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Synthesis and Structures of Niobium(V) Complexes Stabilized by Linear-Linked Aryloxide Trimers

Tsukasa Matsuo and Hiroyuki Kawaguchi*

Coordination Chemistry Laboratories, Institute for Molecular Science, and CREST,
Japan Science and Technology Corporation (JST), Myodaiji, Okazaki 444-8585, Japan

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The preparation and characterization of a series of niobium(V) complexes that incorporate the linear-linked aryloxide trimers 2,6-bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol [H_3(Me-L)] and 2,6-bis(4-methyl-6-*tert*-butylsalicyl)-4-*tert*-butylphenol [$H_3(^t$Bu-L)] are described. The chloride complex [Nb(Me-L)$Cl_2]_2$ (**1**) was prepared in high yield by reaction of $NbCl_5$ with H_3(Me-L) in toluene. In contrast, the analogous reaction with $H_3(^t$Bu-L) gave a mixture of [Nb(^{t}Bu-L)$Cl_2]_2$ (**2**) and [Nb(de-^{t}Bu-L)$Cl_2]_2$ (**3a**). During the formation of **3a**, one of *tert*-butyl groups at the *ortho* position in the ^{t}Bu-L ligand was lost. When the $NbCl_5/H_3(^t$Bu-L) reaction was carried out in acetonitrile, Nb[H(^{t}Bu-L)]Cl_3(NCMe) (**4**) was obtained. Heating a solution of **4** in toluene generated **2** and **3a**. The isolated complex **4** underwent ligand redistribution in acetonitrile to produce Nb[H(^{t}Bu-L)$]_2$Cl(NCMe) (**5**). Treatment of $NbCl_5$ with $Li_3(^t$Bu-L) in toluene afforded **2**. The chloride ligands in **1** and **2** smoothly reacted with 4 equiv of MeMgI and LiS^{t}Bu, resulting in [Nb(R-L)$Me_2]_2$ [R = Me (**6**), ^{t}Bu (**7**)] and Nb(Me-L)(S^{t}Bu)$_2$ (**8**), respectively. A number of the above complexes have been characterized by X-ray crystallography. In the structures of **1**, **2**, and **6**, the R-L ligand is bound to the metal center with a U-coordination mode, while an alternative S-conformation is adopted for **3a** and **8**. Complexes **4** and **5** contain a bidentate H(^{t}Bu-L) diphenoxide–monophenol ligand.

Introduction

The ability of alkoxide and aryloxide ligands to support and promote various important organic/inorganic reactions at metal centers has been known for many years.[1] In this context, they complement the well-studied cyclopentadienyl-based systems, with the major difference being the greater reactivity of the former complexes due to their relatively higher unsaturation and lower coordination numbers for a $(ArO)_nM$ fragment. However, ligand redistribution reaction is a common reaction pathway through which coordinatively unsaturated metal complexes decompose.[2] These undesired ligand redistribution reactions are occasionally a severe obstacle to synthetic efforts. One of strategies for overcoming this problem is to use covalently linked ancillary ligands, thereby limiting ligand mobility and leaving little possibility to reorganize the molecule. This strategy has been a very useful concept in coordination chemistry and has allowed the isolation of transition metal complexes in unstable oxidation states or in unusual coordination geometries and many with diverse highly reactive functionalities.[3−8]

We set out to investigate linear aryloxide trimers H_3(R-L) as new ancillary ligands, in which aryloxide units are

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* To whom correspondence should be addressed. E-mail: hkawa@ims.ac.jp. Fax: +81-564-55-5245.

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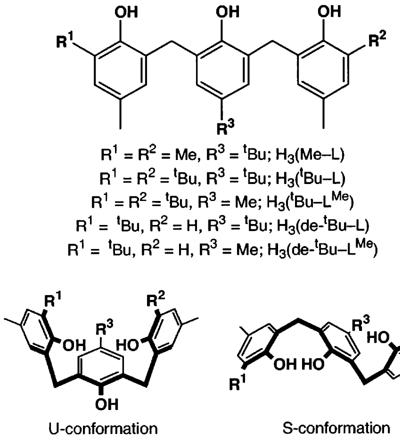
Chart 1



connected at the *ortho* positions through methylene linkers (Chart 1). Although linear aryloxide trimers were being investigated for their use as building blocks for the synthesis of macrocyclic compounds,[9] there are few examples of metal complexes with these trimers in coordination chemistry.[3,7,10−12] Independent from us, Scott and Hofmeister demonstrated the synthesis of compounds having linear-linked aryloxide trimers for lithium, sodium, aluminum, and titanium(IV).[13,14] We have recently exploited these trimers in the formation of tetravalent and trivalent titanium complexes and a reactive niobium derivative which is found to cleave the N≡N triple bond of dinitrogen.[15] In this article we report the full details of the synthesis and structures of a variety of niobium complexes incorporating linear aryloxide trimers.

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive materials were performed under an argon atmosphere using standard Schlenk line techniques. All dried solvents and chemicals commercially available were used as received without further purification. Linear aryloxide trimers, H_3(Me-L), H_3(^{t}Bu-L), and H_3(^{t}Bu-L^{Me}), were synthesized according to the literature procedures.[9d,13,15a] MeMgI was prepared from methyl iodide and magnesium in diethyl ether, while ^{t}BuSLi was obtained by the reaction of 2-methyl-2-propanethiol with butyllithium in toluene at 0 °C. Deuterated chloroform ($CDCl_3$), benzene (C_6D_6), and toluene (C_7D_8) was distilled from calcium hydride or sodium prior to use. Elemental analyses (C, H, N, and S) were carried out on Yanaco CHN Corder MT-6 and Leco-CHNS element analyzers. ^{1}H NMR (500 MHz) spectra were recorded at room temperature using a JEOL LA-500 spectrometer. Chemical shifts (in ppm) for ^{1}H NMR spectra were referenced to residual protic solvent peaks.

Synthesis of [Nb(Me-L)Cl$_2$]$_2$ (1). A mixture of $NbCl_5$ (2.47 g, 9.14 mmol) and H_3(Me-L) (3.83 g, 9.15 mmol) was suspended in toluene (40 mL). The resulting red brown solution was refluxed for 2 h, during which time yellow brown crystals precipitated. After standing at room temperature for 3 h, this material was collected by filtration, washed with ether, and dried in vacuo to afford **1** in 88% (4.66 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 18H, ^{t}Bu), 2.34 (s, 12H, Me), 2.41 (s, 12H, Me), 2.41 (d, $J = 13.5$ Hz, 4H, CH_2), 3.41 (d, $J = 13.5$ Hz, 4H, CH_2), 6.68 (s, 4H, Ar H), 6.98 (s, 4H, Ar H), 7.18 (s, 4H, Ar H). Anal. Calcd for $C_{60}H_{70}O_6Cl_4Nb_2\cdot C_7H_8$: C, 61.57; H 6.02. Found: C, 61.67; H, 6.11.

