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Syntheses and Characterization of Organoimido Complexes of Niobium(V); Potential CVD Precursors

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New niobium imido complexes $(RN)Nb(NEt_2)_3$ (R = Pr^n, Pr^i and Bu^t), potential precursors to grow niobium containing thin films by chemical vapor deposition (CVD), were prepared by reacting the corresponding $(RN)NbCl_3py_2$ complexes (R = Pr^n, Pr^i and Bu^t; py = pyridine) with $LiNEt_2$ in hydrocarbon solvents. The structures of $(RN)NbCl_3py_2$ (R = Pr^i and Bu^t), determined by X-ray crystallography, are mononuclear with distorted octahedral geometries. For each complex, three chloride ligands are cis to the imido ligand and occupy meridional positions. One of two py ligands is cis to and the other is trans to the imido ligand. For $(Pr^iN)NbCl_3py_2$, the $Nb{=}NPr^i$ bond distance (Å) is 1.733(3) and the $\angle Nb{=}N\text{-}Pr^i$ angle (°) is 178.0(3). Crystal data: monoclinic, space group $P2_1/n$, $a = 8.805(2)$, $b = 14.930(4)$, $c = 13.407(3)$ Å, $\beta = 93.37(2)°$, $V = 1759.5(7)$ Å^3, $Z = 4$, $D_c = 1.565$ g cm^{-3}. For $(Bu^tN)NbCl_3py_2$, the $Nb{=}NBu^t$ bond distance (Å) is 1.734(4) and the $\angle Nb{=}N\text{-}Bu^t$ angle (°) is 174.8(4). Crystal data: monoclinic, space group $P2_1/c$, $a = 9.609(1)$, $b = 13.591(6)$, $c = 14.615(2)$ Å, $\beta = 90.05(1)°$, $V = 1908.5(9)$ Å^3, $Z = 4$, $D_c = 1.492$ g cm^{-3}.

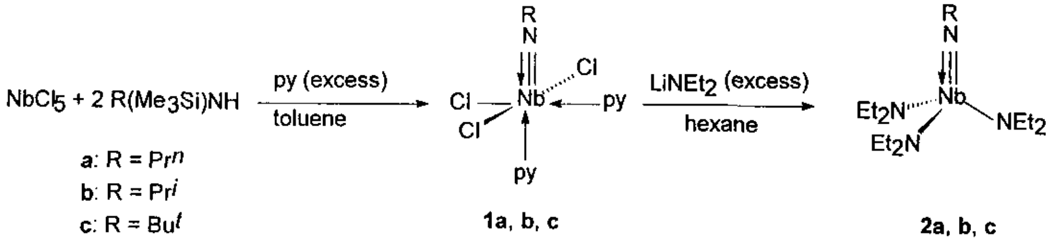
INTRODUCTION

The chemistry of high-oxidation state early transition metal complexes stabilized by organoimido ligands, =NR, have been investigated intensively.[1] There are many potential applications involving these complexes. For example, they may be used in homogeneous catalysis, such as olefin metathesis.[2] Recently, imido complexes have been employed as precursors to grow metal nitride and carbonitride thin films by chemical vapor deposition (CVD).[3] For example, cubic phase tantalum nitride and tungsten nitride thin films can be grown from organoimido complexes $(EtN)Ta(NEt_2)_3$ and $(Bu^tN)_2W(NHBu^t)_2$, respectively.[3a-d] In the first case, the CVD of tantalum nitride, $(\eta^2\text{-}EtN{=}CHMe)Ta(NEt_2)_3$, a precursor of $(EtN)Ta(NEt_2)_3$, is always in the presence with $(EtN)Ta(NEt_2)_3$ due to their similar physical properties.[4] Complete separation of one from the other is difficult. This makes a reaction pathway elucidation complex. To overcome this problem, we have developed a method to synthesize pure $(RN)Ta(NEt_2)_3$ (R = Pr^n, Pr^i and Bu^t) complexes by reacting the corresponding $(RN)TaCl_3py_2$ (py = pyridine) complexes with $LiNEt_2$.[5] $(Bu^tN)Ta(NEt_2)_3$ has been employed successfully as a single-source precursor to grow tantalum nitride thin films by CVD for electronic device applications.[6] Due to the chemical similarity between tantalum and niobium, it is reasonable to assume that organoimido complexes of niobium can be synthesized analogously. Here, we report our preparation and characterization of $(RN)NbCl_3py_2$, (**1a**, R = Pr^n; **1b**, R = Pr^i; **1c**, R = Bu^t), and $(RN)Nb(NEt_2)_3$, (**2a**, R = Pr^n; **2b**, R = Pr^i; **2c**, R = Bu^t). Complexes **2a-c** are liquids at room temperature and volatile under low pressure. These properties make them good candidates for precursors in CVD applications.

