in **2** are very similar.

Deposition of NbP Films from 1. The major goal of this work was to develop molecular precursors to NbP films. Attempts to deposit films from **2** were not successful, since it did not sublime. However, **1** sublimes slowly at 140 °C (0.1 mmHg) with partial decomposition (ca. 50% sublimed yields of **1** were obtained in sublimations carried out on a 1.0 g scale).

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_{24}H_{52}Cl_8Nb_2P_4$	$C_{24}H_{28}Cl_8Nb_2P_4$
fw	934.00	909.76
space group	$P\bar{1}$	*Pbca*
a (Å)	9.904(2)	8.873(2)
b (Å)	10.243(2)	17.394(6)
c (Å)	10.642(1)	21.778(3)
α (deg)	76.33(2)	
β (deg)	67.231(8)	
γ (deg)	73.76(2)	
V (Å^3)	945.7(3)	3361.1(9)
Z	1	4
T (K)	226(2)	298(2)
$\lambda_{\mathrm{Mo\ K\alpha}}$ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.640	1.798
μ (cm^{-1})	13.60	15.25
$R(F)^a$ (%)	2.57^a	2.84^b
$R_w(F)^b$ (%)	3.74^a	6.02^{b,c}

[a] Quantity minimized: $\sum\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R_w = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized: $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]\}^{1/2}$. $R = \sum\Delta/\sum\Delta(F_o)$, $\Delta = |(F_o - F_c)|$. [c] $R_w(F^2)$, %.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Nb−Cl(1)	2.486(1)	Nb−Cl(2)	2.511(1)
Nb−Cl(3)	2.545(1)	Nb−Cl(4)	2.541(1)
Nb−Cl(3A)	2.529(1)	Nb−Cl(4A)	2.543(1)
Nb−P(1)	2.613(1)	Nb−P(2)	2.617(1)
Nb−Nb(A)	2.809(1)		
Cl(1)−Nb−Cl(2)	106.1(1)	Cl(1)−Nb−Cl(3)	81.7(1)
Cl(2)−Nb−Cl(3)	144.0(1)	Cl(1)−Nb−Cl(4)	81.8(1)
Cl(2)−Nb−Cl(4)	143.3(1)	Cl(3)−Nb−Cl(4)	71.8(1)
Cl(1)−Nb−P(1)	71.4(1)	Cl(2)−Nb−P(2)	69.6(1)
Cl(3)−Nb−P(2)	143.3(1)	Cl(4)−Nb−P(2)	79.9(1)
P(1)−Nb−P(2)	113.0(1)	Cl(1)−Nb−Nb(A)	126.6(1)
Cl(2)−Nb−Nb(A)	127.3(1)	Cl(3)−Nb−Nb(A)	56.1(1)
Cl(4)−Nb−Nb(A)	56.5(1)	P(1)−Nb−Nb(A)	123.2(1)
P(2)−Nb−Nb(A)	123.8(1)	Cl(1)−Nb−Cl(3A)	143.8(1)
Cl(2)−Nb−Cl(3A)	81.9(1)	Cl(3)−Nb−Cl(3A)	112.8(1)
Cl(4)−Nb−Cl(3A)	72.6(1)	P(1)−Nb−Cl(3A)	141.4(1)
P(2)−Nb−Cl(3A)	79.1(1)	Nb(A)−Nb−Cl(3A)	56.7(1)
Cl(1)−Nb−Cl(4A)	143.2(1)	Cl(2)−Nb−Cl(4A)	82.5(1)
Cl(3)−Nb−Cl(4A)	72.3(1)	Cl(4)−Nb−Cl(4A)	112.9(1)
P(1)−Nb−Cl(4A)	78.4(1)	P(2)−Nb−Cl(4A)	142.2(1)
Nb(A)−Nb−Cl(4A)	56.4(1)	Cl(3A)−Nb−Cl(4A)	72.1(1)
Nb−Cl(3)−Nb(A)	67.2(1)	Nb−Cl(4)−Nb(A)	67.1(1)

