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Preparation and structural characterization of new alkoxo- and (alkoxo)(amido)(imido)-niobium(V) compounds. Crystal structure of $[NbCl(\mu\text{-}OMe)[N(SiMe_3)_2](NSiMe_3)]_2$

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Abstract

The reactions of $NbCl_5$ with Me_3SiOMe in the appropriate molar ratios have given new alkoxoniobium(V) derivatives of the type $NbCl_{5-x}(OMe)_x$ ($x = 2$ (I), 3 (II)). Reactions of I and II with various ligands afford the corresponding species $NbCl_{5-x}(OMe)_xL$, $x = 2$, $L = OPPh_3$ (III); $L = OAsPh_3$ (IV); $L = THF$ (V); $L = Cl^-$ (VI); $x = 3$, $L = OPPh_3$ (VII); $L = Cl^-$ (VIII). Similar hexacoordinate compounds $NbCl_3(OR)_2(OPPh_3)$, ($R = Me$ (III), $R = Et$ (IX), $R = Pr^i$ (X)) have been obtained by reactions of $NbCl_5(OPPh_3)$ with the relevant Me_3SiOR compounds. Compounds I and II also react with $\{[LiN(SiMe_3)_2]Et_2O\}_2$ to give $[NbCl(\mu\text{-}OMe)[N(SiMe_3)_2](NSiMe_3)]_2$ (XI) and $[Nb(OMe)(\mu\text{-}OMe)[N(SiMe_3)_2](NSiMe_3)]_2$ (XII). All the compounds have been characterized by IR and NMR spectroscopy and the crystal structure of XI has been determined by X-ray diffraction. XI crystallizes in the monoclinic space group $P2_1/c$ with a 10.236(1), b 9.789(1), c 21.201(3) Å, β 102.67(1)° and D_c 1.30 g cm^{-3} for $Z = 4$. A final R value of 0.042 ($R_w = 0.052$) based on 4272 reflections was obtained. The two metal atoms are asymmetrically bridged by the two methoxide ligands. Chloride, amido, and imido ligands complete the coordination spheres of both metal atoms.

Introduction

Alkoxide complexes of a wide variety of transition metals have been much investigated [1], often because they can provide molecular models for metal oxides [2,3]. Furthermore many of the early transition metals form multiple bonds with σ-donating ligands of the first-period elements such as O and N [4]. We describe

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here the isolation and characterization of new alkoxo, and (alkoxo)(amido)(imido) complexes of niobium(V). The crystal structure of $[NbCl(\mu\text{-}OMe)[N(SiMe_3)_2](NSiMe_3)]_2$ has been determined.

Results and discussion

Synthetic studies

Complexes I and II were prepared by reaction of $NbCl_5$ with Me_3SiOMe, according to eq. 1.

$$NbCl_5 + Me_3SiOMe \rightarrow NbCl_{5-x}(OMe)_x + Me_3SiCl \qquad (1)$$

$$\begin{aligned}(\text{I}&: x = 2\\ \text{II}&: x = 3)\end{aligned}$$

Me_3SiOMe has been used previously [5] as an alkoxylating reagent in the preparation of organoalkoxotungsten(VI) complexes because its use avoids reduction of the metal center in the high oxidation state, and also facilitates the selective replacement of the chlorine atoms. With $NbCl_5$ the substitution processes yield I and II, and it was not possible to isolate any complexes with a greater number of OMe groups even when large excess of Me_3SiOMe was used.

Complexes I and II were isolated as air-sensitive hygroscopic white microcrystalline solids. They are soluble in dichloromethane, chloroform, and THF, and insoluble in diethyl ether and aromatic and aliphatic hydrocarbons.