Synthesis of [Nb(^{t}Bu-L)Cl$_2$]$_2$ (2). A hexane solution of butyllithium (1.57 M, 11.0 mL, 17.2 mmol) was added dropwise to H_3(^{t}Bu-L) (2.90 g, 5.77 mmol) in toluene (80 mL) at 0 °C. The solution was stirred at room temperature for 1 h, and then $NbCl_5$ (1.56 g, 5.77 mmol) was added to the resulting white suspension. The color

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of the solution immediately turned red. The mixture was refluxed for 3 h, during which time red microcrystals were formed. After concentration and standing at room temperature for 16 h, the solution was removed by decantation. The red crystalline solid was recrystallized from hot toluene to give **2** as red blocks in 41% yield (1.67 g). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.21 (s, 18H, ^{t}Bu). 1.42 (s, 36H, ^{t}Bu), 2.35 (s, 12H, Me), 2.36 (s, 3H, toluene), 3.31 (d, J = 13.7 Hz, 4H, CH$_2$), 4.97 (d, J = 13.7 Hz, 4H, CH$_2$), 7.04 (s, 4H, Ar H), 7.06 (s, 4H, Ar H), 7.17 (m, 7H, Ar H + toluene), 7.25 (m, 2H, toluene). Anal. Calcd for $C_{68}H_{86}O_6Cl_4Nb_2\cdot C_7H_8$: C, 63.47; H 6.68. Found: C, 63.80; H, 6.69.

Synthesis of [Nb(de-^{t}Bu-L)Cl$_2$] (3a). (a) From NbCl$_5$ and H$_3$(^{t}Bu-L). A mixture of NbCl$_5$ (2.83 g, 10.5 mmol) and H$_3$(^{t}Bu-L) (5.23 g, 10.4 mmol) was suspended in toluene (60 mL). After the reaction mixture was refluxed for 80 min, the solvent was removed in vacuo to afford a red solid. The residue was redissolved in toluene, and then the solution was centrifuged to remove a small amount of **2**. Evaporation of the supernatant gave **3a** as wine-red microcrystals (4.52 g, 72% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.10 (s, 18H, ^{t}Bu), 1.43 (s, 18H, ^{t}Bu), 2.420 (s, 6H, Me), 2.424 (s, 6H, Me), 3.59 (d, J = 15.2 Hz, 2H, CH$_2$), 3.62 (d, J = 15.3 Hz, 2H, CH$_2$), 5.74 (d, J = 15.3 Hz, 2H, CH$_2$), 5.75 (d, J = 15.2 Hz, 2H, CH$_2$), 6.71−7.01 (m, 14H, Ar H). Anal. Calcd for $C_{60}H_{70}O_6Cl_4Nb_2\cdot C_7H_8$: C, 61.57; H 6.02. Found: C, 61.67; H, 6.11.

(b) From Nb[H(^{t}Bu-L)]Cl$_3$(NCMe). A solution of Nb[H(^{t}Bu-L)]Cl$_3$(NCMe) (**4**) (0.69 g, 0.93 mmol) in toluene (20 mL) was refluxed for 1 h, during which time red microcrystals of **2** and **3a** precipitated. Evaporation of the solvent afforded a wine-red solid that was washed with toluene/hexane to give 0.35 g of **3a** in 62% yield.

Synthesis of [Nb(de-^{t}Bu-L^{Me})Cl$_2$] (3b). The same procedure as used for **3a** was followed. Reaction of NbCl$_5$ (1.73 g, 6.40 mmol) and H$_3$(Me-L^{Me}) (2.97 g, 6.44 mmol) in toluene (60 mL) afforded **3b** as red microcrystals in 71% yield (2.57 g). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.42 (s, 36H, ^{t}Bu), 2.34 (s, 6H, Me), 2.42 (s, 12H, Me x 2), 3.59 (d, J = 14.9 Hz, 2H, CH$_2$), 3.62 (d, J = 14.9 Hz, 2H, CH$_2$), 5.74 (d, J = 14.9 Hz, 2H, CH$_2$), 5.75 (d, J = 14.9 Hz, 2H, CH$_2$), 6.75−7.20 (m, 14H, Ph). Anal. Calcd for $C_{54}H_{58}Cl_4Nb_2O_6$: C, 57.36; H 5.17. Found: C, 57.07; H, 5.60.

Synthesis of Nb[H(^{t}Bu-L)]Cl$_3$(NCMe) (4). A solution of NbCl$_5$ (0.90 g, 3.33 mmol) in CH$_3$CN (40 mL) was subjected to the addition of H$_3$(^{t}Bu-L) (1.67 g, 3.32 mmol) at room temperature. The color of the solution immediately changed from yellow to red. The mixture was refluxed for 2 h, and then solvent was removed in vacuo to leave a red solid. The residue was dissolved in CH$_2$Cl$_2$ (10 mL) containing CH$_3$CN (1 mL), and hexane (30 mL) was added. The solution was concentrated to yield **4** as red crystals in 57% (1.41 g). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.17 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu), 1.53 (s, 9H, ^{t}Bu), 2.21 (s, br, MeCN), 2.25 (s, 3H, Me), 2.37 (s, 3H, Me), 1.55 (d, J = 13.9 Hz, 1H, CH$_2$), 4.22 (br, 2H, overlapping CH$_2$ and OH), 4.78 (br, 1H, CH$_2$), 5.29 (d, J = 13.9 Hz, 1H, CH$_2$), 6.77 (s, 2H, Ar H), 7.01 (s, 1H, Ar H), 7.05 (s, 1H, Ar H), 7.18 (s, 1H, Ar H), 7.31 (s, 1H, Ar H). IR (cm^{-1}): 3530 (m, ν_{OH}), 2316 (w, ν_{CN}), 2289 (w, ν_{CN}). Anal. Calcd for $C_{36}H_{47}NO_3Cl_3Nb$: C, 58.35; H, 6.39; N, 1.89. Found: C, 58.02; H, 6.33; N, 1.62.

Synthesis of Nb[H(^{t}Bu-L)]$_2$Cl(NCMe) (5). (a) From Nb[H(^{t}Bu-L)]Cl$_3$(NCMe). Complex **4** (0.47 g, 0.32 mmol) was dissolved into CH$_3$CN (60 mL). The solution was allowed to stand at room temperature for 28 h, yielding 0.12 g of orange needles **5**·CH$_3$CN (31% based on the ligand). Solubility constraints prevent us from acquiring the ^{1}H NMR spectrum of **5**. IR (cm^{-1}): 3516 (s, ν_{OH}), 2280 (w, ν_{CN}), 2251 (w, ν_{CN}, free CH$_3$CN). Anal. Calcd for $C_{72}H_{94}N_2O_6ClNb$: C, 71.36; H, 7.82; N, 2.31. Found: C, 71.20; H, 7.66; N, 2.15.

(b) From NbCl$_5$ and H$_3$(^{t}Bu-L). To a solution of NbCl$_5$ (0.21 g, 0.78 mmol) in CH$_3$CN (10 mL) was added 2 equiv of H$_3$(^{t}Bu-L) (0.78 g, 1.55 mmol). The solution was stirred at 80 °C for 3 h, during which time orange microcrystals of **5** precipitated. This material was collected by filtration, washed with ether, and dried in vacuo to afford **5** in 91% yield (0.83 g).