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

Nb−Cl(1)	2.4906(13)	Nb−Cl(2)	2.4956(13)
Nb−Cl(3)	2.5723(13)	Nb−Cl(4)	2.5223(13)
Nb−Cl(3)#1	2.5530(13)	Nb−Cl(4)#1	2.5227(13)
Cl(3)−Nb#1	2.5529(13)	Cl(4)−Nb#1	2.5226(13)
Nb−P(1)	2.633(2)	Nb−P(2)	2.634(2)
Nb−Nb#1	2.7949(10)		
Cl(1)−Nb−Cl(2)	104.85(5)	Cl(1)−Nb−Cl(4)#1	143.35(4)
Cl(2)−Nb−Cl(4)#1	82.18(4)	Cl(1)−Nb−Cl(4)	82.56(5)
Cl(2)−Nb−Cl(4)	144.52(4)	Cl(4)#1−Nb−Cl(4)	112.72(3)
Cl(1)−Nb−Cl(3)#1	143.67(4)	Cl(2)−Nb−Cl(3)#1	82.38(4)
Cl(4)#1−Nb−Cl(3)#1	72.32(4)	Cl(4)−Nb−Cl(3)#1	72.84(4)
Cl(1)−Nb−Cl(3)	81.98(4)	Cl(2)−Nb−Cl(3)	142.81(4)
Cl(4)#1−Nb−Cl(3)	72.51(4)	Cl(4)−Nb−Cl(3)	72.00(4)
Cl(3)#1−Nb−Cl(3)	113.91(3)	Cl(1)−Nb−P(1)	69.66(5)
Cl(2)−Nb−P(1)	70.62(4)	Cl(4)#1−Nb−P(1)	79.52(4)
Cl(4)−Nb−P(1)	141.63(4)	Cl(3)#1−Nb−P(1)	143.24(4)
Cl(3)−Nb−P(1)	78.19(4)	Cl(1)−Nb−P(2)	73.31(4)
Cl(2)−Nb−P(2)	69.58(4)	Cl(4)#1−Nb−P(2)	140.07(5)
Cl(4)−Nb−P(2)	79.99(4)	Cl(3)#1−Nb−P(2)	76.34(4)
Cl(3)−Nb−P(2)	144.69(5)	P(1)−Nb−P(2)	114.69(4)
Cl(1)−Nb−Nb#1	127.40(4)	Cl(2)−Nb−Nb#1	127.74(4)
Cl(4)#1−Nb−Nb#1	56.36(3)	Cl(4)−Nb−Nb#1	56.36(3)
Cl(3)#1−Nb−Nb#1	57.29(3)	Cl(3)−Nb−Nb#1	56.62(3)
P(1)−Nb−Nb#1	122.92(4)	P(2)−Nb−Nb#1	122.37(4)
Nb#1−Cl(3)−Nb	66.09(3)	Nb#1−Cl(4)−Nb	67.28(3)

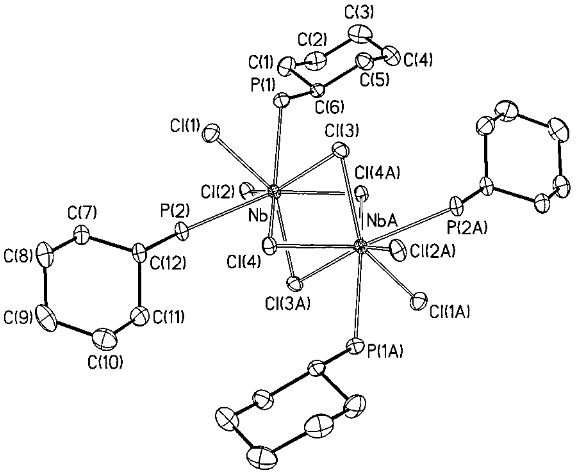


Figure 1. Perspective view of **1** with thermal ellipsoids at the 30% probability level.

Accordingly, **1** was deemed sufficiently volatile to allow film fabrication trials. Depositions were conducted on Corning 7059 glass and crystalline silicon at 400, 500, and 600 °C using **1** as the precursor in a horizontal hot-walled reactor. Details of the reactor configuration have been previously described.[35] The films were specular or matte in appearance and were silver-colored. The precursor did not sublime quantitatively. Some of the precursor decomposed in the precursor vial to give silver-colored granules with a metallic sheen. The powder X-ray diffraction spectrum of these granules was consistent with that of NbP.[36] This experiment indicates that **1** decomposes in the solid state to bulk NbP at about the same temperature at which it sublimes.

