1982 *Inorg. Chem.* **1997,** *36,* 1982−1986

Notes

Mononuclear Niobium Imido and Oxo Complexes Supported by *N,N′*-Bis(trimethylsilyl)benzamidinate Ligands. X-ray Structures of $[Nb(NBu^t)\{PhC(NSiMe_3)_2\}Cl_2(py)]$ and $[Nb(O)\{(4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$

Peter J. Stewart, Alexander J. Blake, and Philip Mountford*

Department of Chemistry, University of Nottingham,
Nottingham NG7 2RD, U.K.

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Introduction

The study of transition metal oxo and imido compounds continues to be an area of substantial interest.[1−8] An wide variety of ancillary ligand sets has now been used to support these multiply bonded functional groups resulting in very different reactivity patterns and structural motifs. Somewhat surprisingly, amidinate ligands[9,10] [having the general formula $RC(NR')_2$] have been relatively little used in metal imido or oxo chemistry.[11−16] Recently, several research groups have reported interesting and novel reaction chemistry of amidinate-supported early transition metal complexes in general,[17−22] and we were interested to develop synthetic routes to new group 5 amidinate complexes containing metal−ligand multiple bonds. Here we describe the synthesis and properties of some mononuclear niobium imido and oxo complexes supported by *N,N′*-bis(trimethylsilyl)benzamidinato ligands. [Note: Although for ease of representation all niobium−imido or −oxo linkages are drawn "Nb═NR" or "Nb═O", the formal metal−ligand multiple bond order in the complexes described herein is probably best thought of as three (pseudo-$\sigma^2\ \pi^4$; triple bond) rather than as two.[2]]

Experimental Section

General Methods and Instrumentation. All manipulations were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or drybox techniques. All solvents and pyridine were predried over activated molecular sieves and refluxed over the appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. $CDCl_3$ and CD_2Cl_2 were dried over freshly ground calcium hydride at rt (rt = room temperature), distilled under vacuum, and stored under N_2 in Young's ampules. Other reagents were used as received (Aldrich). NMR samples were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young's Teflon valve.

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer. The spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. ^{13}C NMR assignments were supported by DEPT-135 and DEPT-90 experiments as appropriate. IR spectra were recorded on a Nicolet 205 FTIR spectrometer in the range 4000−400 cm^{-1}. Samples were prepared in the drybox as Nujol mulls between CsBr plates, and data are quoted in wavenumbers (ν, cm^{-1}). Elemental analyses were carried out by the analysis department of this laboratory or by Canadian Microanalytical Service Ltd.

Literature Preparations. $Li[(4\text{-}C_6H_4R)C(NSiMe_3)_2]$ (R = H or Me),[23] $PhC(NSiMe_3)(N\{SiMe_3\}_2)$,[24] $[Nb(NBu^t)Cl_3(py)_2]$,[25] and $[Nb(O)Cl_3(THF)_2]$[26] were prepared according to literature methods.

$[Nb(NBu^t)\{PhC(NSiMe_3)_2\}_2Cl]$ (1). A solution of $Li[PhC(NSiMe_3)_2]$ (0.495 g, 1.83 mmol) in THF (20 mL) was added over 10 min to a stirred solution of $[Nb(NBu^t)Cl_3(py)_2]$ (0.390 g, 0.91 mmol) in THF (20 mL) at −40 °C. The solution was allowed to warm to room temperature and then stirred for 15 h. The volatiles were removed under reduced pressure, and the solid residue was redissolved in hexane (30 mL) and filtered. The solvent was then removed under reduced pressure to give **1** as a spectroscopically pure yellow powder. Yield: 0.55 g (83%). Recrystallization from hexane gave analytically pure yellow crystals of **1**.