Synthesis of [Nb(Me-L)Me$_2$]$_2$ (6). A solution of MeMgI (4.45 mmol) in Et$_2$O (5 mL) was added dropwise to a suspension of **1** (1.29 g, 1.11 mmol) in toluene (80 mL) at −78 °C. The mixture was allowed to return to room temperature and stirred for a further 4 h. After the reaction mixture was centrifuged to remove an insoluble material, the dark-yellow supernatant was evaporated to dryness. The resulting residue was recrystallized from Et$_2$O, yielding **6** as yellow crystals (0.64 g, 44%). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ −0.42 (s, 6H, Nb−Me), 1.04 (s, 18H, ^{t}Bu), 1.27 (s, 6H, Nb−Me), 2.20 (s, 24H, the methyl protons of Me-L are overlapped), 3.16 (d, J = 13.0 Hz, 4H, CH$_2$), 4.89 (d, J = 13.0 Hz, 4H, CH$_2$), 6.75 (s, 4H, Ar H), 6.89 (s, 4H, Ar H), 7.00 (s, 4H, Ar H). ^{13}C{^{1}H} NMR (125.65 MHz, C$_6$D$_6$): δ 34.3, 32.7 (Nb−Me). Anal. Calcd for $C_{60}H_{74}O_6Nb_2\cdot 2C_4H_{10}O$: C, 66.66; H, 7.73. Found: C, 66.15; H, 7.56.

Synthesis of [Nb(^{t}Bu-L)Me$_2$]$_2$ (7). (a) From [Nb(^{t}Bu-L)Cl$_2$]$_2$ (2). The same procedure as used for **6** was followed. Reaction of MeMgI (2.3 mmol) in Et$_2$O (4 mL) with **2** (0.57 g, 0.43 mmol) in THF (60 mL) afforded **7** as yellow crystals (0.21 g, 39% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.03 (s, 6H, Nb−Me), 1.14 (s, 18H, ^{t}Bu), 1.39 (s, 36H, ^{t}Bu), 1.67 (s, 6H, Nb−Me), 2.32 (s, 6H, Me), 3.21 (d, J = 13.5 Hz, 4H, CH$_2$), 4.63 (d, J = 13.5 Hz, 4H, CH$_2$), 7.01 (s, 4H, Ar H), 7.04 (s, 4H, Ar H), 7.15 (s, 4H, Ar H). Anal. Calcd for $C_{72}H_{98}O_6Nb_2\cdot 2C_7H_8$: C, 72.25; H, 8.04. Found: C, 71.61; H, 7.92. Solubility constraints prevent us from acquiring the ^{13}C NMR spectrum of **7**.

(b) From Nb[H(^{t}Bu-L)]Cl$_3$(NCMe) (4). Addition of MeMgI (2.14 mmol) in Et$_2$O (6 mL) to **4** (0.79 g, 1.07 mmol) in toluene (80 mL) followed by workup similar to the above provided 0.20 g of **7** in 30% yield.

Synthesis of Nb(Me-L)(S^{t}Bu)$_2$ (8). Addition of butyllithium (2.36 mL, 3.71 mmol, 1.57 M in hexane) to a toluene solution of 2-methyl-2-propanethiol (0.42 mL, 3.72 mmol) at 0 °C gave a white suspension. After the suspension was stirring for 30 min, **1** (1.03 g, 0.89 mmol) was added. The mixture was stirred at 80 °C for 3 h, during which time a red color appeared and LiCl precipitated. The solution was centrifuged to remove an insoluble material. Concentration of the supernatant and cooling to −30 °C provided **7** as orange crystals (0.93 g, 76% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.26 (s, 9H, ^{t}Bu), 1.64 (s, 18 H, S^{t}Bu), 2.25 (s, 6H, Me), 2.56 (s, 6H, Me), 3.3 (br, 2H, CH$_2$), 4.4 (br, 2H, CH$_2$), 6.83 (s, 2H, Ar H), 6.94 (s, 2H, Ar H), 7.04 (s, 2H, Ar H). Anal. Calcd for $C_{36}H_{49}O_3S_2Nb$: C, 62.96; H, 7.19; S, 9.34. Found: C, 62.71; H, 7.09; S, 8.97.

Analysis of the Fluxionality of 8 in Solution. Complex **8** (15 mg) was dissolved in toluene-d_8, and the NMR tube was sealed under an argon atmosphere. ^{1}H NMR spectra were taken at 9 temperatures ranging from −20 to 80 °C. Line shape analysis of the methylene region was carried out at each temperature using the gNMR program.[16] The k_1 values obtained at given temperature are as follows: −19.9 °C, 17; −9.7 °C, 42; −0.2 °C, 88; 19.9 °C, 5.6 × 10^2; 30 °C, 9.5 × 10^2; 40 °C, 2.1 × 10^3; 50 °C, 4.0 × 10^3;

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(16) Budzellar, P. H. M. *gNMR for Windows version 4.1*; Cherwell Scientific Ltd.: Oxford, U.K., 1999.

Table 1. Crystallographic Data for $[Nb(R\text{-}L)Cl_2]_2$ (R = Me (**1**), ^{t}Bu (**2**)), $[Nb(de\text{-}^tBu\text{-}L^{Me})_2Cl_2]_2$ (**3b**), $Nb[H(^tBu\text{-}L)]Cl_3(NCMe)$ (**4**), $Nb[H(^tBu\text{-}L)]_2Cl(NCMe)$ (**5**), $[Nb(^tBu\text{-}L)Cl_2]_2$ (**6**), and $Nb(Me\text{-}L)(S^tBu)_2$ (**8**)