Complexes I and II behave as coordinatively unsaturated species, and react with σ-donating ligands to give the corresponding hexacoordinate complexes, according to eq. 2:

$$NbCl_{5-x}(OMe)_x + L \rightarrow NbCl_{5-x}(OMe)_xL \qquad (2)$$

$$\begin{aligned}(\text{III}&: x = 2, L = OPPh_3;\\ \text{IV}&: x = 2, L = OAsPh_3;\\ \text{V}&: x = 2, L = THF;\\ \text{VI}&: x = 2, L = Cl^-;\\ \text{VII}&: x = 3, L = OPPh_3;\\ \text{VIII}&: x = 3, L = Cl^-)\end{aligned}$$

Analogous disubstituted compounds can be isolated when $NbCl_5(OPPh_3)$ reacts with Me_3SiOR (see eq. 3) even when a large excess of the alkoxide is used:

$$NbCl_5(OPPh_3) + Me_3SiOR \rightarrow NbCl_3(OR)_2(OPPh_3) \qquad (3)$$

$$\begin{aligned}(\text{III}&: R = Me;\\ \text{IX}&: R = Et;\\ \text{X}&: R = Pr^i)\end{aligned}$$

The hexacoordinate complexes III–X are air sensitive hygroscopic white microcrystalline solids. They are more stable toward the hydrolysis than complexes I and II, and are less soluble in dichloromethane, chloroform, and THF, and insoluble in aromatic and aliphatic hydrocarbons. We thus decided to study the reactions of complexes I and II with $[LiN(SiMe_3)_2Et_2O]_2$ and found that on treatment with an

0.5 molar proportion of the latter they give the binuclear complexes containing both organoamido and organoimido ligands, according to eq. 4:

$$\begin{aligned}&NbCl_x(OMe)_{5-x} + [LiN(SiMe_3)_2Et_2O]_2 \rightarrow \\ &\quad [NbCl_{x-2}[N(SiMe_3)_2](NSiMe_3)(OMe)_{3-x}(\mu\text{-}OMe)]_2 + Me_3SiOMe \qquad (4)\\ &\qquad\qquad (XI\text{: } x=3;\\ &\qquad\qquad XII\text{: } x=2)\end{aligned}$$

The presence of the organoimido ligand, $NSiMe_3$, can be accounted for in terms of the spontaneous elimination of one of the OMe ligands followed by abstraction of a $SiMe_3$ group of the initially organoamido ligand, $N(SiMe_3)_2$, to give Me_3SiOMe. This process may be especially favoured by the presence of a strong bond Si–O in the latter product.

Complexes XI and XII are air sensitive hygroscopic white microcrystalline solids and are soluble in the common organic solvents.

All the compounds were characterized by analysis (see Table 1).

Spectroscopic studies

IR spectroscopy. The IR spectra of all the reported alkoxo compounds show the band due to the ν(O–O) stretching vibration at ca. 1200 cm^{-1}. For all these compounds the ν(Nb–O) stretching vibration is observed between 550–650 cm^{-1},

Table 1

Analyses of alkoxo- and (alkoxo)(amido)(imido)-niobium(V) complexes

Complex		Analyses (found (calcd.) (%))			Yield (%)
		C	H	N	
I	$NbCl_3(OCH_3)_2$	8.9 (9.2)	2.5 (2.3)		97
II	$NbCl_2(OCH_3)_3$	13.6 (14.0)	3.6 (3.5)		96
III	$NbCl_3(OCH_3)_2OPPh_3$	44.5 (44.5)	4.4 (3.9)		72
IV	$NbCl_3(OCH_3)_2OAsPh_3$	40.0 (41.2)	3.5 (3.6)		58
V	$NbCl_3(OCH_3)_2THF$	20.9 (21.6)	4.2 (4.3)		65
VI	$NbCl_4(OCH_3)_2^-\ PPh_4^+$	49.5 (49.1)	4.0 (4.1)		98
VII	$NbCl_2(OCH_3)_3OPPh_3$	46.9 (47.1)	4.6 (4.5)		57
VIII	$NbCl_3(OCH_3)_3^-\ PPh_4^+$	52.4 (51.3)	4.2 (4.6)		91
IX	$NbCl_3(OCH_2CH_3)_2OPPh_3$	46.0 (46.5)	4.8 (4.4)		77
X	$NbCl_3(OCH(CH_3)_2)_2OPPh_3$	47.6 (48.4)	5.3 (4.9)		60
XI	$NbCl(OCH_3)(N(SiMe_3)_2)(NSiMe_3)$	29.3 (29.5)	8.2 (7.3)	7.2 (6.9)	20
XII	$Nb(OCH_3)_2(N(SiMe_3)_2)(NSiMe_3)$	32.7 (32.8)	8.2 (8.3)	7.0 (7.0)	40