^1H NMR ($CDCl_3$, 300 MHz, 25 °C): 7.35 (m, 10 H, overlapping *o*-, *m*- and *p*-C_6H_5), 1.42 (s, 9 H, NBu^t) −0.03 (s, 36 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 25 °C): 178.5 (C_6H_5C), 140.9, (*ipso*-C_6H_5), 128.8, 128.03, 126.5 (3 × *o*-, *m*- or *p*-C_6H_5), 67.6 ($NCMe_3$), 31.5 ($NCMe_3$), 2.6 ($SiMe_3$). IR: 1945 (w), 1881 (w), 1677 (w), 1641 (w), 1591 (w), 1546 (s), 1403 (s), 1318 (s), 1246 (vs), 1178 (w), 1162 (w), 1133 (w), 1096 (w), 1074 (w), 1030 (w), 1005 (m), 995 (m), 980 (vs), 899 (m), 842 (vs), 786 (m), 761 (s), 741 (s), 716 (m), 702 (m), 634 (w), 616 (w), 560 (w), 500 (m), 446 (w) cm^{-1}. Anal. Calcd (found) for $C_{30}H_{54}ClN_5NbSi_4$: C, 49.6 (48.6); H, 7.6 (7.6); N, 9.6 (9.6).

$[Nb(NBu^t)\{PhC(NSiMe_3)_2\}Cl_2(py)]$ (2). This compound was obtained as an admixture with **1**. A solution of $Li[PhC(NSiMe_3)_2]$ (0.162 g, 0.60 mmol) in THF (15 mL) was added over 10 min to a stirred solution of $[Nb(NBu^t)Cl_3(py)_2]$ (0.245 g, 0.60 mmol) in THF (15 mL) at −40 °C. The solution was allowed to warm to room temperature and then stirred for 23 h. The volatiles were removed under reduced pressure, and the solid residue was redissolved in CH_2Cl_2 (20 mL) and filtered. The solvent was then removed, and ^1H NMR showed the resulting yellow solid (0.34 g) to be a mixture of **1** and **2**. Recrystallization from hexane failed to separate the two components. Yield of **2** (by ^1H NMR): 68%.

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Table 1. X-ray Data Collection and Processing Parameters for [Nb(NBu^t){PhC(NSiMe$_3$)$_2$}Cl$_2$(py)]·0.25C$_6$H$_{14}$ (**2**·0.25C$_6$H$_{14}$) and [Nb(O){(4-C$_6$H$_4$Me)C(NSiMe$_3$)$_2$}$_2$Cl] (**4**)

complex	**2**·0.25C$_6$H$_{14}$	**4**
molecular formula	C$_{22}$H$_{37}$Cl$_2$N$_4$NbSi$_2$·0.25C$_6$H$_{14}$	C$_{28}$H$_{50}$CN$_4$NbOSi$_4$
fw	599.09	736
temp/°C	−123(1)	−53(2)
wavelength/Å	0.710 73	0.710 73
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens		
a/Å	10.972(3)	10.573(9)
b/Å	17.100(4)	11.173(8)
c/Å	17.777(3)	17.03(1)
α/deg	91.37(2)	100.65(6)
β/deg	95.51(2)	93.92(6)
γ/deg	93.03(2)	106.90(6)
V/Å^3	3313.9(10)	1875.4(3)
Z	4	2
D(calcd)/g·cm^{-3}	1.20	1.24
abs coeff/mm^{-1}	0.613	0.53
F(000)	1250	736
cryst size/mm	0.75 × 0.67 × 0.60	0.58 × 0.54 × 0.50
θ range for data collcn/deg	2.52−25.00	2.51−25.00
index ranges	$-13 \le h \le 12$, $-20 \le k \le 20$, $0 \le l \le 21$	$-11 \le h \le 12$, $-12 \le k \le 11$, $-19 \le l \le 18$
reflcns collcd	11 217	6566
indepdt reflcns	11 217	5026
R(merge)		0.048
abs corr	ψ scans	ψ scans
max and min transm	0.501 and 0.441	0.823 and 0.739
decay corr/%	none	11.2
obsd reflcns (criterion)	10313 [$I > 3\sigma(I)$]	3769 [$I > 2\sigma(I)$]
no. of restraints applied	14	0
no. of params refined	585	352
weighting scheme	Chebychev polynomial	unit weights
extinction coeff	41(16)	none
final R indices: R,^{a} R_w^{b}	0.035, 0.041	0.057, 0.064
goodness-of-fit	0.964	1.33
final $(\Delta/\sigma)_{max}$	0.580	0.099
largest resid peaks/e Å^{-3}	0.18, −0.19	1.99, −0.27