	1·$2CH_2Cl_2$	**2**·C_7H_8	**3b**·$2C_7H_8$	**4**	**5**·CH_3CN	**6**·$2C_4H_{10}O$	**8**·$1/2C_7H_8$
formula	$C_{60}H_{66}O_6Cl_8Nb_2$	$C_{75}H_{94}O_6Cl_4Nb_2$	$C_{68}H_{74}O_6Cl_4Nb_2$	$C_{36}H_{47}NO_3Cl_3Nb$	$C_{72}H_{94}N_2O_6ClNb$	$C_{68}H_{94}O_8Nb_2$	$C_{39.5}H_{53}O_3S_2Nb$
M_r	1352.61	1419.19	1314.95	741.04	1211.90	1225.30	732.88
T/K	193	123	173	173	173	173	173
cryst size/mm	0.30 × 0.20 × 0.02	0.15 × 0.05 × 0.05	0.40 × 0.25 × 0.20	0.35 × 0.15 × 0.10	0.15 × 0.04 × 0.02	0.30 × 0.20 × 0.20	0.25 × 0.25 × 0.20
cryst system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a/Å	27.4464(13)	12.621(6)	10.607(3)	18.921(2)	13.2637(10)	11.841(4)	9.772(2)
b/Å	16.640(2)	12.594(4)	14.566(4)	9.3838(9)	17.850(1)	15.601(5)	27.527(6)
c/Å	13.7110(4)	14.256(6)	21.501(6)	22.820(3)	29.325(2)	17.967(7)	14.509(3)
α/deg		66.44(2)	85.513(9)				
β/deg	103.7695(9)	85.86(2)	89.343(9)	115.228(4)	93.814(4)	91.094(4)	94.385(3)
γ/deg		64.99(2)	71.501(5)				
V/Å^3	6081.8(5)	1870(1)	3140.2(13)	3665.2(7)	6927.4(8)	3318.4(18)	3891.5(13)
Z	4	1	2	4	4	2	4
D_c/g cm^{-3}	1.477	1.260	1.391	1.343	1.162	1.226	1.251
μ(Mo Kα)/cm^{-1}	7.76	4.97	5.85	5.81	2.61	3.95	4.50
reflcns collcd	28 867	14 249	24 469	29 352	55 006	24 368	30 321
unique reflcns	6956	8130	13 680	8247	15 854	7504	8879
refined params	352	428	795	435	839	399	473
GOF on F^2	1.05	1.00	1.04	1.01	1.02	1.04	1.02
$R1$ $[I > 2\sigma(I)]^a$	0.060	0.084	0.039	0.067	0.072	0.036	0.044
wR2 (all data)^b	0.169	0.242	0.098	0.200	0.230	0.092	0.130

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR2 = [\Sigma(w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

60 °C, 7.8 × 10^3; 80 °C, 2.4 × 10^4. Activation parameters were determined from Eyring plots of the above data.

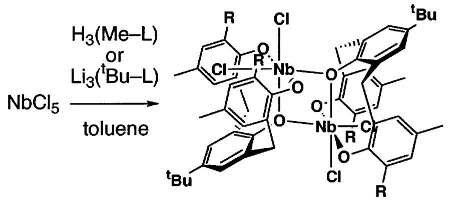
X-ray Crystallography. Crystallographic data are summarized in Table 1. X-ray-quality single crystals were obtained from CH_2Cl_2/hexane (for **1**·$2CH_2Cl_2$ as brown blocks), toluene (for **2**·C_7H_8, **3b**·$2C_7H_8$, and **8** as red needles, wine-red blocks, and orange blocks, respectively), CH_3CN (for **4** and **5**·CH_3CN as red blocks and orange needles, respectively), and Et_2O (for **8** as yellow blocks). Crystals were immersed in Paraton-N oil on a nylon loop and transferred to a Rigaku Mercury CCD diffractometer equipped with a Rigaku GNNP low-temperature device. Data were collected under a cold nitrogen stream using graphite monochromated Mo Kα radiation (λ = 0.710 70 Å). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) program.[17] Corrections for Lorentz−polarization effects and absorption were performed.

All structures were solved by direct methods and refined on F^2 by the full-matrix least-squares method using CrystalStructure (Rigaku) software package.[18] In the case of **1**, **2**, and **4**, methyl carbons of the *para-tert*-butyl group of the R-L ligand were disordered with occupancy factors of 50:50. The crystal solvents in **1**·$2CH_2Cl_2$, **2**·C_7H_8, and **8**·$1/2C_7H_8$ were disordered over two site positions, and the individual components were resolved and refined. Anisotropic refinement was applied to all non-hydrogen atoms except for the distorted atoms. The disordered atoms were isotropically refined, and no hydrogen atoms on the disordered atoms were included. The phenolic OH protons for **4** and **5** were located from Fourier difference syntheses and isotropically refined, while the other hydrogen atoms were put at calculated positions with C−H distances of 0.97 Å. Additional crystallographic data are given in the Supporting Information.

Results and Discussion

Synthesis of $[Nb(R\text{-}L)Cl_2]_2$ [R = Me (1), ^{t}Bu (2)]. Aryloxides complexes of early transition metals are typically synthesized by reactions of metal chlorides with either ArOH, ArOM (M = Li, Na, K), or $ArOSiMe_3$. In this study, we began to examine the reactions between $NbCl_5$ and $H_3(R\text{-}L)$. The course and outcome of the reaction chemistry are dependent on the identity of the outer aryloxide ring substituents of the tridentate R-L^{3-} ligands. The reaction of $NbCl_5$ with 1 equiv of $H_3(Me\text{-}L)$ in toluene under reflux led to elimination of HCl and formation of the chloride complex $[Nb(Me\text{-}L)Cl_2]_2$ (**1**) as brown crystals in 88% isolated yield. Spectroscopic data and combustion analysis of **1** are in agreement with its formulation. In the ^{1}H NMR spectrum of **1**, the methylene proton signals appear as a pair of doublets along with two methyl and one *tert*-butyl signals, indicating the rigid and symmetric conformation of the Me-L ligand. In addition, **1** was characterized by X-ray structural analysis.

The molecular structure of **1** is shown in Figure 1, and



(1)

1 R = Me, 88%
2 R = ^{t}Bu, 41%

selected bond distances and angles are given in Table 2. The metal center is in a pseudooctahedral environment consisting of one Me-L tridentate ligand, one central aryloxide [O(2A)] of another Me-L ligand, and two mutually cis chlorides. The tridentate Me-L ligand meridionally coordinates to niobium in the U-conformation (Scheme 1), which is consistent with its ^{1}H NMR spectrum. The two $Nb(Me\text{-}L)Cl_2$ fragments are related by a crystallographic inversion center, and the Nb_2O_2 core is thus required to be planar. A notable feature of the tridentate Me-L^{3-} ligand in the U-conformation concerns the narrow Nb−O(2)−C(8) angles of the central aryloxide [108.2(3)°] relative to the corresponding angles of the outer aryloxides (average 150.6°), because of the constrained

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(17) (a) CrystalClear Software Package, Rigaku and Molecular Structure Corp., 1999. (b) Pflugrath, J. W. *Acta Crystallogr.* **1999**, *D55*, 1718−1725.

(18) Crystal Structure Analysis Package, Rigaku and Molecular Structure Corp., 2001.