RESULTS AND DISCUSSION

The synthetic procedure employed here, as shown in Scheme I, parallels the method we used to prepare $(RN)TaCl_3py_2$ and $(RN)Ta(NEt_2)_3$.[5] The air- and moisture-sensitive organoimido complexes $(RN)NbCl_3py_2$, **1a-c**, were conveniently prepared in good yields by reacting $NbCl_5$ with the corresponding amines $R(Me_3Si)NH$ and pyridine in hydrocarbon solvents. **1b** and **1c** were structurally characterized by single crystal X-ray diffraction (see below). Simple metathesis reactions between complexes **1a-c** and $LiNEt_2$ generated $(RN)Nb(NEt_2)_3$, **2a-c**, in good yields. All three complexes are air- and moisture-sensitive liquids at room temperature. In mass spectra, they all showed M^+ signals corresponding to the *m/z* values for the $(RN)Nb(NEt_2)_3^+$ molecular ions. NMR data show resonance signals which can be assigned to the alkyl groups on the imdo and the amido ligands. Based on the data, complexes **2** are proposed to have structures resembling those of tris(dimethylamido)(tertbutylimido)tantalum(V) and

Scheme I Syntheses of 1 and 2



tris(dimethylamido)(2,6-diisopropylphenylimido)niobium (V).[7,8] Both complexes were structurally characterized to show a distorted tetrahedral geometry about the MN_4 cores. All complexes **2** are volatile liquids at 60 °C under vacuum. It is generally recognized that for CVD applications, precursor molecules in liquid phase usually provide more uniform vaporization than those in solid phase.[9] Our preliminary investigation indicated that using **2a** as a single-source precursor, good quality niobium carbonitride thin films can be grown by low pressure chemical vapor deposition.[10] For example, a smooth metallic-shining thin film, characterized to have a bulk composition of $NbC_{0.2}N_{0.7}O_{0.2}$ by wavelength dispersive spectroscopy (WDS), was deposited at 550 °C under a pressure of 0.01 torr. XRD study showed that the film was cubic (a = 4.32 Å), close to the XRD angles of cubic NbN (a = 4.392 Å). High resolution X-ray photoelectron spectra (XPS) of the film, after surface layers were removed by Ar sputtering for one minute, showed binding energies of $Nb_{3d_{5/2}}$, $Nb_{3d_{3/2}}$, C_{1s}, N_{1s}, and O_{1s} electrons at 203.5, 206.2, 282.4, 397.2, and 530.6 eV, respectively. The data supported that the film was a niobium nitride with carbon and oxygen atoms incorporated as carbide and oxide.[11] It is also possible to develop CVD processes to grow other niobium containing thin films, such as niobium oxide, using complexes **2**.