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): 9.07 (2 H, d, $J = 4.9$ Hz, o-NC$_5$H$_5$), 7.83 (1 H, t, $J = 7.6$ Hz, p-NC$_5$H$_5$), 7.37 (5 H, m, m-NC$_5$H$_5$ and o- and p-C$_6$H$_5$), 7.02 (m, 2 H, m-C$_6$H$_5$) 1.46 (s, 9H, NBu^t) −0.12 (s, 18 H, SiMe$_3$). The NMR assignments are made by comparison of the spectrum for the mixture of **1** and **2** with that of pure **1**.

[Nb(O){PhC(NSiMe$_3$)$_2$}$_2$Cl] (3). A solution of Li[PhC(NSiMe$_3$)$_2$] (0.592 g, 2.19 mmol) in THF (20 mL) was added over 10 min to a stirred solution of [Nb(O)Cl$_3$(THF)$_2$] (0.392 g, 1.09 mmol) in THF (20 mL) at −45 °C. The solution was allowed to warm to room temperature and then stirred for 18 h. The volatiles were removed under reduced pressure, and the solid residue was redissolved in hexane, filtered, and concentrated. Cooling at −25 °C for 16 h afforded **3** as yellow crystals which were washed with pentane (2 × 10 mL) and dried *in vacuo*. Yield: 0.538 (74%).

^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): 7.42, 7.28 (10 H, m, o-, m- and p-C$_6$H$_5$), −0.01 (36 H, s, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 25 °C): 181.8 (C$_6$H$_5$*C*), 139.4, (*ipso*-C$_6$H$_5$), 129.5, 128.2, 126.3 (3 × o-, m-, or p-C$_6$H$_5$), 1.9 (SiMe$_3$). IR: 1538 (s), 1312 (s), 1248 (s), 1156 (w), 1011 (m), 978 (s), 927 [s, ν(Nb=O)], 841 (vs), 763 (s), 738 (s), 704 (s), 620 (w), 508 (m), 448 (w). Anal. Calcd (found) for C$_{26}$H$_{46}$ClN$_4$NbOSi$_4$: C, 46.5 (44.8); H, 6.9 (7.1); N, 8.3 (7.9).

[Nb(O){(4-C$_6$H$_4$Me)C(NSiMe$_3$)$_2$}$_2$Cl] (4). A solution of Li[(4-C$_6$H$_4$Me)C(NSiMe$_3$)$_2$] (0.435 g, 1.35 mmol) in THF (30 mL) was added over 15 min to a stirred solution of [Nb(O)Cl$_3$(THF)$_2$] (0.241 g, 0.67 mmol) in THF (30 mL) at −50 °C. The solution was allowed to warm to room temperature and then stirred for 60 h. The volatiles were removed under reduced pressure, and the solid residue was redissolved in hexane (30 mL) and filtered. Concentration to 15 mL and then cooling to −25 °C afforded **4** as yellow crystals which were washed with hexane (2 × 5 mL) and dried *in vacuo*. Yield: 0.068 g (15%).

^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): 7.18 (8 H, s, overlapping o- and m-C$_6$*H*$_4$Me), 2.39 (6 H, s, C$_6$H$_4$*Me*), 0.02 (36 H, s, SiMe$_3$). IR: 1612 (w), 1548 (m), 1299 (s), 1247 (s), 1011 (w), 980 (vs), 930 [vs, ν(Nb=O)], 839 (vs), 763 (m), 714 (m), 644 (w), 475 (w). Anal. Calcd (found) for C$_{28}$H$_{50}$ClN$_4$NbOSi$_4$: C, 48.1 (48.2); H, 7.2 (7.6); N, 8.0 (7.9).