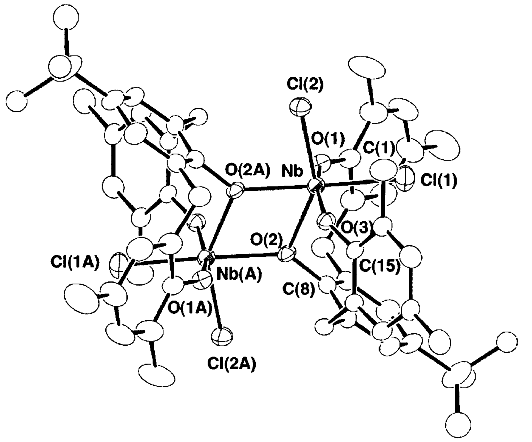


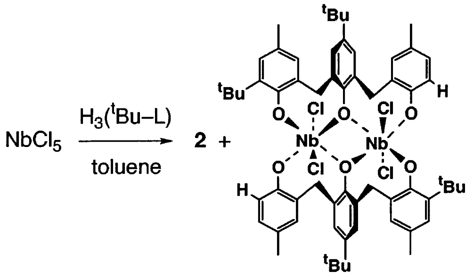
Figure 1. Molecular structure of [Nb(Me-L)Cl$_2$]$_2$ (**1**). One set of the disordered methyl carbons of *tert*-groups of the Me-L ligands is shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Nb(Me-L)Cl$_2$]$_2$ (**1**), [Nb(^{t}Bu-L)$_2$Cl$_2$]$_2$ (**2**), and [Nb(Me-L)Me$_2$]$_2$ (**6**)

	1	2	6
Nb−O(1)	1.874(4)	1.902(4)	1.899(2)
Nb−O(2)	2.097(4)	2.058(4)	2.061(2)
Nb−O(3)	1.862(4)	1.904(4)	1.886(2)
Nb−O(2A)	2.151(4)	2.237(4)	2.320(2)
Nb−Nb(A)	3.554(1)	3.649(1)	3.7095(9)
Nb−Cl(1)	2.352(2)	2.365(2)	
Nb−Cl(2)	2.327(2)	2.335(2)	
Nb−C(29)			2.156(2)
Nb−C(30)			2.189(3)
O(1)−Nb−O(2)	86.9(2)	91.5(2)	89.34(6)
O(2)−Nb−O(3)	86.3(2)	90.7(2)	90.42(7)
O(1)−Nb−O(3)	163.1(2)	168.0(2)	168.42(7)
O(2)−Nb−O(2A)	66.39(16)	63.69(16)	64.41(6)
Nb−O(2)−Nb(A)	113.61(16)	116.31(16)	115.59(6)
Nb−O(1)−C(1)	148.0(4)	151.6(4)	151.2(1)
Nb−O(2)−C(8)	108.2(3)	102.6(3)	101.45(12)
Nb−O(3)−C(15)	153.1(4)	153.0(4)	155.9(2)
Nb(A)−O(2)−C(8)	138.1(3)	141.1(3)	143.0(1)
Cl(1)−Nb−Cl(2)	96.54(6)	104.59(6)	
C(29)−Nb−C(30)			101.21(11)

geometry of the linked ligand. The bridging Nb−O distances are asymmetric, and the Nb−O(2) distance [2.097(4) Å] is shorter than the Nb−O(2A) distance [2.151(4) Å]. As expected, the bridging Nb−O distances (average 2.124 Å) are longer than the terminal Nb−O distances (average 1.868 Å). The Nb−Cl(1) distance of 2.352(2) Å is elongated relative to the Nb−Cl(2) distance of 2.327(2) Å, reflecting the stronger Nb−O(2) interaction trans to Cl(2) in comparison with the Nb−O(2A) interaction trans to Cl(1).

When H$_3$(^{t}Bu-L) was used instead of H$_3$(Me-L), the analogous reaction gave a red solution. After removal of volatiles in vacuo, analysis of the crude products by ^{1}H NMR spectroscopy showed resonances corresponding to the formation of [Nb(^{t}Bu-L)Cl$_2$]$_2$ (**2**) and [Nb(de-^{t}Bu-L)Cl$_2$]$_2$ (**3a**) in the intensity ratio of 15:85. According to ^{1}H NMR spectroscopy, we found no rapid conversion of **2** into **3a**. The ^{1}H NMR spectrum of **2** is analogous to that of **1** and suggests that these compounds possess similar structures. In the ^{1}H NMR spectrum of **3a**, the presence of the asymmetric de-^{t}Bu-L ligand leads to two methyl and two *tert*-butyl singlets with relative integrations of 1:1:3:3. Additionally, there are four doublets due to the methylene linkers. After the crude product was washed with toluene/hexane, **3a** was obtained as analytically pure wine-red microcrytals in 72% yield. Unfortunately, attempts to isolate **2** from the reaction mixture have yet to be successful. However, the structures of both **2** and **3a** have been determined by X-ray diffraction.



(2)

3a, 72%

The structure of **2** is a cenrtosymmetric dimer analogous to **1**. Selected bond distances and angles are given in the second column of Table 2. The slight differences observed between **1** and **2** are due to the nature of the substituents at *ortho* positions of the outer aryloxide rings, possibly generating slightly differing steric and electronic effects. In comparison with **1**, the Nb−Nb separation is 0.095 Å longer in **2**. A corresponding trend is observed in the planar Nb$_2$O$_2$ dimer ring, and the Nb−O(2A) distance of **2** is elongated relative to that of **1**. In contrast, the Nb−O(2) distance of **2** [2.058(4) Å] is slightly shorter than that of **1** [2.097(4) Å]. This is ascribed to the more obtuse O(1)−Nb−O(3) angle in the linked aryloxide trimer [163.1(2)° in **1** vs. 168.0(2)° in **2**].

In the case of **3a**, the disorder problem prevents us from discussing its metric parameters in detail.[19] Thus the ^{t}Bu-L^{Me} derivative, which has the methyl group at the *para* position of the central aryloxide (Scheme 1), was chosen for a structural study. Complex [Nb(de-^{t}Bu-L^{Me})Cl$_2$]$_2$ (**3b**) was prepared by the analogous reaction of NbCl$_5$ with H$_3$(^{t}Bu-L^{Me}) in toluene. Complete solution of X-ray diffraction data for **3b** was possible (Figure 2), and the molecular structure is similar to that of **3a** as determined from the preliminary X-ray analysis. Selected bond distances and angles are listed in Table 3. The structure of **3b** shows a binuclear geometry with octahedral niobium centers, each possessing four aryloxides and two mutually trans chlorides. The most notable feature in the structure is that the two ligands adopt an S-conformation and span both metal centers. The niobium atoms are bridged by the two central aryloxides of the ligand. This conformation of the tridentate ligands in **3b** contrasts with that observed for **1** and **2**. The remaining *tert*-butyl groups of the de-^{t}Bu-L^{Me} ligands in **3b** are located away from each other, resulting in a solid-state molecular geometry with approximately C_2 symmetry. We note that

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(19) Crystal data for **3a**: monoclinic, $P2_1/a$ (No. 14), $a = 16.696(5)$ Å, $b = 22.044(7)$ Å, $c = 22.570(7)$ Å, $\beta = 103.783(5)°$, $V = 8067.7(4)$ Å^3, $Z = 4$.