In order to understand whether the different imido R groups could affect the Nb=NR bond lengths, both **1b** and **1c** were structurally characterized by single crystal X-ray diffraction. Single crystals of **1b** and **1c** were grown from toluene solutions at -15 °C. Selected bond distances and bond angles are listed in Tables 1 and 2 for **1b** and **1c**, respectively. The ORTEP drawings of **1b** and **1c** are shown in Figs. 1 and 2, respectively. In general, each complex has a distorted octahedral geometry about the metal center. Cis to the imido ligand, there are three Cl ligands arranged in mer geometry. The remaining coordination sites, one trans to and one cis to the imido ligand, are occupied by pyridine ligands. The difference in cis-trans Nb-N(py) distances reflects the strong trans influence of the imido ligands. This type of structure has been observed for related tantalum complexes.[5,12] When the metal-imido moieties are compared for **1b** and **1c**, it is found that the Nb=N(imido) distances are identical and the Nb=N-R angles, almost linear, are indistinguishable. Apparently, changing R from an isopropyl group to a tertbutyl group generated negligible effects on the niobium-imido bonding. Recently, the structure of a closely related monomeric complex (Bu^{t}N)NbCl$_3$(dme) (dme = 1,2-dimethoxyethane) has been reported.[13] Its "(Bu^{t}N)NbCl$_3$" moiety is essentially identical to that of **1c**. The structures of dimeric complexes related to **1b**, [NbCl$_3$(NR)(NH$_2$R)]$_2$ (R = Pr^i and 2,6-diisopropylphenyl), have been reported also.[14] These dimers have edge-shared bioctahedron structures. Large steric differences between the isopropyl and the 2,6-diisopropylphenyl groups of these complexes affected their general structural features only

Table 1. Selected Bond Distances and Bond Angles of **1b**

Bond Distance (Å)	
Nb-Cl(1)	2.406(1)
Nb-Cl(2)	2.382(1)
Nb-Cl(3)	2.409(1)
Nb-N(1)	1.733(3)
Nb-N(2)	2.463(3)
Nb-N(3)	2.307(3)
N(1)-C(1)	1.451(6)
Bond Angle (°)	
Cl(1)-Nb-Cl(2)	94.74(4)
Cl(1)-Nb-Cl(3)	162.56(4)
Cl(1)-Nb-N(1)	97.4(1)
Cl(1)-Nb-N(2)	83.19(8)
Cl(1)-Nb-N(3)	83.93(8)
Cl(2)-Nb-Cl(3)	94.62(4)
Cl(2)-Nb-N(1)	99.3(1)
Cl(2)-Nb-N(2)	85.22(8)
Cl(2)-Nb-N(3)	166.46(8)
Cl(3)-Nb-N(1)	95.6(1)
Cl(3)-Nb-N(2)	82.97(8)
Cl(3)-Nb-N(3)	83.53(8)
N(1)-Nb-N(2)	175.4(1)
N(1)-Nb-N(3)	94.3(1)
N(2)-Nb-N(3)	81.3(1)
Nb-N(1)-C(1)	178.0(3)

Table 2. Selected Bond Distances and Bond Angles of **1c**

Bond Distance (Å)	
Nb-Cl(1)	2.381(2)
Nb-Cl(2)	2.400(2)
Nb-Cl(3)	2.419(1)
Nb-N(1)	1.734(4)
Nb-N(2)	2.313(4)
Nb-N(3)	2.480(4)
N(1)-C(1)	1.465(7)
Bond Angle (°)	
Cl(1)-Nb-Cl(2)	94.55(6)
Cl(1)-Nb-Cl(3)	93.75(6)
Cl(1)-Nb-N(1)	98.4(2)
Cl(1)-Nb-N(2)	170.1(1)
Cl(1)-Nb-N(3)	87.2(1)
Cl(2)-Nb-Cl(3)	161.2(6)
Cl(2)-Nb-N(1)	96.1(1)
Cl(2)-Nb-N(2)	84.9(1)
Cl(2)-Nb-N(3)	81.9(1)
Cl(3)-Nb-N(1)	99.4(1)
Cl(3)-Nb-N(2)	84.1(1)
Cl(3)-Nb-N(3)	81.6(1)
N(1)-Nb-N(2)	91.6(2)
N(1)-Nb-N(3)	174.2(2)
N(2)-Nb-N(3)	82.9(1)
Nb-N(1)-C(1)	174.8(4)

slightly. When **1b** is compared to [NbCl$_3$(NPr^i)(NH$_2$Pr^i)]$_2$, it is clear that the "(Pr^{i}N)NbCl$_3$" moieties of these complexes are basically indistinguishable.