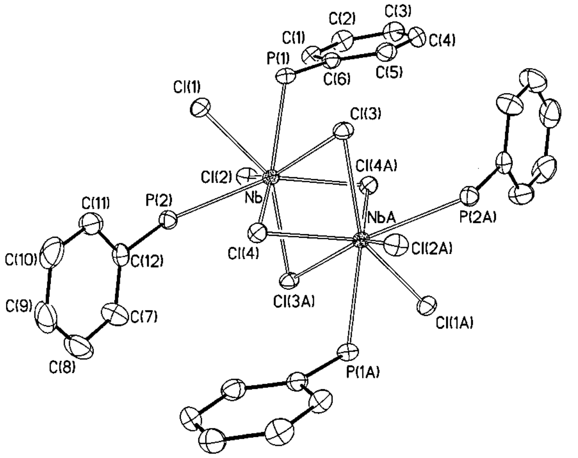


Figure 2. Perspective view of **2** with thermal ellipsoids at the 30% probability level.

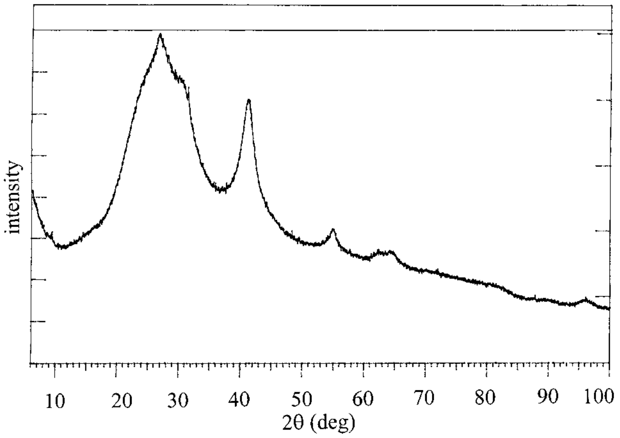


Figure 3. X-ray diffraction spectrum of a film deposited on Corning 7059 glass at 600 °C using **1** as the precursor. The broad reflection centered at $2\theta = 24°$ is from the substrate.

A film deposited at 600 °C was analyzed by X-ray diffraction (Figure 3). The film exhibited preferred orientation along the reflections with $2\theta = 27$, 32, and 41.5°. The *d* spacing for the deposited NbP film was 2.18 Å, which is identical to the value given in the JCPDS reference file.[36] The films deposited at 400 and 500 °C were specular and silver-colored but were too thin to give observable reflections in the X-ray diffraction spectra. X-ray photoelectron spectroscopy was used to determine the surface composition of a film deposited at 600 °C. Such analysis showed the presence of two types of niobium environments (Nb $3d^{5/2} = 207.9$, 203.3 eV; 70:30 ratio), oxygen (O 1s = 532.6 eV), carbon (C 1s = 285.6 eV), and two kinds of phosphorus ionizations (P 2p = 133.8, 128.9 eV; 70:30 ratio). The first Nb $3d^{5/2}$ binding energy is similar to that reported for Nb_2O_5 (Nb $3d^{5/2} = 207.5$ eV).[37] The first P 2p ionization, 133.8 eV, is consistent with the binding energy of the phosphate ion.[37] The second P 2p peak, 128.9 eV, is consistent with values for reported metal phosphides.[37] After sputtering with argon ions for 45 min, the main niobium ionization was centered at 203.0 eV; the ionization at 207.9 eV was significantly reduced in intensity. The ratio between these two ionizations was 70:30. Presumably, the Nb $3d^{5/2}$ peak at 203.0 eV is due to NbP. The phosphorus region still contained two peaks after sputtering (P 2p = 133.8, 129.0 eV), but the ratio had changed to 20:80. The ionization at 129.0 eV probably corresponds to the phosphido ion of NbP. The oxygen (O 1s = 531.4 eV) and carbon (C 1s = 285.0 eV) peaks, although still present after sputtering, were significantly reduced in intensity. The X-ray photoelectron spectroscopic data suggest a surface that is terminated by niobium phosphate.