Crystal Structure Determination of [Nb(NBu^t){PhC(NSiMe$_3$)$_2$}Cl$_2$(py)]·0.25C$_6$H$_{14}$ (2·0.25C$_6$H$_{14}$) and [Nb(O){(4-C$_6$H$_4$Me)C(NSiMe$_3$)$_2$}$_2$Cl] (4). Crystal data collection and processing parameters are given in Table 1. Crystals were mounted on a glass fiber with RS3000 oil and transferred to the goniometer head of a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[27] An absorption correction based on ψ scans was applied to the data, and equivalent reflections were merged. The structures were solved by direct methods (SIR92[28]). Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Ligand non-hydrogen atoms were refined anisotropically. Further examination of a Fourier difference synthesis for **2** revealed residual electron density which was sucessfully modeled as a quarter-occupancy (half chemical occupancy × half crystallographic site occupancy) hexane molecule of crystallization and refined in the isotropic approximation subject to "soft" similarity restraints.[29] H atoms were placed in estimated positions with C−H = 0.96 Å and $U_{iso} = 1.3U_{equiv}$ or U_{iso} of the atom to which they were bonded and were refined "riding" on their supporting atom. For **2** a Chebychev[30] weighting scheme was applied in the final stages of refinement and an overall secondary extinction parameter[31] was applied. For **4**, examination of the refined secondary extinction parameter and $|F_o|$ and $|F_c|$ for the

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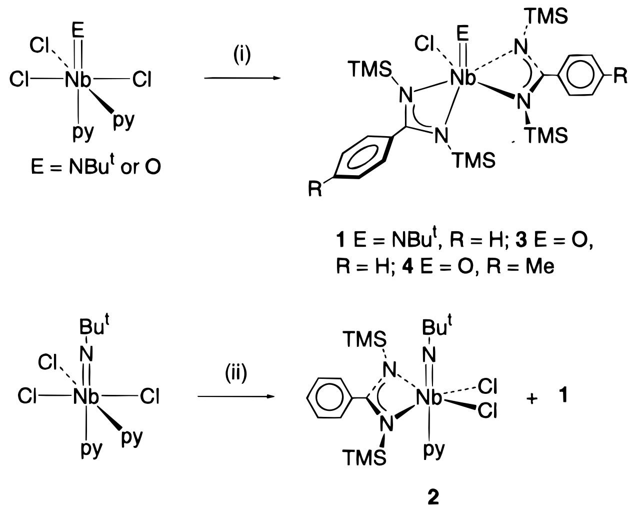
Scheme 1. Synthetic Routes to Mononuclear Niobium Imido and Oxo Complexes Supported by *N,N′*-Bis(trimethylsilyl)benzamidinato Ligands[a]



[a] Reagents and conditions: (i) Li[$RC_6H_4C(NSiMe_3)_2$] (2 equiv), THF, 15 h, for **1** 83%, **3** 74%, **4** 15%; (ii) Li[$PhC(NSiMe_3)_2$] (1 equiv), THF, 23 h, **2** 68% (by NMR analysis of the mixture).

strongest reflections and an agreement analysis suggested that no extinction correction or weighting scheme needed to be applied. A large peak (1.99 e Å^{-3}) in the final Fourier difference synthesis for **4** located 0.96 Å from Nb(1) is attributed to residual absorption effects.

All crystallographic calculations were performed using SIR92[28] and CRYSTALS-PC.[32] Full listings of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See the Notice to Authors, Issue No. 1.

Results and Discussion

Although a variety of amidinate ligands of the general formula $RC(NR')_2$ have been described in the literature, we were particularly attracted by the *N,N′*-bis(trimethylsilyl)benzamidinato derivatives $ArC(NSiMe_3)_2$ (Ar = Ph or substituted phenyl) because of the ease of preparation of their lithium salts[33] and the solubility properties they generally impart to their metal complexes. The benzamidinate-supported vanadium imido complexes [V(NR){$PhC(NSiMe_3)_2$}X_2] (X = Cl, R = Bu^t or 4-C_6H_4-Me; X = OPh, R = Bu^t) and [V(NR){$PhC(NSiMe_3)_2$}$_2$Cl] (R = Bu^t or 4-C_6H_4Me) have recently been prepared.[13] However, no imido or oxo derivatives of the heavier group 5 elements with benzamidinate coligands have previously been reported.