In conclusion, we have synthesized and characterized new niobium imido complexes (RN)NbCl$_3$py$_2$ and (RN)Nb(NEt$_2$)$_3$. Investigations are underway to study the potential applications of (RN)Nb(NEt$_2$)$_3$ complexes as the precursors to grow Nb containing thin films by CVD.

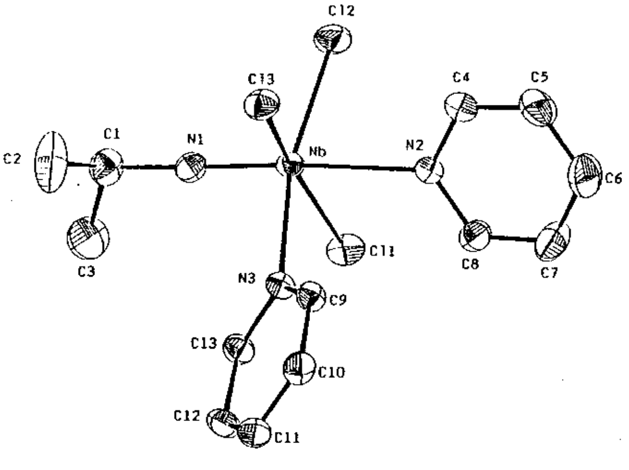


Fig. 1. ORTEP drawing of (Pr^{i}N)NbCl$_3$py$_2$ (**1b**) showing the atom numbering scheme.

EXPERIMENTAL SECTION

General Procedures

All chemicals and solvents were manipulated under dry and oxygen-free environments. NbCl$_5$ was purchased from Strem and used without further purification. RNH$_2$ and pyridine were supplied by Merck and degassed before use. Me$_3$SiCl was obtained from Janssen and used as received. LiNEt$_2$ was prepared from HNEt$_2$ and Bu^{n}Li (Janssen) in hexane. All ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300 and 75-MHz, respectively, on a Varian Unity-300 spectrometer at +25 °C. Mass spectra were measured (Vacuum Generator Trio-2000) by the direct insertion method. Elements were analyzed with a Heraeus CHN-O-Rapid Analyzer.

Preparation of (Bu^{t}N)NbCl$_3$py$_2$, 1a

To NbCl$_5$ (2.1 g, 7.6 mmol) dissolved in a mixture of toluene (120 cm^3) and ether (5 cm^3), a mixture of Me$_3$SiCl (1.4 cm^3, 11 mmol), Bu^{t}NH$_2$ (1.9 cm^3, 22 mmol) and pyridine (2.2 cm^3, 27 mmol) in toluene (80 cm^3) was added at 0 °C. The mixture was stirred overnight then filtered. A yellow solid was separated after the filtrate was concentrated. Recrystallization of the solid from toluene at -15 °C gave crystals suitable for analysis. (2.1 g, 65% based on Nb). ^{1}H NMR (benzene-d_6, ppm): 1.47 (s, 9H, Me_3CN), 6.31 (t, 2H, m-C$_6$H$_5$N), 6.57 (br, 2H, m-C$_6$$H_5$N), 6.70 (t, 1H, p-C$_6$$H_5$N), 6.87 (br, 1H, p-C$_6$$H_5$N), 8.82 (d, 2H, o-C$_6$$H_5$N), 9.17 (br, 2H, o-C$_6$$H_5$N). ^{13}C NMR (benzene-$d_6$, ppm): 29.5 ($Me_3$CN), 70.8 (Me$_3$CN), 123.8 (m-C$_6H_5$N), 137.6 (p-C$_6H_5$N), 139.0 (p-C$_6H_5$N), 151.5 (o-C$_6H_5$N), 152.8 (o-C$_6H_5$N). Mass (EI,