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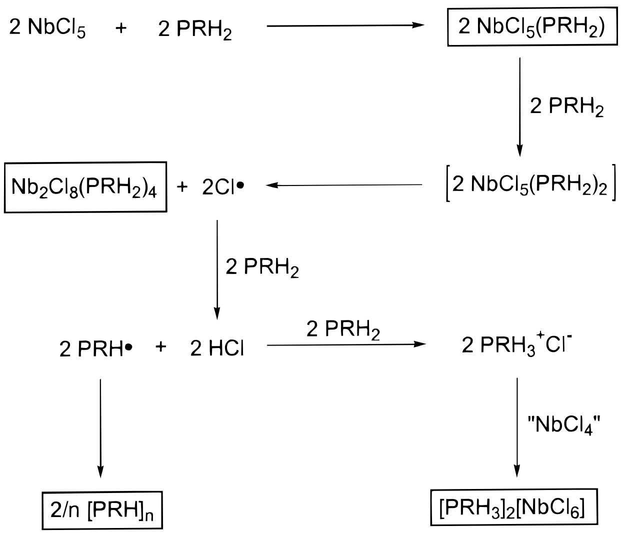
(35) Winter, C. H.; Lewkebandara, T. S.; Sheridan, P. H.; Proscia, J. W. *Mater. Res. Soc. Symp. Proc.* **1993**, *282*, 293.

(36) *Inorganic Phases*; JCPDS-International Centre for Diffraction Data: Swarthmore, PA, 1988; Card No. 17-882.

(37) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp., Physical Electronics Division: Eden Prairie, MN, 1979.

Scheme 1. Proposed Reaction Process



Rutherford backscattering spectrometry was used to determine the stoichiometry of an NbP film deposited at 600 °C on a silicon substrate. The backscattering spectrum revealed a phosphorus-rich stoichiometry of $Nb_{1.00}P_{1.20}$. In addition, traces of carbon, oxygen, and chlorine were detected, but the backscattering peaks for these elements were barely above the noise level and were correspondingly difficult to quantify. We estimate that the total concentration of these elements was less than 10% relative to niobium.

Discussion

We have documented an interesting reaction course that occurs upon treatment of niobium pentachloride with primary phosphines. The niobium(IV) products **1** and **2** are obtained in good yields and possess dimeric structures that are very similar to tertiary phosphine adducts of niobium(IV) chloride that have been documented by the groups of Nielson and Cotton.[25−28] It is clear that the dimeric framework adopted by **1** and **2** is very stable, since this structure type seems to be generally adopted by complexes of the empirical formula $NbCl_4(PR_3)_2$ ($R = H$, alkyl, aryl). Despite the fact that **1** has a niobium(IV) oxidation state, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra exhibited reasonably sharp resonances. Such behavior implies that the d^1 metal centers couple in an antiferromagnetic fashion to afford a complex that has substantial diamagnetic character, at least at ambient temperature. The diamagnetic character of **1** also suggests that the dimeric structure observed in the solid state is retained in solution. By contrast, Cotton and co-workers reported that the tertiary phosphine adduct $Nb_2Cl_8(PMe_2Ph)_4$, which possesses a structure similar to that of **1** and **2**, dissolves in dichloromethane with a drastic change in color and exhibits an ESR spectrum in this medium.[26,27] These observations suggest dissociation of the dimer to $NbCl_4(PMe_2Ph)_2$ in dichloromethane. Retention of the dimeric structure of **1** in solution probably reflects the smaller steric profile of a primary phosphine compared to a tertiary phosphine and argues that $Nb_2Cl_8(PMe_2Ph)_4$ dissociates in dichloromethane to relieve steric crowding.

The origin of the hydrogen atom that is incorporated in **3** and **4** has been probed. A proposed mechanistic sequence that is consistent with the experimental data is outlined in Scheme 1. Treatment of niobium pentachloride with 1 equiv of a primary phosphine affords the adduct $NbCl_5(PRH_2)$, which is stable in the absence of additional phosphine. This initial step is supported by the isolation and characterization of **5**. In the presence of additional phosphine, $NbCl_5(PRH_2)$ reacts to form the dimeric niobium(IV) complex $Nb_2Cl_8(PRH_2)_4$, isolated examples of which include **1** and **2**. To account for the reduction to niobium(IV), we propose the formation of a seven-coordinate transition state or intermediate, which can eliminate a chlorine atom with concomitant reduction of the niobium(V) center. A similar process was proposed by Poli in the reaction of $CpNbCl_4$ with excess trimethylphosphine.[31] Poli suggested that the chlorine atom abstracts a hydrogen atom from toluene solvent to afford hydrogen chloride, which then reacts with trimethylphosphine to give trimethylphosphonium chloride. Our results suggest that the hydrogen source for **3** is not dichloromethane solvent but rather additional cyclohexylphosphine. This proposal is supported by the lack of deuterium incorporation when the synthesis of **3** is conducted in dichloromethane-d_2 and by the spectroscopic detection of oligomeric phosphines derived from cyclohexylphosphine. We note that Poli's system utilized trimethylphosphine, which has no phosphorus−hydrogen bonds to be abstracted by chlorine atoms, leaving toluene solvent as the most likely hydrogen atom source. Once formed, the hydrogen chloride reacts with the primary phosphine to form a primary phosphonium chloride. The phosphonium ions are isolated as highly insoluble hexachloroniobate(IV) salts, which presumably form by capture of two chloride ions by a niobium(IV) chloride species. While mechanistically interesting, the formation of **3** and **4** can be avoided through use of $NbCl_4(THF)_2$ in place of niobium pentachloride.