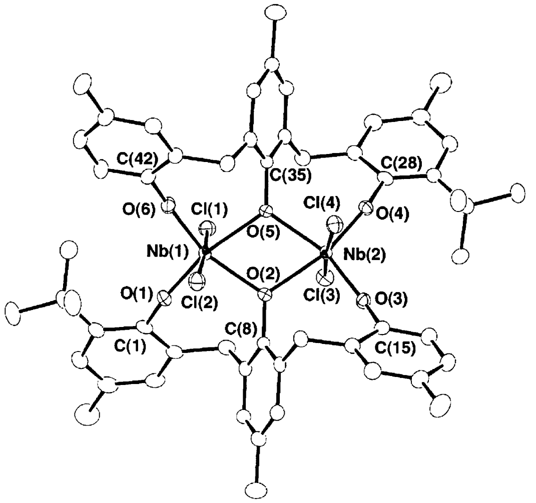


Figure 2. Molecular structure of [Nb(de-^{t}Bu-L^{Me})Cl$_2$]$_2$ (**3b**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Nb(de-^{t}Bu-L^{Me})$_2$Cl$_2$]$_2$ (**3b**)

Nb(1)−O(1)	1.852(2)	Nb(2)−O(2)	2.133(2)
Nb(1)−O(2)	2.093(2)	Nb(2)−O(3)	1.847(2)
Nb(1)−O(5)	2.136(2)	Nb(2)−O(4)	1.846(2)
Nb(1)−O(6)	1.839(2)	Nb(2)−O(5)	2.118(2)
Nb(1)−Cl(1)	2.391(1)	Nb(2)−Cl(3)	2.402(1)
Nb(1)−Cl(2)	2.420(1)	Nb(2)−Cl(4)	2.412(1)
Nb(1)−Nb(2)	3.4721(3)		
O(1)−Nb(1)−O(2)	97.01(7)	O(2)−Nb(2)−O(3)	92.65(7)
O(1)−Nb(1)−O(5)	159.17(7)	O(2)−Nb(2)−O(4)	157.00(7)
O(1)−Nb(1)−O(6)	105.31(8)	O(2)−Nb(2)−O(5)	69.72(6)
O(2)−Nb(1)−O(5)	70.13(6)	O(3)−Nb(2)−O(4)	105.90(7)
O(2)−Nb(1)−O(6)	154.52(7)	O(3)−Nb(2)−O(5)	153.58(7)
O(5)−Nb(1)−O(6)	91.39(7)	O(4)−Nb(2)−O(5)	96.55(7)
Cl(1)−Nb(1)−Cl(2)	175.33(2)	Cl(3)−Nb(2)−Cl(4)	174.21(2)
Nb(1)−O(1)−C(1)	156.1(2)	Nb(2)−O(2)−C(8)	126.02(13)
Nb(1)−O(2)−C(8)	123.51(13)	Nb(2)−O(3)−O(15)	151.1(2)
Nb(1)−O(5)−C(35)	126.15(13)	Nb(2)−O(4)−O(28)	156.1(2)
Nb(1)−O(6)−C(42)	155.1(2)	Nb(2)−O(5)−O(35)	124.40(13)
Nb(1)−O(2)−Nb(2)	110.46(7)	Nb(1)−O(5)−Nb(2)	109.41(7)

the ^{t}Bu-L^{3-} ligand cannot coordinate in a manner similar to those of de-^{t}Bu-L and de-^{t}Bu-L^{Me} found in **3a,b**, because of steric congestion between the bulky *tert*-butyl groups. The terminal and bridging Nb−O distances average 1.846 and 2.120 Å, respectively, which are comparable to the corresponding distances found in **1** and **2**. The Nb−Nb separation in **3b** is 3.4721(3) Å, and this is significantly shorter than those in **1** and **2**.

The reaction between NbCl$_5$ and H$_3$(^{t}Bu-L) involves loss of one of the *tert*-butyl groups of ^{t}Bu-L^{3-}, resulting in the formation of **3a**. The de-*tert*-butylation occurred regioselectively at one of the *ortho* positions of the ligand. The leaving *tert*-butyl group is captured by a Cl$^-$ nucleophile, because 2-chloro-2-methylpropane was detected in the reaction mixture by ^{1}H NMR and GC-MS spectra. This retro-Friedel−Crafts reaction is one example of what is likely to be a general tendency to lose a *tert*-butyl group in some manner in calixarene and phenol derivatives.[20] We felt that the retro-Friedel−Crafts process was promoted by the acidic Nb(V) metal center and speculated that a less acidic niobium compound [NbCl$_5$(NCCH$_3$)] might prevent the de-*tert*-butylation reaction of the ^{t}Bu-L ligand. This proved to be the case, as shown in eq 3.

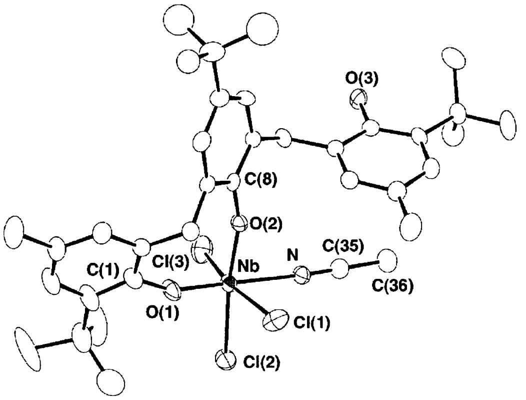
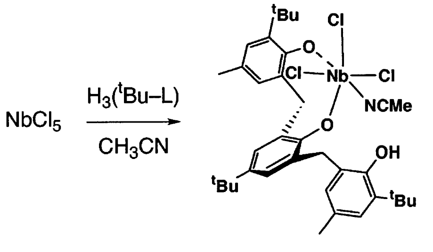


Figure 3. Molecular structure of Nb[H(^{t}Bu-L)]Cl$_3$(NCMe) (**4**). One set of the disordered methyl carbons of *para tert*-groups of the ^{t}Bu-L ligands is shown.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Nb[H(^{t}Bu-L)]Cl$_3$(NCMe) (**4**)

Nb−O(1)	1.839(3)	Nb−Cl(1)	2.386(2)
Nb−O(2)	1.847(3)	Nb−Cl(2)	2.409(1)
Nb−N	2.274(4)	Nb−Cl(3)	2.363(2)
N−C(35)	1.142(6)		
Cl(1)−Nb−Cl(2)	87.12(6)	Cl(1)−Nb−Cl(3)	163.94(5)
Cl(1)−Nb−O(1)	95.7(1)	Cl(1)−Nb−O(2)	92.83(11)
Cl(1)−Nb−N	81.57(11)	Cl(2)−Nb−Cl(3)	87.60(6)
Cl(2)−Nb−O(1)	95.14(11)	Cl(2)−Nb−O(2)	171.48(10)
Cl(2)−Nb−N	85.80(10)	Cl(3)−Nb−O(1)	99.8(1)
Cl(3)−Nb−O(2)	90.17(11)	Cl(3)−Nb−N	82.93(11)
O(1)−Nb−O(2)	93.3(1)	O(1)−Nb−N	177.1(2)
O(2)−Nb−N	85.76(13)	Nb−N−C(35)	173.3(4)
Nb−O(1)−C(1)	158.4(3)	Nb−O(2)−C(8)	161.3(3)



(3)