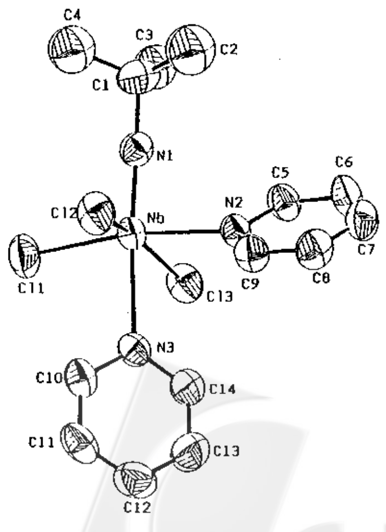


Fig. 2. ORTEP drawing of (Bu^{t}N)NbCl$_3$py$_2$ (**1a**) showing the atom numbering scheme. Only one orientation of the disordered Bu^t group is shown.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters of **1b**

	x	y	z	Biso
Nb	0.05853(4)	0.151743(23)	0.213485(24)	2.818(13)
Cl1	0.16813(11)	0.08558(8)	0.07072(7)	4.05(4)
Cl2	0.28190(12)	0.13496(8)	0.32097(9)	4.89(5)
Cl3	-0.10583(12)	0.18170(8)	0.34703(7)	4.05(4)
N1	0.0799(4)	0.26279(22)	0.17948(24)	3.46(13)
N2	0.0069(4)	-0.00537(21)	0.25605(23)	3.31(13)
N3	-0.1679(3)	0.13350(20)	0.12018(21)	2.89(12)
C1	0.0964(5)	0.3567(3)	0.1545(3)	4.68(20)
C2	-0.0305(9)	0.4109(4)	0.1913(6)	8.6(4)
C3	0.1141(7)	0.3685(4)	0.0450(4)	6.9(3)
C4	0.0089(5)	-0.0320(3)	0.3513(3)	4.32(20)
C5	-0.0213(6)	-0.1185(4)	0.3780(4)	5.57(24)
C6	-0.0551(7)	-0.1813(3)	0.3055(4)	6.4(3)
C7	-0.0586(6)	-0.1546(3)	0.2077(4)	5.48(24)
C8	-0.0271(5)	-0.0667(3)	0.1862(3)	4.00(18)
C9	-0.2896(4)	0.0909(3)	0.1536(3)	3.21(15)
C10	-0.4269(4)	0.0857(3)	0.0995(3)	3.75(18)
C11	-0.4422(5)	0.1252(3)	0.0069(3)	4.03(18)
C12	-0.3187(5)	0.1675(3)	-0.0293(3)	4.04(17)
C13	-0.1842(4)	0.1704(3)	0.0289(3)	3.43(16)
H1	0.189	0.379	0.188	5.5
H2a	-0.041	0.403	0.261	8.5
H2b	-0.020	0.473	0.178	8.5
H2c	-0.127	0.392	0.158	8.5
H3a	0.198	0.334	0.022	7.3
H3b	0.023	0.349	0.007	7.3
H3c	0.130	0.430	0.028	7.3
H4	0.032	0.012	0.404	5.0
H5	-0.018	-0.135	0.448	6.2
H6	-0.076	-0.243	0.324	6.9
H7	-0.084	-0.197	0.154	6.2
H8	-0.029	-0.048	0.116	4.8
H9	-0.280	0.063	0.219	4.0
H10	-0.512	0.055	0.126	4.4
H11	-0.538	0.124	-0.031	4.7
H12	-0.326	0.194	-0.095	4.7
H13	-0.097	0.200	0.002	4.2