Initial deposition studies demonstrate that **1** functions as a molecular precursor to slightly phosphorus-rich NbP films using a CVD reactor. It was found that a deposition temperature of 600 °C was required to obtain films that were sufficiently thick for analysis. This deposition temperature can be contrasted with the 1050 °C required to obtain NbP films from niobium pentachloride, phosphorus trichloride, and hydrogen.[10] The low volatility of **1** is a distinct limitation in its use as a precursor. In fact, **1** partially decomposes to bulk NbP at temperatures required for its vapor transport. Future source compound development should focus on monomeric complexes to achieve higher volatility. Interestingly, monomeric **5** decomposes before it sublimes and is therefore not a viable source compound. RBS analysis of the films deposited at 600 °C demonstrates that the bulk of the film is NbP containing $\leq$10% of carbon, chlorine, and oxygen. However, XPS studies indicate that the surface of the film is terminated by phosphate ions rather than phosphido ions. The formation of surface phosphate undoubtedly occurs rapidly upon exposure to ambient atmosphere. The formation of niobium(V) phosphate on the film surface is probably the key to the air stability and remarkable chemical resistance of NbP films.[10] The formation of phosphate phases in the presence of oxygen donors seems to be a general feature in the attempted deposition of early transition metal phosphide phases. Watson, Connor, and Whyman reported that film depositions using the precursors $M(CO)_5(PH_3)$ ($M = Cr$, Mo, W) yielded metal phosphate films rather than metal phosphide films.[38] Apparently, the carbon monoxide ligands serve as the oxygen source. Of relevance to this study, Watson, Connor, and Whyman found that the metal phosphate films were unaffected by immersion in aqueous hydrochloric acid for several hours. The stability of these metal phosphate phases toward chemical attack supports our proposal that it is the phosphate-terminated surface of the NbP films that leads to their stability in air.

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(38) Watson, I. M.; Connor, J. A.; Whyman, R. *Thin Solid Films* **1991**, *201*, 337.

Experimental Section

General Considerations. All synthetic manipulations were carried out under argon using either drybox or Schlenk-line techniques. Dichloromethane was distilled from calcium hydride. Diethyl ether was distilled from sodium/benzophenone ketyl. Chloroform-*d* and dichloromethane-d_2 were dried over 4 Å molecular sieves. Niobium pentachloride, cyclohexylphosphine, and phenylphosphine were obtained from commercial vendors and were used as received. $NbCl_4(THF)_2$ was prepared according to a literature method.[22]

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained at 400, 100, and 161 MHz, respectively, in the indicated solvents. Infrared spectra were obtained using Nujol mulls. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. X-ray diffraction spectra were obtained on a Rigaku Rotaflex powder diffractometer equipped with a rotating-anode source. X-ray photoelectron spectroscopy was carried out on an SSX-100 ESCA spectrometer using Al Kα radiation. Rutherford backscattering spectrometry was performed by the Michigan Ion Beam Laboratory, Ann Arbor, MI.