Reaction of [Nb(NBu^t)$Cl_3(py)_2$][25] with 2 equiv of Li[PhC($NSiMe_3)_2$] in THF followed by recrystallization from hexane afforded the bis(benzamidinato)niobium imido derivative [Nb(NBu^t){$PhC(NSiMe_3)_2$}$_2$Cl] (**1**) in 71% yield. The compound shows a single $SiMe_3$ resonance in its ^{1}H and ^{13}C NMR spectra. This could indicate either a static C_{2v} symmetrical structure with mutually *trans* imido and chloride ligands or a highly fluxional compound with mutually *cis* imido and chloride ligands as shown in Scheme 1. Although the latter geometry should, in principle, feature four $SiMe_3$ resonances in the ^{1}H and ^{13}C NMR spectra, we favor it by comparison with the crystallographically characterized vanadium imido [V(N-4-C_6H_4Me){$PhC(NSiMe_3)_2$}$_2$Cl] and niobium oxo [Nb(O){(4-C_6H_4R)C($NSiMe_3)_2$}$_2$Cl] (R = H (**3**) or Me (**4**); *vide infra*) analogues. These are all fluxional in solution, the oxo complexes also showing only one $SiMe_3$ environment in their NMR spectra.

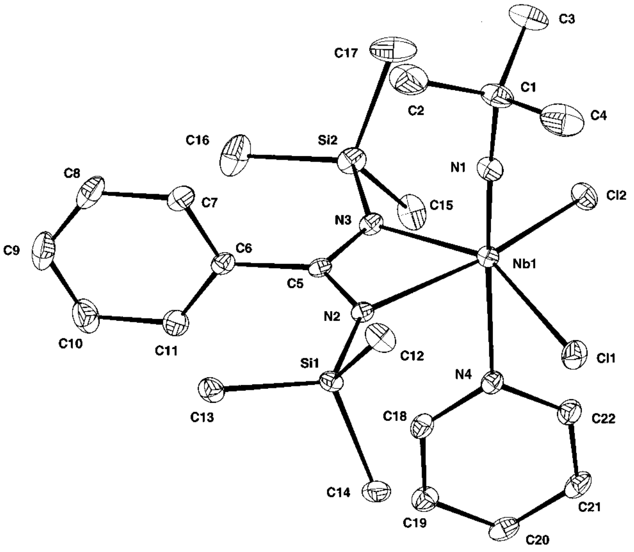


Figure 1. CAMERON[41] plot of one of the two crystallographically independent molecules of [Nb(NBu^t){$PhC(NSiMe_3)_2$}Cl_2(py)] (**2**). Hydrogen atoms and the hexane molecule of crystallization omitted for clarity. Thermal ellipsoids are drawn at the 20% probablility level.

Attempts to prepare mono(benzamidinato)niobium imido complexes from reaction of [Nb(NBu^t)$Cl_3(py)_2$] with 1 equiv of Li[$PhC(NSiMe_3)_2$] gave an essentially inseparable mixture of **1** and [Nb(NBu^t){$PhC(NSiMe_3)_2$}Cl_2(py)] (**2**). Attempts to prepare **2** by comproportionation of **1** and [Nb(NBu^t)$Cl_3(py)_2$] in either CH_2Cl_2 or $CDCl_3$ (by NMR) returned only unreacted starting materials. Furthermore, attempted synthesis of **2** from $PhC(NSiMe_3)$(N{$SiMe_3$}$_2$)[24] and [Nb(NBu^t)$Cl_3(py)_2$] gave irreproducible mixtures. These appeared to contain **2**, but a pure substance could not be separated. Hence **2** was only spectroscopically characterized as an admixture with **1**. However, cooling of a hexane solution containing **1** and [Nb(NBu^t){$PhC(NSiMe_3)_2$}Cl_2(py)] (**2**) afforded a few X-ray-quality crystals of **2**. The crystals contain a half-occupancy hexane molecule of crystallization and two crystallographically independent molecules of **2** in the asymmetric unit. The molecular structure of **2** is shown in Figure 1, and selected bond lengths and angles are given in Table 2.