Table 4. Atomic Coordinates and Isotropic Thermal Parameters of **1c**

	x	y	z	Biso
Nb	0.21385(5)	0.18362(3)	0.24974(3)	3.349(18)
Cl1	0.21159(17)	0.31878(12)	0.35339(10)	5.39(7)
Cl2	0.33441(16)	0.07537(12)	0.35253(10)	5.14(6)
Cl3	0.03379(15)	0.25243(11)	0.15334(9)	4.55(6)
N1	0.3589(4)	0.2170(3)	0.1864(3)	3.79(19)
N2	0.1811(4)	0.0440(3)	0.1618(3)	3.40(18)
N3	0.0085(4)	0.1192(3)	0.3332(3)	3.71(18)
C1	0.4890(6)	0.2399(5)	0.1387(5)	5.6(3)
C2	0.5379(18)	0.1375(14)	0.1005(12)	8.6(4)
C2′	0.5942(22)	0.1631(16)	0.1631(15)	10.8(6)
C3	0.4584(14)	0.3182(11)	0.0666(9)	63.(3)
C3′	0.4727(21)	0.2470(16)	0.0370(14)	10.2(5)
C4	0.5937(17)	0.2697(13)	0.2132(11)	7.8(4)
C4′	0.5538(25)	0.3242(19)	0.1971(16)	12.5(7)
C5	0.1874(6)	0.0521(4)	0.0706(3)	4.06(24)
C6	0.1746(7)	-0.0262(4)	0.0130(4)	5.0(3)
C7	0.1533(6)	-0.1178(4)	0.0491(4)	5.0(3)
C8	0.1468(6)	-0.1285(4)	0.1417(4)	4.9(3)
C9	0.1612(6)	-0.0462(4)	0.1957(4)	4.22(24)
C10	-0.0008(6)	0.1276(4)	0.4238(4)	4.3(3)
C11	-0.1152(7)	0.0954(5)	0.4727(4)	5.2(3)
C12	-0.2220(7)	0.0510(5)	0.4282(4)	5.8(3)
C13	-0.2135(7)	0.0402(5)	0.3353(4)	6.1(3)
C14	-0.0982(6)	0.0764(5)	0.2907(4)	5.0(3)
H5	0.202	0.117	0.044	4.7
H6	0.181	-0.017	-0.052	5.6
H7	0.143	-0.175	0.009	5.7
H8	0.131	-0.193	0.169	5.5
H9	0.159	-0.054	0.261	4.9
H10	0.077	0.159	0.457	5.0
H11	-0.119	0.105	0.539	5.8
H12	-0.302	0.027	0.462	6.5
H13	-0.288	0.007	0.302	6.6
H14	-0.096	0.071	0.225	5.7

m/z, ^{35}Cl, ^{93}Nb): 254 [M - 2 py - Me]$^+$. A satisfactory analysis was not obtained.

Preparation of (Pr^{i}N)NbCl$_3$py$_2$, 1b, and (Pr^{n}N)NbCl$_3$py$_2$, 1c

By using Pr^{i}NH$_2$ and Pr^{n}NH$_2$, **1b** and **1c** were synthesized by a procedure similar to the one used to prepare **1a**.

1b ^{1}H NMR (benzene-*d*$_6$, ppm): 1.32 (d, 6H, *Me*$_2$CHN), 4.23 (m, 1H, Me$_2$C*H* N), 6.51 (t, 2H, m-C$_6$*H*$_5$N), 6.65 (br, 2H, m-C$_6$*H*$_5$N), 6.95 (t, 1H, p-C$_6$*H*$_5$N), 7.02 (br, 1H, p-C$_6$*H*$_5$N), 8.74 (d, 2H, o-C$_6$*H*$_5$N), 9.12 (br, 2H, o-C$_6$*H*$_5$N). ^{13}C NMR (chloroform-*d*, ppm): 22.6 (*Me*$_2$CHN), 66.3 (Me$_2$*C*HN), 124.2 (m-*C*$_6$H$_5$N), 124.5 (m-*C*$_6$H$_5$N), 138.5 (p-*C*$_6$H$_5$N), 139.9 (p-*C*$_6$H$_5$N), 151.1 (o-*C*$_6$H$_5$N), 152.4 (o-*C*$_6$H$_5$N). Mass (EI, *m/z*, ^{35}Cl, ^{93}Nb): 240 [M - 2 py - Me]$^+$. Anal. Calcd. for NbC$_{13}$H$_{17}$N$_3$Cl$_3$: C, 37.66; H, 4.13; N, 10.14. Found: C, 37.29; H, 4.18; N, 9.92.