Preparation of Octachlorotetrakis(cyclohexylphosphine)diniobium(IV) (1). A 100-mL Schlenk flask was charged with niobium pentachloride (0.53 g, 2.0 mmol) and dichloromethane (25 mL). Using a syringe, cyclohexylphosphine (0.57 g, 4.9 mmol) was added to this suspension. The resultant brown-red mixture was stirred for 18 h at ambient temperature. Over this period, a purple precipitate formed and the dichloromethane layer took on a brown-red color. The purple precipitate was collected on a medium-porosity glass frit in the glovebox and was washed with dichloromethane (15 mL) and vacuum-dried to afford **3** (0.36 g, 68% based on niobium pentachloride). Analytical and spectroscopic data for **3** are given below. The clear brown-red filtrate was layered with diethyl ether (20 mL). The crystallization system was allowed to equilibrate for 24 h. The resultant crystals were isolated by cannulating away the solvent and vacuum-drying to afford **1** as brown-red crystals (0.39 g, 85% based on niobium pentachloride): mp 155−160 °C (dec); IR (Nujol, cm^{-1}) 2413 (ν_{P-H}, w), 2396 (ν_{P-H}, w), 2368 (ν_{P-H}, m), 2363 (ν_{P-H}, m), 1449 (s), 1354 (w), 1344 (w), 1295(w), 1270 (w), 1214 (w), 1180 (w), 1126 (m), 1059 (m), 1027 (w), 1003 (m), 916 (w), 893 (s), 869 (s), 841 (s), 819 (m), 733 (w); ^1H NMR ($CDCl_3$, δ) 4.69 (br d, $J_{HP} = 355.6$ Hz, $P\boldsymbol{H}_2$), 2.39 (br s, $C\boldsymbol{H}PH_2$), 2.14, 1.77, 1.36 (br s, $PCH(C\boldsymbol{H}_2)_2(C\boldsymbol{H}_2)_2C\boldsymbol{H}_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 33.88 (s, $PCH(\boldsymbol{C}H_2)_2(CH_2)_2CH_2$), 32.23 (s, $P\boldsymbol{C}H(CH_2)_2(CH_2)_2CH_2$), 26.84 (br s, $PCH(CH_2)_2(\boldsymbol{C}H_2)_2CH_2$), 25.62 (s, $PCH(CH_2)_2(CH_2)_2\boldsymbol{C}H_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm) −2.62 (br s). Anal. Calcd for $C_{24}H_{52}Cl_8Nb_2P_4$: C, 30.86; H, 5.61. Found: C, 28.88; H, 5.31.

Preparation of Octachlorotetrakis(phenylphosphine)diniobium(IV) (2). A 100-mL Schlenk flask was charged with niobium pentachloride (2.02 g, 7.50 mmol) and dichloromethane (15 mL). Using a syringe, a solution of phenylphosphine (1.70 g, 14.6 mmol) in dichloromethane (15 mL) was added to this mixture. After the addition, the resultant dark red mixture was stirred at ambient temperature for 18 h. During this time, a purple precipitate formed. The precipitate (containing **4**; vide infra) was removed by filtration through a medium-porosity glass frit in a drybox. The resultant dark red filtrate was layered with diethyl ether (15 mL). The crystallization system was allowed to equilibrate for 24 h. The resultant crystals were isolated by cannulating away the solvent and vacuum-drying to afford **2** as dark red crystals (1.503 g, 88% based on niobium pentachloride): mp 170−175 °C dec; IR (Nujol, cm^{-1}) 2409 (ν_{P-H}, w), 2393 (ν_{P-H}, w), 2386 (ν_{P-H}, w), 1484 (w), 1437 (m), 1333 (w), 1306 (w), 1106 (w), 1069 (w), 1048 (w), 1038 (w), 1023 (w), 1001 (w), 917 (w), 872 (s), 847 (m), 737 (m), 732 (m), 703 (w), 687 (m), 668 (w). NMR data could not be obtained because **2** was insoluble in all common solvents after isolation as a solid. Anal. Calcd for $C_{24}H_{28}Cl_8Nb_2P_4$: C, 31.68; H, 3.10. Found: C, 28.01, 28.11; H, 2.96, 2.96.

The purple precipitate was probably **4**, in analogy with **3**. Due to the insolubility of compound **2**, however, **4** could not be isolated as a single compound. The infrared spectrum of the purple precipitate showed absorptions for **2**, as well as absorptions consistent with a phosphonium ion (ν_{PH} 2408, 2392, 2385 cm^{-1}). No further attempts were made to separate **2** from **4**.