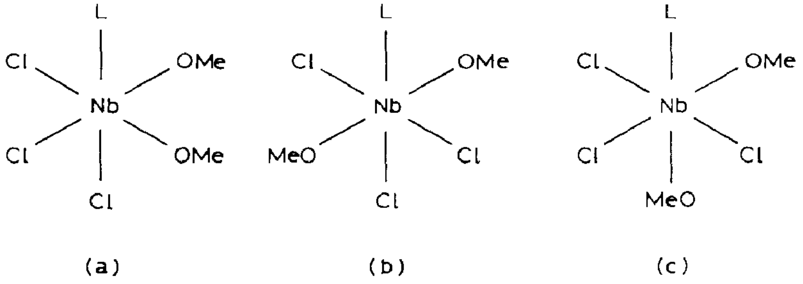

Fig. 1. Possible different isomers for complexes III–V.

but it cannot easily be assigned because it overlaps with strong bands from the other ligands.

NMR spectroscopy. The ^{1}H spectra at room temperature of the complexes I–VIII show several broad peaks between 4.75–4.10 ppm (see Table 2) due to the methyl protons of the OMe groups, which are not equivalent. Complexes I and II show a temperature dependent behaviour which can be attributed to a dynamic equilibrium between various dimeric units with σ-alkoxo groups. This behaviour has been previously reported for the Nb(OMe)$_5$ complex [6]. At low temperatures the ^{1}H NMR spectra show several peaks corresponding to the various isomers, and it is not possible to assign the resonances corresponding to terminal or bridging OMe groups in an octahedral arrangement for both niobium atoms.

For the complexes III–V the pattern observed in the methoxy region, consisting of two signals (see Table 2) with a proton integration ratio of 3 to 3, is in agreement with formation of an octahedral complex with two non-equivalent methoxy ligands (Fig. 1c).

The ^{1}H NMR data for complexes IX and X also suggest a similar octahedral geometry involving two non equivalent ethoxy or isopropoxy ligands (see Table 2). The spectroscopic data for complex VI (see Table 2) do not permit a choice between the two possible isomers with the methoxy groups in *cis* or *trans* dispositions.

The ^{1}H NMR spectra of complexes VII and VIII show several peaks (see Table 2) in the methoxy region, probably as a consequence of the existence of a mixture of two isomers in solution (Fig. 2). For the complex VIII the (b) and (c) isomers are equivalent.

In addition, the ^{1}H NMR spectra of all the complexes with σ-donating ligands show the resonances due to the L protons (see Table 2).

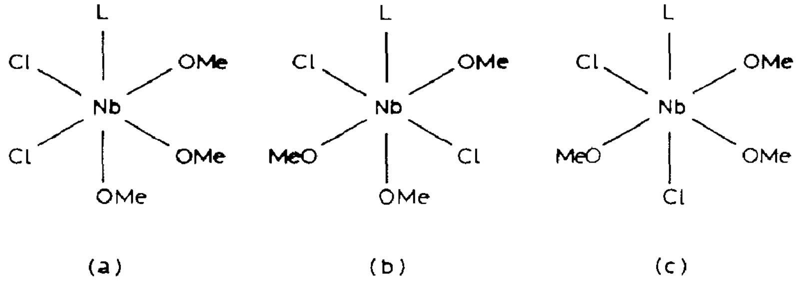

Fig. 2. Possible isomers for complexes VII and VIII.