4, 57%

The reaction of NbCl$_5$ with 1 equiv of H$_3$(^{t}Bu-L) in acetonitrile under reflux afforded Nb[H(^{t}Bu-L)]Cl$_3$(CH$_3$CN) (**4**), which was isolated as dark red crystals in 57% yield by recrystallization from CH$_2$Cl$_2$/hexane. The ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for the formation of **2** or **3a**. The formulation of **4** was inferred from the spectroscopic data and combustion analysis, and the structural data were obtained by X-ray analysis (Figure 3, selected bond distances and angles in Table 4). Molecules of **4** contain a pseudooctahedral niobium(V) center with a acetonitrile ligand and three meridionally arranged chloride ligands. The coordination sphere is completed by a bidentate

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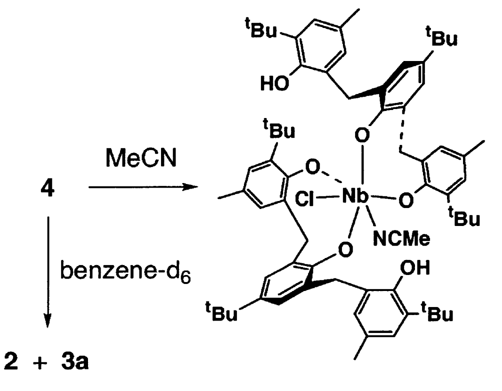
(20) (a) Takeshita, M.; Nishio, S.; Shinkai, S. *J. Org. Chem.* **1994**, *59*, 4032−4034. (b) Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem.* **1996**, *61*, 2511−2516. (c) de Mendoza, J.; Carramolino, M.; Cuevas, F.; Nieto, P. M.; Prados, P.; Reinhoudt, D. N.; Verboom, W.; Ungaro, R.; Casnati, A. *Synthesis* **1994**, 47−50. (d) Sartori, G.; Bigi, F.; Maggi, R.; Porta, C. *Tetrahedron Lett.* **1994**, *35*, 7073−7076.

H(^{t}Bu-L)$^{2-}$ diphenoxide−monophenol ligand, and one outer phenolic oxygen [O(3)] is not bound to niobium. The Nb−O and Nb−Cl distances are within the ranges found in **1**, **2**, and **3b**. The Nb−N distance of 2.274(4) Å is comparable to that of $NbCl_5(NCMe)$ (2.236(4) Å),[21] and the binding of the acetonitrile molecule is linear [Nb−N−C(35) of 173.3(4)° and N−C(35)−C(36) of 179.8(6)°].

Compound **4** was characterized by ^1H NMR and IR spectroscopy. A characteristic feature of the ^1H NMR spectrum in $CDCl_3$ is the presence of four methylene signals along with three *tert*-butyl and two methyl signals, reflecting the asymmetric coordination of the ancillary H(^{t}Bu-L)$^{2-}$ ligand. The signal of the OH proton accidentally overlaps with one of methylene signals (δ 4.22), but the IR spectrum clearly exhibits the OH stretching vibration at 3530 cm^{-1}. The presence of the acetonitrile molecule is characterized by the ν(CN) IR absorptions at 2316 and 2289 cm^{-1}, which are slightly higher than that of free acetonitrile (2251 cm^{-1}). This small increase in ν(CN) stretching frequency is consistent with η^1-coordination of acetonitrile.[22]

As expected, the retro-Friedel−Crafts reaction was inhibited by the presence of acetonitrile in the $NbCl_5$/H_3(^{t}Bu-L) reaction. However, once isolated, analytically pure **4** is found to be labile in solution. For example, upon heating a benzene-d_6 solution of **4** at 80 °C in sealed tube, we noticed the formation of **2** and **3a** in a 1:4 ratio according to the ^1H NMR spectra. On the other hand, upon standing an acetonitrile solution of **4** at room-temperature resulted in the precipitation of Nb[H(^{t}Bu-L)]$_2$Cl(NCMe) (**5**) as orange plates, where a ligand redistribution reaction took place. This complex was alternatively synthesized in 91% yield by treating $NbCl_5$ with 2 equiv of H_3(^{t}Bu-L) in CH_3CN at 80 °C for 3 h. The combustion analysis of **5** was in agreement with the proposed formulation, while the IR spectrum exhibits ν(OH) and ν(CN) bands at 3516 and 2280 cm^{-1}, respectively. However, we were unable to obtain other spectroscopic data for **5** due to its insolubility in common organic solvents. Single crystals of **5** suitable for X-ray diffraction were obtained from a dilute CH_3CN solution of **4** at room temperature.



(4)

5, 31%

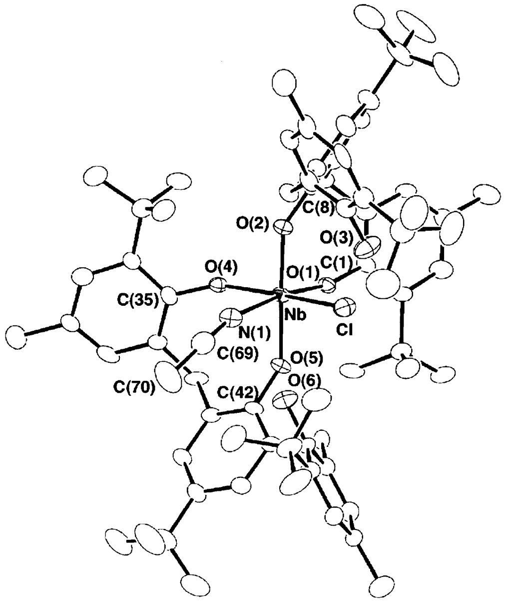


Figure 4. Molecular structure of Nb[H(^{t}Bu-L)]$_2$Cl(NCMe) (**5**).

Table 5. Selected Bond Distances (Å) and Angles (deg) for Nb[H(^{t}Bu-L)]$_2$Cl(NCMe) (**5**)

Nb−O(1)	1.869(4)	Nb−Cl	2.480(2)
Nb−O(2)	1.919(4)	Nb−N(1)	2.296(5)
Nb−O(4)	1.898(4)	N1−C(69)	1.140(8)
Nb−O(5)	1.933(4)		
O(1)−Nb−O(2)	94.6(2)	O(1)−Nb−O(4)	105.6(2)
O(1)−Nb−O(5)	93.2(2)	O(1)−Nb−Cl	94.81(13)
O(1)−Nb−N(1)	171.3(2)	O(2)−Nb−O(4)	91.0(2)
O(2)−Nb−O(5)	168.4(2)	O(2)−Nb−Cl	83.86(12)
O(2)−Nb−N(1)	92.2(2)	O(4)−Nb−O(5)	95.3(2)
O(4)−Nb−Cl	159.27(12)	O(4)−Nb−N(1)	79.7(2)
O(5)−Nb−Cl	86.88(12)	O(5)−Nb−N(1)	79.3(2)
Cl−Nb−N(1)	80.4(1)	Nb−N(1)−C(69)	153.6(5)
Nb−O(1)−C(1)	159.3(4)	Nb−O(2)−C(8)	147.0(4)
Nb−O(4)−C(35)	153.2(4)	Nb−O(5)−C(42)	145.5(4)