Spectroscopic and analytical data for bis(cyclohexylphosphonium) hexachloroniobate(IV) (3): mp 128−132 °C dec; IR (Nujol, cm^{-1}) 2446 (ν_{P-H}, s), 2405 (ν_{P-H}, s), 1352 (m), 1328 (m), 1301 (m), 1275 (m), 1217 (m), 1183 (w), 1127 (w), 1078 (w), 1053 (m), 1037 (m), 1009 (m), 980 (s), 918 (m), 892 (m), 857 (m), 773 (w), 736 (w). NMR data could not be obtained because **3** was insoluble in all common solvents. Anal. Calcd for $C_{12}H_{28}Cl_6NbP_2$: C, 26.69; H, 5.23; Cl, 39.40. Found: C, 26.97; H, 5.29; Cl, 39.15.

Preparation of 1 from Tetrachlorobis(tetrahydrofuran)niobium(IV). A 100-mL Schlenk flask was charged with $NbCl_4(THF)_2$ (0.55 g, 1.44 mmol) and toluene (25 mL). Using a syringe, cyclohexylphosphine (0.35 g, 3.01 mmol) was added to this suspension. The reaction mixture was stirred for 18 h. During this time, the reaction solution became brown and a brown-red precipitate formed. The brown-red precipitate was collected on a medium-porosity glass frit in a drybox. The solid was washed with toluene (15 mL) and dried under vacuum to afford the first portion of **1** (0.39 g, 58%). The volume of the filtrate obtained from filtration of the brown-red solid was reduced to about 20 mL under reduced pressure. The flask was cooled to −20 °C. Brown-red crystals of **1** formed over 24 h. The crystals were isolated and dried under vacuum to afford a second portion of **1** (0.13 g, 19%). The combined yield of **1** was 77%. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and infrared spectra of the crystals and precipitate were identical with those of **1** prepared as described above.

Preparation of Pentachloro(cyclohexylphosphine)niobium(V) (5). A 100-mL Schlenk flask was charged with niobium pentachloride (1.08 g, 4.00 mmol) and dichloromethane (25 mL). The flask and its contents were cooled to −78 °C. Cyclohexylphosphine (0.35 g, 3.0 mmol) was added by syringe to this stirred suspension. After the addition, the resultant orange mixture was stirred at −78 °C for 1 h. The mixture was then warmed to room temperature and was stirred for an additional 13 h. Filtration of the reaction solution through a 1-cm pad of Celite on a coarse glass frit, followed by removal of the volatile components under reduced pressure, afforded **5** as a bright orange powder (1.02 g, 88% based on cyclohexylphosphine): mp 78−83 °C dec; IR (Nujol, cm^{-1}) 2387 (ν_{P-H}, w), 2367 (ν_{P-H}, w), 2347 (ν_{P-H}, w), 1443 (s), 1346 (w), 1327 (w), 1297 (m), 1274 (w), 1258 (w), 1209 (w), 1179 (m), 1125 (m), 1086 (w), 1078 (w), 1053(s), 1041 (s), 1003 (m), 921 (s), 893 (s), 864 (m), 831 (s), 818 (s), 785 (w); ^1H NMR ($CDCl_3$, δ) 4.60 (dd, $J_{HP} = 347$ Hz, $J_{HH} = 6.0$ Hz, $P\boldsymbol{H}_2$), 2.38 (br m, $PC\boldsymbol{H}(CH_2)_2(CH_2)_2CH_2$), 2.21, 1.85, 1.43 (br m, $PCH(C\boldsymbol{H}_2)_2(C\boldsymbol{H}_2)_2C\boldsymbol{H}_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 32.63 (d, $J_{CP} = 5.2$ Hz, $PCH(\boldsymbol{C}H_2)_2(CH_2)_2CH_2$), 30.57 (d, $J_{CP} = 17.8$ Hz, $P\boldsymbol{C}H(CH_2)_2(CH_2)_2CH_2$), 26.57 (d, $J_{CP} = 9.6$ Hz, $PCH(CH_2)_2(\boldsymbol{C}H_2)_2CH_2$), 25.33 (s, $PCH(CH_2)_2(CH_2)_2\boldsymbol{C}H_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm) −40.07 (s, PH_2). Anal. Calcd for $C_6H_{13}Cl_5NbP$: C, 18.65; H, 3.39. Found: C, 15.73; H, 3.02.