Table 2

^{1}H and ^{13}C {^{1}H} NMR chemical shifts for alkoxo- and (alkoxo)(amido)(imido)-niobium(V) complexes

Compound	^{1}H (internal standard TMS) [a]			^{13}C {^{1}H} NMR (ppm)		
	H(O-C*H*R)	H(O-CH-*R*)	L or N(SiMe$_3$)$_2$ and NSiMe$_3$	OCH$_3$	N(SiMe$_3$)$_2$	N(SiMe$_3$)
I	4.75					
II	4.43; 4.60					
III	4.68(s, 3); 4.10(s, 3)		7.58(m, 15) Ph			
IV	4.63(s, 3); 4.38(s, 3)		7.75(m, 15) Ph			
V	4.75(s, 3); 4.49(s, 3)		4.49(t, 4) CH_2-O 2.05(t, 4) CH_2-CH$_2$			
VI	4.48(s, 6)		7.63(m, 20) Ph			
VII	4.00(s, 3); 4.50(s, 3) 4.05(s, 3); 4.55(s, 3)		7.50(m, 15); 8.00 (m, 15)			
VIII	4.37(s, 3); 4.32(s, 3) 4.28(s, 3)		7.72(m, 20)			
IX	5.00(q, 2); 4.40(q, 2)	1.46(t, 3); 1.27(t, 3) J(H-H = 7.2 (Hz)	7.70(m, 15)			
X	5.49(m, 1); 4.78(m, 1)	1.50(d, 6); 1.20(d, 6) J(H-H) = 6.2 (Hz)	7.73(m, 15)			
XI	4.06(s, 3)		0.48(s, 9) N(SiMe$_3$)$_2$; 0.10(s, 9) NSiMe$_3$ 0.43(s, 9)	[b] 68.20	2.40; 1.84	4.79
XII	4.36(s, 6)		0.45(s, 18) N(SiMe$_3$)$_2$; 0.10(s, 9) NSiMe$_3$	[c] 64.26	2.99	3.15

[a] In CDCl$_3$. [b] In CD$_2$Cl$_2$. [c] In C$_6$D$_6$.

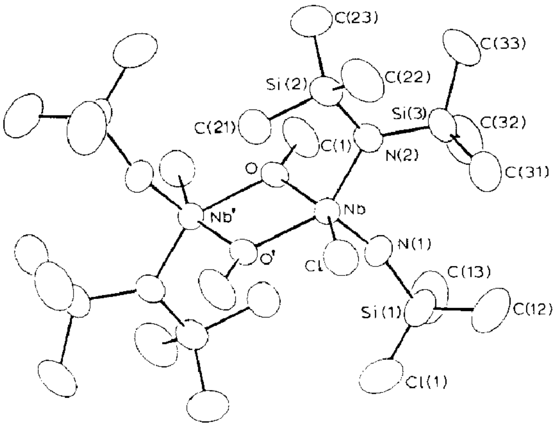

Fig. 3. View of the complex $[NbCl(\mu\text{-}OMe)(N(SiMe_3)_2)(NSiMe_3)]_2$.

The ^1H NMR spectra of complexes XI and XII show the resonances due to the methoxy, organoamido, and organoimido groups (see Table 2). Singlets are observed for the OMe and $SiMe_3$ protons, and the chemical shifts are in agreement with those previously [7] observed for organoamido tantalum(V) complexes.

The $^{13}C\ \{^1H\}$ NMR spectra of XI and XII (see Table 2) show the resonances due to the OMe and $SiMe_3$ carbon atoms, in agreement with the crystal structure of XI discussed below.

Crystal structure of $[NbCl(\mu\text{-}OMe)(N(SiMe_3)_2)(NSiMe_3)]_2$

Figure 3 displays a view of the molecule and the atom numbering used. Table 3 lists the atomic coordinates, and bond lengths and angles and some torsion angles are shown in Table 4.