1c ^{1}H NMR (benzene-*d*$_6$, ppm): 1.07 (t, 3H, *Me*CH$_2$CH$_2$N), 1.71 (m, 2H, MeC*H*$_2$CH$_2$N), 4.01 (t, 2H, MeCH$_2$C*H*$_2$N), 6.47 (m, 2H, m-C$_6$*H*$_5$N), 6.65 (m, 2H, m-C$_6$*H*$_5$N), 6.89 (t, 1H, p-C$_6$*H*$_5$N), 6.98 (t, 1H, p-C$_6$*H*$_5$N), 8.69 (d, 2H, o-C$_6$*H*$_5$N), 9.16 (br, 2H, o-C$_6$*H*$_5$N). ^{13}C NMR (chloroform-*d*, ppm): 11.9 (*Me*CH$_2$CH$_2$N), 23.7 (Me*C*H$_2$CH$_2$N), 67.2 (MeCH$_2$*C*H$_2$N), 124.1 (m-*C*$_6$H$_5$N), 124.5 (m-*C*$_6$H$_5$N), 138.5 (p-*C*$_6$H$_5$N), 139.9 (p-*C*$_6$H$_5$N), 150.9 (o-*C*$_6$H$_5$N), 151.8 (o-*C*$_6$H$_5$N). Mass (EI, *m/z*, ^{35}Cl, ^{93}Nb): 226 [M - 2 py - Et]$^+$. Anal. Calcd. for NbC$_{13}$H$_{17}$N$_3$Cl$_3$: C, 37.66; H, 4.13; N,

Table 5. Crystallographic Data for **1b** and **1c**

	1b	**1c**
Formula	$C_{13}H_{17}N_3Cl_3Nb$	$C_{14}H_{19}N_3Cl_3Nb$
Formula weight	414.56	428.59
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.805(2)	9.609(1)
b (Å)	14.930(4)	13.591(6)
c (Å)	13.407(3)	14.615(2)
β (°)	93.37(2)	90.05(1)
V(Å)^3	1759.5(7)	1908.5(9)
Z	4	4
ρcalc, g cm^{-3}	1.565	1.492
λ (Å)	0.7107	0.7107
F(000)	825	828
Unit cell detn.: No.; (2θ range)	25; (18.74-38.86°)	25; (19.20-29.30°)
Scan type	θ/2θ	θ/2θ
Scan width (°)	2(0.65 + 0.35tan(θ))	2(0.70 + 0.35tan(θ))
Scan speed (°/min)	2.06-8.24	2.06-8.24
2θ (max)	50.0	50.0
hkl ranges	(-10; 10)(0; 17)(0; 15)	(-11; 11)(0; 16)(0; 17)
μ, cm^{-1}	11.087	10.234
Crystal size, mm	0.40 × 0.50 × 0.60	0.50 × 0.50 × 0.50
Transmission	0.934; 1.000	0.894; 1.000
T, °K	298	298
No. of measured reflns.	3095	3361
No. of obsd. reflns. (I > 2.0 sig(I))	2599	2784
No. of unique reflns.	3095	3361
R_F[a], R_w[b]	0.027, 0.031	0.037, 0.044
GoF[c]	1.40	1.83
Refinement program	NRCVAX	NRCVAX
No. of atoms	37	34
No. of refined parameters	182 (2599 out of 3095 reflns.)	188 (2784 out of 3361 reflns.)
Minimize function	$\Sigma(w(F_o - F_c)^2)$	$\Sigma(w(F_o - F_c)^2)$
Unit weights were used	yes	
g (2nd. ext. coeff.) × 10^4	0.73(8)	0.91(4)
(δ/σ)max	0.0043	0.0624
(D -map)max.min e/A^3	-0.380; 0.570	-0.270; 0.780

[a] $R_F = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $R_w = [\Sigma(w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$.

[c] $GoF = [\Sigma(w(F_o - F_c)^2)/(\text{No. of reflections} - \text{No. of parameters})]^{1/2}$.

[d] **1b** 3 standard reflections monitored every 3600 seconds, intensity decay 3%.

[e] **1c** standard reflections: No. 3; Variation < 2%, 4 σ; every 3600 seconds; Bu^t disorder.