Reaction of 5 with Cyclohexylphosphine. A 100 mL Schlenk flask was charged with **5** (0.61 g, 1.5 mmol) and dichloromethane (25 mL). Cyclohexylphosphine (0.37 g, 3.1 mmol) was added by syringe to this solution. The reaction mixture turned brown-red immediately and was stirred for 18 h. A purple precipitate was collected on a medium-porosity glass frit and vacuum-dried to afford **3** (0.22 g, 52%). The filtrate was layered with diethyl ether (25 mL). The crystallization flask was allowed to equilibrate for 24 h. The resultant brown-red crystals were isolated and dried under vacuum to afford **1** (0.34 g, 66%). Compounds **1** and **3** were identified by comparison of their spectral properties with those of materials prepared as described above.

Preparation of 1 and 3 in Dichloromethane-d_2. In a glovebox, a 10-mL glass vial was charged with niobium pentachloride (0.54 g, 2.0 mmol) and a stir bar. Dichloromethane-d_2 (5.0 mL) was added, followed by cyclohexylphosphine (0.44 g, 3.8 mmol). The resultant brown-red mixture was stirred for 18 h at ambient temperature. A purple precipitate was collected by filtration through a medium-porosity glass frit. The purple solid was dried under vacuum and subsequently identified as **3** (0.22 g, 40%) by comparison of its infrared spectrum with that of material prepared as described above. The filtrate was cooled to −20 °C for 24 h. A brown-red crystalline solid was isolated by removal of the solvent and identified as **1** (0.13 g, 28%) by comparison of its NMR spectra with those of material prepared as described above. The infrared spectra of **1** and **3** prepared herein were identical to material that was prepared in protiodichloromethane.

For the NMR experiment, a mixture of **1** and **3** was prepared as above by starting from niobium pentachloride (0.16 g, 0.6 mmol) and cyclohexylphosphine (0.18 g, 1.5 mmol) in dichloromethane-d_2 (2.0 mL). Insoluble **3** was removed by filtration through a plug of Celite on a coarse glass frit to afford a solution containing **1** and products of cyclohexylphosphine oxidation: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ppm) 23.50 (br s), −3.53 (br m, **1**), −69.04 (br s), −87.80 (br s). For discussion, see text.

NbP Film Deposition from 1. Film depositions were carried out in a horizontal hot-wall reactor, the details of which have been previously described.[35] The precursor (ca. 1 g) was finely ground and placed in a vial. The vial was placed in the sealed end of a 1 in. diameter quartz tube located in a tube furnace. The substrates were situated directly ahead of the precursor vial in the reactor. Corning 7059 low-sodium glass substrates were wiped with a Kimwipe until visually clean just prior to use, while silicon substrates were used as received. The open end of the tube was fitted with a vacuum adapter. Depositions were conducted at low pressure (ca. 0.01 mmHg). The substrates were equilibrated at the deposition temperatures for ca. 1 h prior to deposition, with the precursor region of the tube outside the furnace. Once the substrates were equilibrated at the deposition temperature, the precursor vial was placed just inside the furnace (temperature 150−200 °C), resulting in sublimation of the precursor over the heated substrates. Depositions were carried out for 15.0 min with substrate temperatures of 400, 500, and 600 °C. Details of the film analysis are described in the text.

Crystallographic Structure Determinations for 1 and 2. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were selected and mounted in thin-walled glass capillaries under nitrogen, and the capillaries were then flame-sealed. Diffraction data were collected on a Siemens P4 diffractometer. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\theta \leq 25°$).

No evidence of symmetry higher than triclinic was observed in either the photographic or the diffraction data for **1**, and the systematic absences in the diffraction data for **2** are uniquely consistent with the space group *Pbca*. *E* statistics suggested the centrosymmetric space group option $P\bar{1}$ for **1**, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Absorption corrections were applied to the data of **2** but were ignored for **1** because there was <10% variation in the integrated ψ-scan intensity data. The molecules of **1** and **2** each lie on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms on phosphorus were located from the difference map, and their distances in **1** were fixed to an average phosphorus−hydrogen distance. All other hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELXTL (5.03) or SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. We are grateful to the National Science Foundation for support of this research and the Institute for Manufacturing Research of Wayne State University for fellowships to K.C.J. and J.T.S. The Rutherford backscattering spectrometry was performed at the Michigan Ion Beam Laboratory by Dr. Victor Rotberg.

Supporting Information Available: X-ray photoelectron spectra, an RBS spectrum, and an X-ray diffraction spectrum for NbP films, an ORTEP diagram and listings of crystallographic data, atomic coordinates, thermal parameters, bond lengths, and bond angles for **1**, and an X-ray crystallographic file, in CIF format, for the structure determination of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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