The compound **2** has a six-coordinate niobium(5+) center with a pyridine ligand *trans* to the *tert*-butylimido group. The other 4 coordination sites are occupied by two *cis* chloride ligands which are *trans* to a bidentate $PhC(NSiMe_3)_2$. The Nb−N(imido) bond length in **2** [1.749(2) and 1.745(2) Å for the crystallographically independent molecules] is similar to the corresponding values for other niobium(5+) *tert*-butylimido bonds [range 1.731(3)−1.756(3) Å for three complexes].[34−36] The Nb−N(pyridine) bond length [2.478(2) and 2.490(2) Å] is very similar to that in *trans*-[Nb(NBu^t)Cl_4(py)]$^-$.[34] A search of the Cambridge Structural Database[37,38] showed that the Nb−Cl distances are normal for a complex of this type. The two Nb−N(benzamidinate) bond lengths [2.199(2) and 2.195(2); 2.196(2) and 2.193(2) Å] are the same within error and are

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Nb(NBu^t)\{PhC(NSiMe_3)_2\}Cl_2(py)]$ (**2**)[a]

Nb(1)−N(1)	1.749(2) [1.745(2)]	N(1)−C(1)	1.451(3) [1.446(3)]
Nb(1)−N(2)	2.199(2) [2.196(2)]	N(2)−Si(1)	1.753(2) [1.753(2)]
Nb(1)−N(3)	2.195(2) [2.193(2)]	N(2)−C(5)	1.329(3) [1.326(3)]
Nb(1)−N(4)	2.478(2) [2.490(2)]	N(3)−Si(2)	1.754(2) [1.755(2)]
Nb(1)−Cl(1)	2.3919(6) [2.3872(6)]	N(3)−C(5)	1.330(3) [1.325(3)]
Nb(1)−Cl(2)	2.3850(6) [2.3896(6)]	C(5)−C(6)	1.495(3) [1.498(3)]
N(1)−Nb(1)−N(2)	98.09(8) [97.67(7)]	N(4)−Nb(1)−Cl(1)	79.86(4) [82.45(4)]
N(1)−Nb(1)−N(3)	99.75(8) [97.39(7)]	N(1)−Nb(1)−Cl(2)	96.76(6) [98.53(6)]
N(2)−Nb(1)−N(3)	61.01(6) [61.03(6)]	N(2)−Nb(1)−Cl(2)	152.45(5) [152.56(5)]
N(1)−Nb(1)−N(4)	177.26(8) [179.60(7)]	N(3)−Nb(1)−Cl(2)	93.66(5) [94.95(5)]
N(2)−Nb(1)−N(4)	83.79(6) [82.50(6)]	N(4)−Nb(1)−Cl(2)	82.32(4) [81.45(5)]
N(3)−Nb(1)−N(4)	82.90(6) [83.02(6)]	Cl(1)−Nb(1)−Cl(2)	105.44(2) [104.53(2)]
N(1)−Nb(1)−Cl(1)	97.94(7) [97.17(6)]	N(2)−C(5)−N(3)	114.1(2) [114.4(2)]
N(2)−Nb(1)−Cl(1)	95.33(4) [95.22(5)]	N(2)−C(5)−C(6)	123.0(2) [123.1(2)]
N(3)−Nb(1)−Cl(1)	152.15(5) [153.58(5)]	N(3)−C(5)−C(6)	122.8(2) [122.5(2)]

[a] The values in brackets correspond to those of the other crystallographically independent molecule of **2** in the asymmetric unit.