10.14. Found: C, 37.35; H, 4.15; N, 9.89.

Preparation of $(Bu^tN)Nb(NEt_2)_3$, 2a

To **1a** (2.0 g, 4.8 mmol) suspended in hexane (60 cm^3), $LiNEt_2$ (1.8 g, 23 mmol) suspended in hexane (60 cm^3) was added slowly. The mixture turned brown gradually as it was stirred overnight. After filtration, the filtrate was concentrated to a brown liquid. Purification by vacuum distillation (60 °C, 10^{-1} mm Hg) gave a yellow liquid (0.51 g, 28% based on Nb). ^1H NMR (benzene-d_6, ppm): 1.16 (t, 18H, *Me*CH_2N), 1.41 (s, 9H, *Me*$_3$CN), 3.47 (q, 12H, MeC*H*$_2$N). ^{13}C NMR (benzene-d_6, ppm): 17.3 (*Me*CH_2N), 26.9 (*Me*$_3$CN), 48.5 ($MeCH_2N$), 63.8 (Me_3CN). Mass (EI, *m/z*, ^{93}Nb): 380 [M]$^+$. A satisfactory carbon analysis was not obtained.

Preparation of $Nb(NPr^i)(NEt_2)_3$, 2b, and $Nb(NPr^n)(NEt_2)_3$, 2c

2b and **2c** were synthesized by a procedure similar to the one used to prepare **2a**.

2b ^1H NMR (benzene-d_6, ppm): 1.16 (t, 18H, *Me*CH_2N), 1.28 (d, 6H, *Me*$_2$CHN), 3.42 (q, 12H, MeC*H*$_2$N), 4.11 (m, 1H, Me_2C*H*N). ^{13}C NMR (benzene-d_6, ppm): 17.3 (*Me*CH_2N), 26.9 (*Me*$_2$CHN), 48.6 ($MeCH_2N$), 63.8

($\mathrm{Me_2\mathit{C}HN}$). Mass (EI, *m/z*, ^{93}Nb): 366 [M]$^+$. A satisfactory analysis was not obtained.

2c ^{1}H NMR (benzene-d_6, ppm): 0.99 (t, 3H, $\mathit{Me}\mathrm{CH_2CH_2N}$), 1.20 (t, 18H, $\mathit{Me}\mathrm{CH_2N}$), 1.70 (m, 2H, $\mathrm{MeC\mathit{H}_2CH_2N}$), 3.43 (q, 12H, $\mathrm{MeC\mathit{H}_2N}$), 3.88 (t, 2H, $\mathrm{MeCH_2C\mathit{H}_2N}$). ^{13}C NMR (benzene-$d_6$, ppm): 11.9 ($\mathit{Me}\mathrm{CH_2CH_2N}$), 17.3 ($\mathit{Me}\mathrm{CH_2N}$), 27.3 ($\mathrm{Me\mathit{C}H_2CH_2N}$), 48.5 ($\mathrm{Me\mathit{C}H_2N}$), 65.5 ($\mathrm{MeCH_2\mathit{C}H_2N}$). Mass (EI, *m/z*, ^{93}Nb): 366 [M]$^+$. A satisfactory carbon analysis was not obtained.

Structural Determinations

Single crystals of **1b** and **1c** were sealed in glass capillaries under an inert atmosphere. Data were collected on a Nonius CAD-4 using graphite-monochromated Mo K_α radiation, and the structures were solved by the heavy-atom method; all data reduction and structural refinements were performed with the NRCC SDP package. Selected bond distances and angels are listed in Tables 1 and 2 for **1b** an **1c**, respectively. Atomic coordinates and isotropic thermal parameters of **1b** and **1c** are respectively shown in Tables 3 and 4. Crystal data, conditions for crystallographic data collection, and structure refinements are summarized in Table 5. For **1c**, the methyl groups of Bu^t group are disorder with half occupancies. They are designated as C(2), C(3), C(4) and C(2)′, C(3)′, C(4)′, and refined isotropically.

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Key Words

Niobium complex; Organoimido ligands; CVD precursors.

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