The asymmetric unit consists of the $NbCl(\mu\text{-}OMe)(N(SiMe_3)_2)(NSiMe_3)$ fragment, the dimer being centrosymmetric around a crystallographic inversion center. The two niobium atoms are asymmetrically bridged by two methoxide groups, with Nb–O bond lengths of 2.104(3) and 2.157(2) Å, respectively. The coordination around the metallic centres is intermediate between a tetragonal pyramid and trigonal bipyramid.

The presence of an imido group is the most interesting feature of the compound. Terminal imido groups can be arranged in two ways, one as a linear four-electron donor ligand as in $Ta(NBu^t)(NMe_2)_3$ [8], with the Ta–N–R angle of exactly 180° owing to symmetry requirements, and the other as a bent two-electron donor ligand, as in $Mo(NPh)_2(S_2CNEt_2)_2$ [9], where the Mo–N–R bond angles are 139.4(4)° and 169.4(4)°, respectively.

The title compound has a Nb–N(1) bond length of 1.748(3) Å and a Nb–N(1)–Si(1) angle of 161.7(3)°; these data can be compared with those for other imidoniobium compounds, viz.: $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$ [10], 1.733(7) Å and 175.1(7)°; $Nb(p\text{-}NC_6H_4Me)(S_2CNEt_2)_3$ [11], 1.783(3) Å and 167.4(3)°; $[Nb_2Cl_8(MeCn)_2C_4H_6N_2)^{2-}$ [12], 1.752(6) Å and 172.5(7)°, the second of these, with the largest bond length and the smallest angle, has pentagonal bipyramidal geometry around the niobium atoms, while the others have octahedral environments. Our Nb–N(1) bond length of 1.748(3) Å must be regarded as a true triple

Table 3

Atomic parameters for $Nb_2Cl_2Si_6O_2N_4C_{20}H_{60}$ coordinates and thermal parameters as $U_{eq} = \frac{1}{3}\Sigma(U_{ij}a_i^\star a_j^\star \times a_i a_j \cos(a_i a_j))\times 10^5$

Atom	x	y	z	U_{eq}
Nb	0.08737(3)	0.09901(3)	0.56499(1)	3720(50)
Cl	−0.02252(12)	0.28420(13)	0.60682(6)	6568(96)
Si(1)	0.11194(17)	−0.08592(15)	0.70601(6)	6622(95)
Si(2)	0.24325(12)	0.31253(12)	0.49964(7)	5454(81)
Si(3)	0.39997(11)	0.19566(15)	0.62803(7)	5785(83)
O	0.10580(23)	−0.04337(26)	0.49309(13)	4196(92)
N(1)	0.12530(37)	−0.00156(40)	0.63474(16)	5340(129)
N(2)	0.25766(29)	0.19573(33)	0.56355(16)	4516(108)
C(1)	0.23193(44)	−0.10760(59)	0.49654(32)	7653(215)
C(11)	−0.06847(88)	−0.9770(90)	0.70640(34)	10033(334)
C(12)	0.19621(93)	0.01508(81)	0.77696(29)	9877(321)
C(13)	0.19117(90)	−0.25623(69)	0.70672(38)	10165(324)
C(21)	0.06654(49)	0.30664(53)	0.45071(26)	6488(175)
C(22)	0.27261(67)	0.49118(57)	0.53090(43)	9226(291)
C(23)	0.35591(71)	0.26719(89)	0.44436(35)	9351(306)
C(31)	0.36083(62)	0.29432(79)	0.69672(31)	8565(249)
C(32)	0.45533(65)	0.01904(77)	0.65410(40)	9640(293)
C(33)	0.54726(51)	0.27589(94)	0.60302(39)	9741(313)

Table 4

Relevant bond distances (Å), angles (°) and torsion angles (°) with e.s.d.'s in parentheses