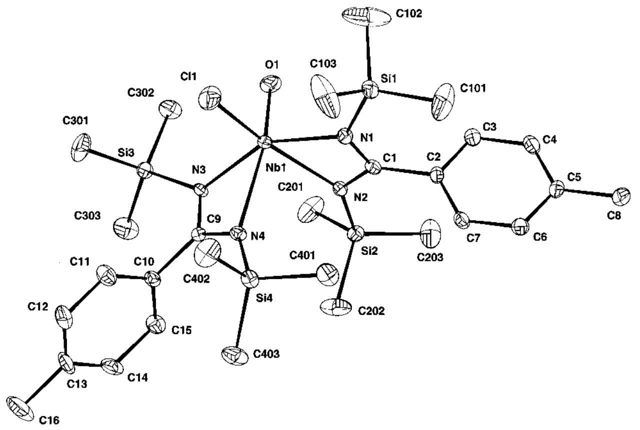

Figure 2. CAMERON[41] plot of $[Nb(O)\{(4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$ (**4**). Hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level.

comparable with those of **3** and **4** (*vide infra*), the only other structurally characterized niobium benzamidinate complexes.

We were also interested to prepare oxo analogues of **1**. Addition of 2 equiv of $Li[PhC(NSiMe_3)_2]$ to $[Nb(O)Cl_3(THF)_2]$[26] gave the desired bis(benzamidinate) derivative $[Nb(O)\{PhC(NSiMe_3)_2\}_2Cl]$ (**3**) in 74% yield. Attempts to prepare mono(benzamidinato)niobium oxo complexes gave only intractable mixtures. Crystals of **3** were obtained from hexane solution but were disordered about a crystallographic 2-fold rotation axis which bisects the Cl−Nb=O angle. In order to obtain a crystallographically well-behaved bis(benzamidinato)niobium oxo complex we prepared the 4-methyl analogue $[Nb(O)\{(4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$ (**4**) from $Li[(4\text{-}C_6H_4Me)C(NSiMe_3)_2]$ and $[Nb(O)Cl_3(THF)_2]$. The ^1H NMR spectra of **3** and **4** are very similar, and both show a single $SiMe_3$ resonance indicative of either a fluxional complex or a static C_{2v} symmetry solution structure.

Cooling a hexane solution of $[Nb(O)\{(4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$ (**4**) afforded X-ray-quality crystals. The molecular structure of **4** is shown in Figure 2, and selected bond lengths and angles are given in Table 3. The structure of **4** confirms that shown in Scheme 1 and is analogous to that proposed for $[Nb(NBu^t)\{PhC(NSiMe_3)_2\}_2Cl]$ (**1**).

The compound **4** has a six-coordinate Nb(5+) center with mutually *cis* oxo and chloro ligands. One $PhC(NSiMe_3)_2$ ligand has one N donor atom *cis* [N(3)] and one approximately *trans* [N(4)] to the oxo ligand. The other $PhC(NSiMe_3)_2$ ligand has both N donor atoms *cis* to the oxo ligand. The niobium−oxo bond length in **4** [Nb(1)−O(1) = 1.781(5) Å] is the longest reported for a neutral niobium oxo complex.[1,37] The $PhC(NSiMe_3)_2$ ligand which has both N donor atoms *cis* to the oxo ligand has very similar Nb−N bond lengths [Nb(1)−N(1) = 2.195(6) Å, Nb(1)−N(2) = 2.189(6) Å], which are also comparable to those found in **2**. In the other $PhC(NSiMe_3)_2$ ligand, the *cis* (with respect to the oxo ligand) Nb−N bond length [Nb(1)−N(3) = 2.085(5) Å] is shorter than any of the other Nb−N(benzamidinate) bonds encountered, whereas the *trans* Nb−N bond length [Nb(1)−N(4) = 2.402(6) Å] is much longer. The very substantial difference of 0.317(8) Å between the *cis* and *trans* bond lengths reflects the strong *trans* influence of the multiply bonded oxo ligand. The Nb−Cl bond length [Nb(1)−Cl(1) = 2.333(3) Å] is slightly shorter than the Nb−Cl bonds in **5** and is normal in this type of complex.[1,37]

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Nb(O)\{(4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$ (**4**)