Bond distances		Torsion angles		Bond angles	
Nb–Cl	2.403(1)	N(1)–Nb–N(2)–Si(2)	−176.5(2)	N(1)–Nb–N(2)	104.4(2)
Nb–O	2.104(3)	O–Nb–N(2)–Si(2)	80.2(2)	O–Nb–N(2)	94.9(1)
Nb–N(1)	1.748(3)	Cl–Nb–N(2)–Si(2)	−75.7(2)	O–Nb–N(1)	101.6(1)
Nb–N(2)	1.990(3)	N(1)–Nb–N(2)–Si(3)	−9.7(2)	Cl–Nb–N(2)	97.4(1)
				Cl–Nb–N(1)	98.5(1)
Si(1)–N(1)	1.753(4)	O–Nb–N(2)–Si(3)	−113.1(2)	Cl–Nb–O	152.9(1)
				C(12)–Si(1)–C(13)	110.5(4)
Si(1)–C(11)	1.852(9)	Cl–Nb–N(2)–Si(3)	91.0(2)	C(11)–Si(1)–C(13)	112.3(4)
Si(1)–C(12)	1.848(7)	N(2)–Nb–N(1)–Si(1)	140.9(8)	C(11)–Si(1)–C(12)	108.5(3)
				N(1)–Si(1)–C(13)	108.3(3)
Si(1)–C(13)	1.853(7)	O–Nb–N(1)–Si(1)	−120.8(8)	N(1)–Si(1)–C(12)	109.8(3)
Si(2)–N(2)	1.754(4)	Cl–Nb–N(1)–Si(1)	40.9(8)	N(1)–Si(1)–C(11)	107.4(3)
				C(22)–Si(2)–C(23)	111.8(3)
Si(2)–C(21)	1.878(5)	Cl–Nb–O–C(1)	162.0(3)	C(21)–Si(2)–C(23)	107.3(3)
Si(2)–C(22)	1.871(6)	N(1)–Nb–O–C(1)	−60.8(3)	C(21)–Si(2)–C(22)	106.5(2)
				N(2)–Si(2)–C(23)	111.7(3)
Si(2)–C(23)	1.869(8)	N(2)–Nb–O–C(1)	45.0(3)	N(2)–Si(2)–C(22)	110.8(3)
Si(3)–N(2)	1.765(3)	C(11)–Si(1)–N(1)–Nb	19.4(9)	N(2)–Si(2)–C(21)	108.3(2)
				C(32)–Si(3)–C(33)	105.1(3)
Si(3)–C(31)	1.863(7)	C(12)–Si(1)–N(1)–Nb	−98.4(8)	C(31)–Si(3)–C(33)	109.1(3)
Si(3)–C(32)	1.865(8)	C(13)–Si(1)–N(1)–Nb	140.9(8)	C(31)–Si(3)–C(32)	110.6(3)
				N(2)–Si(3)–C(33)	111.0(3)
Si(3)–C(33)	1.877(7)	C(21)–Si(2)–N(2)–Nb	−0.9(3)	N(2)–Si(3)–C(32)	112.0(3)
O–C(1)	1.423(5)	C(22)–Si(2)–N(2)–Nb	115.6(3)	N(2)–Si(3)–C(31)	108.8(2)
				Nb–O–C(1)	118.7(3)
		C(23)–Si(2)–N(2)–Nb	−118.9(3)	Nb–N(1)–Si(1)	161.7(3)
				Si(2)–N(2)–Si(3)	120.9(2)
				Nb–N(2)–Si(3)	124.4(2)
				Nb–N(2)–Si(2)	113.4(2)

bond, although the departure from linearity of the Nb–N(1)–Si(1) linkage is slightly bigger than expected. This can be explained in terms of the steric effects of the bulky imido- and amidosilyl ligands, but these may also be some influence of the strong $-M$ effect of the $SiMe_3$ group.

The Nb–N(2) bond length corresponding to the amido ligand is 1.990(3) Å, which is shorter than that usually found for a Nb–N single bond and may indicate some π-electron contribution. The three bonds of the N(2) atom deviated slightly from planarity, N(2) being 0.123(3) Å from the plane defined by NbSi(2)Si(3).

Packing in the unit cell is determined by Van der Waals forces and there are no significant intermolecular contacts.

Experimental

All operations were carried out under vacuum or in an inert atmosphere with Schlenk type glassware. Solvents were dried and distilled under N_2 and degassed before use. $NbCl_5$ was purchased from Fluka and was purified by sublimation before use. $Me_3Si(OR)$, R = Me, Et, Pr^i) were prepared by the reaction of hexamethyldisilazane with the appropriate alcohol in the presence of a few drops of Me_3SiCl. $[Li[N(SiMe_3)_2]Et_2O]_2$ and $NbCl_5OPPh_3$ were prepared as previously described [13,14]. IR spectra were recorded with Nujol mulls between CsI plates in the region 4000–200 cm^{-1} using a Perkin–Elmer 599 spectrophotometer. Carbon and hydrogen analyses were performed with a Perkin–Elmer 240B microanalyzer. ^1H and ^{13}C NMR spectra were recorded on Varian FT 80A instruments.

$NbCl_{5-x}(OMe)_x$ (I, II)

Me_3SiOMe (0.770 g, 7.40 mmol) was added to a suspension of $NbCl_5$ (1.000 g, 3.70 mmol) in 25 ml of dichloromethane at −78 °C. The stirred mixture was allowed to warm to room temperature. The resulting yellow solution was concentrated under reduced pressure (10 ml) and then 20 ml of hexane were added, to give a white crystalline solid, which was washed with hexane, dried under vacuum and identified as complex I.

Complex II was prepared similarly when three or more equivalents of Me_3SiMe were used.

$NbCl_{5-x}(OR)_xL$ (III–X)

$OPPh_3$ (1.110 g, 4.00 mmol) was added to $NbCl_3(OMe)_2$ in toluene (15 ml). The solution was stirred at room temperature for 24 h. The white microcrystalline solid which separated was filtered off, repeatedly washed with cold toluene, and dried under vacuum. It was identified as complex III.

Complexes IV and VII were prepared similarly. Complex V was prepared by use of THF as solvent, and recrystallized from a THF/hexane mixture. Complexes VI and VIII were prepared from PPh_4Cl in dichloromethane, and complexes IX and X were prepared in THF.

$[NbCl_{x-2}(OMe)_{3-x}(\mu\text{-}OMe)[N(SiMe_3)_2](NSiMe_3)]_2$ (XI, XII)

$[Li[N(SiMe_3)_2]Et_2O]_2$ (1.850 g, 7.66 mmol) was added to $NbCl_3(OMe)_2$ (1.000 g, 3.83 mmol) in diethyl ether (20 ml). After 12 h stirring at room temperature the solution was pumped to dryness and the resulting solid extracted with hexane (10 ml), and the extract was kept at −20 °C to give compound XI as a white crystalline solid.

Compound XII was prepared similarly from $NbCl_2(OMe)_3$.

Crystal structure of compound XI

Crystal data: $NbClSi_3ON_2C_{10}H_{30}$, monoclinic, $P2_1/c$, t, a 10.236(1), b 9.789(1), c 21.201(3) Å, β 102.67(1)°, V 2072.6(4) Å^3, D_c 1.30 g cm^{-3}, M 406.98, $F(000) = 848$, μ 8.509 cm^{-1}, $Z = 4$.

Unit cell parameters were determined from a least-squares fit of 50 reflexions within $2 < \theta < 30°$. A white crystal of XI was mounted on a Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.7107 Å). 5976 reflexions were measured up to θ 30°, with bisecting geometry and $\omega/2\theta$ scan mode. 4272 reflexions were considered as observed on the criterion $I > 3\sigma(I)$ ($R_{int} = 0.01$). The data were corrected for Lorentz, polarization, and absorption [15] factors.