Nb(1)−O(1)	1.781(5)	N(2)−Si(2)	1.757(6)
Nb(1)−Cl(1)	2.333(3)	N(2)−C(1)	1.324(9)
Nb(1)−N(1)	2.195(6)	N(3)−Si(3)	1.775(6)
Nb(1)−N(2)	2.189(6)	N(3)−C(9)	1.376(8)
Nb(1)−N(3)	2.085(5)	N(4)−Si(4)	1.754(6)
Nb(1)−N(4)	2.402(6)	N(4)−C(9)	1.299(8)
N(1)−Si(1)	1.772(6)	C(1)−C(2)	1.50(1)
N(1)−C(1)	1.339(9)	C(9)−C(10)	1.50(1)
O(1)−Nb(1)−Cl(1)	99.6(2)	Cl(1)−Nb(1)−N(4)	89.0(2)
O(1)−Nb(1)−N(1)	103.2(2)	N(1)−Nb(1)−N(4)	94.5(2)
Cl(1)−Nb(1)−N(1)	94.0(2)	N(2)−Nb(1)−N(4)	83.4(2)
O(1)−Nb(1)−N(2)	96.2(3)	N(3)−Nb(1)−N(4)	60.0(2)
Cl(1)−Nb(1)−N(2)	153.3(2)	N(1)−C(1)−N(2)	114.2(6)
N(1)−Nb(1)−N(2)	61.3(2)	N(1)−C(1)−C(2)	121.9(6)
O(1)−Nb(1)−N(3)	100.2(2)	N(2)−C(1)−C(2)	123.9(6)
Cl(1)−Nb(1)−N(3)	98.9(2)	N(3)−C(9)−N(4)	115.3(6)
N(1)−Nb(1)−N(3)	150.9(2)	N(3)−C(9)−C(10)	122.1(6)
N(2)−Nb(1)−N(3)	99.3(2)	N(4)−C(9)−C(10)	122.5(6)
O(1)−Nb(1)−N(4)	159.6(2)		

For a range of complexes of the type $[Nb(O)L_n]$, the presence of a terminal oxo ligand is characterized by a strong, sharp ν(Nb=O) absorption in the range 890−950 cm^{-1}. The frequency is sensitive to the metal coordination number and the nature of the ligand field. The values of ν(Nb=O) for **3** and **4** (927 and 930 cm^{-1}, respectively) are within the range found for six-coordinate, niobium(5+) oxo complexes in general[39] but slightly higher that for *trans*-[Nb(O)(F)(oep)] [ν(Nb=O) *ca.* 910 cm^{-1}; oep = octaethylporphyrin],[40] which also has a comparable Nb=O bond length [1.749(3) Å] to that of $[Nb(O)\{(4\text{-}C_6H_4Me)C(NSiMe_3)_2\}_2Cl]$ (**4**).

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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Additions and Corrections

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Girlie Naomi A. Nallas, Sumner W. Jones, and Karen J. Brewer*: Bipyrimidine-Bridged Mixed-Metal Trimetallic Complexes of Ruthenium(II) with Rhodium(III) or Iridium(III), $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$.

Page 6974. Reference 8 was incorrect. The correct reference is as follows: (8) (a) Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Ricevuto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211. (b) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (c) Campagna, S.; Giannetto, A.; Serroni, S.; Denti, G.; Trusso, S.; Mallamace, F.; Micali, N. *J. Am. Chem. Soc.* **1995**, *117*, 1754. (d) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750. (e) Balzani, V.; Moggi, L.; Scandola, F. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 1. (f) Serroni, S.; Campagna, S.; Denti, G.; Keyes, T. E.; Vos, J. G. *Inorg. Chem.* **1996**, *35*, 4513. (g) Juris, A.; Venturi, M.; Pontoni, L.; Resino, I. R.; Balzani, V.; Serroni, S.; Campagna, S.; Denti, G. *Can. J. Chem.* **1995**, *73*, 1875. (h) Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1992**, *114*, 2944. (i) Serroni, S.; Juris, A.; Campagna, S.; Venturi, M.; Denti, G.; Balzani, V. *J. Am. Chem. Soc.* **1994**, *116*, 9086. (j) Roffia, S.; Marcaccio, M.; Paradisi, C.; Paolucci, F.; Balzani, V.; Denti, G.; Serroni, S.; Campagna, S. *Inorg. Chem.* **1993**, *32*, 3003.

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