The structure was solved by MULTAN 80 [16], which gave the position of the niobium atom and DIRDIF [17], and refined by full matrix least-squares. 40% of the hydrogen atoms were found from a difference synthesis, and the rest were placed in calculated positions. All of them were included in the refinement with fixed isotropic temperature factors. An empirical weighting scheme [18] was used so as to give no trends in $\langle w\, \Delta^2 F\rangle$ vs. $\langle F_o\rangle$ and vs $\langle \sin\theta/\lambda\rangle$. Final mixed refinement gave $r = 0.042$ ($R_w = 0.052$) for 163 variables with $(\Delta/\sigma)_{max} = 0.05$ and $(\Delta/\sigma)_{av} = 0.004$. Maximal residual electron density was 0.64 eÅ^{-3}. Scattering factors were taken from International Tables for X-ray Crystallography [19]. Calculations performed with X-ray system [20] and PARST [21] on VAX-11/750 computer.

References

1 D.C. Bradley, R.C. Mehrotra, and P.D. Gaur, Metal Alkoxides, Academic Press, London, New York, San Francisco, 1978.
2 D.C. Bradley, Coord. Chem. Rev., 2 (1967) 299.
3 M.H. Chisholm, J. Solid State Chem., 57 (1985) 120.
4 W.A. Nugent, B.L. Haymore, Coord. Chem. Rev., 31 (1980) 123.
5 L.B. Handy, K.G. Sharp, and F.F. Brinckman, Inorg. Chem., 11 (1972) 523.
6 L.G. Hubert-Pfalzgraf, Inorg. Chim. Acta, 12 (1975) 229.
7 D.C. Bradley, M.B. Hursthouse, K.M. Abdul Malik, and B.C. Yuru, Inorg. Chim. Acta, 44 (1980) L5.
8 W.A. Nugent, and R.L. Harlow, J. Chem. Soc. Chem. Comm., (1978) 579.
9 B.L. Haymore, E.A. Maatta, and R.A.D. Wentworth, J. Am. Chem. Soc., 101 (1979) 2063.
10 F.A. Cotton, S.A. Duraj, and W.J. Roth, J. Am. Chem. Soc., 106 (1984) 4749.
11 L. Seng Tan, G.V. Goeden, and B.L. Haymore, Inorg. Chem., 22 (1983) 1744.
12 P.A. Finn, M.S. King, P.A. Kilty, and R.E. McCarley, J. Am. Chem. Soc., 97 (1975) 220.
13 M.F. Lappert, M.J. Slade, A. Singh, J.L. Atwood, R.D. Rogers, and R. Shakir, J. Am. Chem. Soc., 105 (1983) 302.
14 D. Brown, J.F. Easey, and J.G.H. du Peer, J. Chem. Soc. A, (1966) 258.
15 N. Walker, and D. Stuart, Acta Cryst., A, 39 (1983) 158.
16 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq, and M.H. Woolfson (1980). MULTAN80. A system of computer programs for automatic solution of crystal structures from X-ray diffraction data. Univ. of York, England, and Louvain, Belgium.
17 P.T. Beurskens, W.P. Bosman, H.M. Doesburg, R.O. Gould, Th.E.M. van der Hark, P.A.J. Prick, J.H. Noordik, G. Beurskens, and V. Parthasarathi (1981). DIRDIF Manual 81. Crystallography Laboratory, Nijmegen, Netherlands.

18 M. Martinez-Ripoll, and F.H. Cano, 1975. PESOS. A computer program for the automatic treatment of weighting schemes. Instituto Rocasolano, Madrid, Spain.
19 International Tables for X-Ray Crystallography, 1974, Vol. IV. Birmingham. Kynoch Press.
20 J.M. Stewart, F.A. Kundell, and J.C. Baldwin (Eds.), 1976, The X-Ray System. Computer Science Center. Univ. of Maryland. College Park. Maryland.
21 M. Nardelli, Comput. Chem., 7 (1983) 95.