The molecular structure of **5** is presented in Figure 4, and selected bond distances and angles are given in Table 5. The structure shows that two diphenoxide−monophenol ligand are bound to niobium in a bidentate fashion. Like **4**, a phenolic group of each H(^{t}Bu-L) ligand [O(3) and O(6)] acts as a pendant arm. The 2.63(7) Å O(3)−H···Cl and 3.278(5) Å O(3)···Cl distances found in **5** are appropriate for intramolecular hydrogen bonding, and the O(3)−H···Cl angle is 152(8)°. The geometry at niobium is best described as an octahedron, and the nitrile and chloride ligands are coordinated to the niobium center cis to each other. The Nb−O distances range from 1.869(4) to 1.933(4) Å, with a slight elongation of the Nb−O bonds trans to O [O(2) and O(5)]. The Nb−N and Nb−Cl distances are relatively long compared to those in **4**, reflecting the increased number of strong aryloxide donors. The bent Nb−N(1)−C(69) angle [153.6(5)°] implies a sterically crowed niobium center in the solid state.

The elimination of hydrochloric acid as a byproduct from the reaction of $NbCl_5$ with H_3(^{t}Bu-L) causes the degradation of the ^{t}Bu-L ligand, so we have sought an alternative synthetic method for the desired compound **2**. Scott et al. have reported the preparations of solvated lithium salts of linked aryloxide trimers in THF and Et_2O. For our purpose,

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(22) Farona, M. F.; Kraus, K. F. *Inorg. Chem.* **1970**, *9*, 1700−1704.

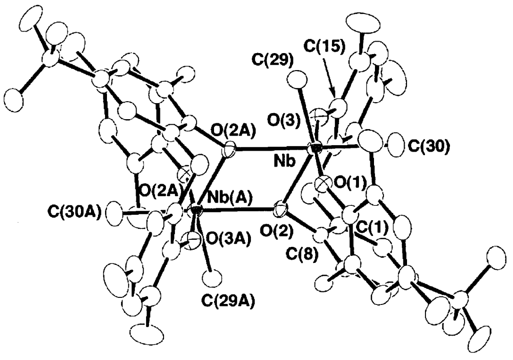
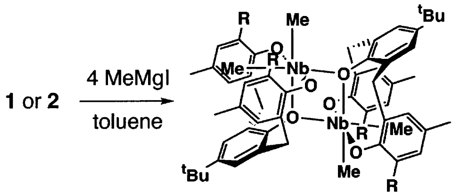


Figure 5. Molecular structure of $[Nb(Me\text{-}L)Me_2]_2$ (**6**).

treatment of $H_3(^t\text{Bu-L})$ with 3 equiv of butyllithium in toluene afforded unsolvated $Li_3(^t\text{Bu-L})$ as a white powder. The conversion of $H_3(^t\text{Bu-L})$ to trilithio salts was confirmed by its IR spectrum, which showed no ν(OH) absorption. The stoichiometric reaction of $Li_3(^t\text{Bu-L})$ with $NbCl_5$ in toluene under reflux produced **2** as red crystals. Multigram quantities of the ^{t}Bu-L derivative **2** were prepared in 41% isolated yield through this metathesis.

Synthesis of Methyl and *tert*-Butyl Mercaptan Derivatives. The chloride complexes **1** and **2** proved to be versatile precursors to organometallic and coordination complexes via halide displacement reactions with MeMgI and LiS^{t}Bu. Addition of 4 equiv of MeMgI in Et_2O to the chloride complexes in toluene at −78 °C followed by standard workup afforded $[Nb(R\text{-}L)Me_2]_2$ [R = Me (**6**), 44%; ^{t}Bu (**7**), 39%] as yellow crystals. The formation of the methyl complexes was found to be sensitive to the alkylating reagent, as the analogous reactions with methyllithium resulted in a mixture of **6** (or **7**) and the corresponding solvated lithium salt of R-L^{3-}.[13] Alkylation of **4** with 3 equiv of MeMgI provided an alternative route to the target methyl complex **7** in 30% yield. These methyl complexes, **6** and **7**, were characterized by NMR spectra and combustion analyses. In the ^{1}H NMR spectra, the resonance patterns due to the R-L^{3-} ligand are entirely analogous to those of the parent complexes, **1** and **2**. The Nb−CH_3 resonances appear as inequivalent signals at δ −0.42 and 1.27 for **6** and at δ 0.03 and 1.67 for **7**, indicating a rigid conformation of the R-L ligand in solution. Single crystals of **6** suitable for an X-ray analysis were grown from a saturated Et_2O solution at −30 °C.



(5)

6 R = Me, 44%
7 R = ^{t}Bu, 39%

Structural analysis revealed the molecular geometry for **6** shown in Figure 5, and selected bond distances and angles are given in the third column of Table 2. Like **1**, the compound **6** exists as a central-aryloxide-bridged dimer in the solid state and the molecule lies across a crystallographic inversion center. The structure of **6** is broadly analogous to that of **1** with the methyl groups replacing the chloride ligands, although the dimer of **6** appears to possess a considerably weaker bridging niobium−oxygen interaction as judged by the Nb−O(2A) distances [2.320(2) Å in **6** but 2.151(4) Å in **1**]. This reflects the stronger σ donor property of the methyl ligand relative to the chloride ligand. The Nb−Me distances of 2.156(2) and 2.189(3) Å are in agreement with the values quoted in the literature for niobium−alkyl bonds.[23]

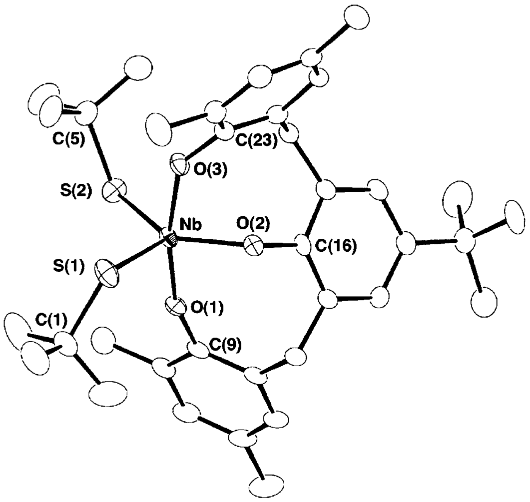


Figure 6. Molecular structure of $Nb(Me\text{-}L)(S^t\text{Bu})_2$ (**8**).

We then examined the reaction of the Me-L complex **1** with ^{t}BuSLi, anticipating that the bulky thiolate ligand might affect the coordination mode of the tridentate Me-L ligand. While the reaction of **1** with 4 equiv of ^{t}BuSLi in THF gave complicated mixtures, $Nb(Me\text{-}L)(S^t\text{Bu})_2$ (**8**) was obtained as orange crystals in 76% yield when the reaction was carried out in toluene at 60 °C. Although attempts to prepare mixed thiolate/alkoxide complexes frequently result in complicated mixturers,[24] **8** is robust toward ligand redistribution reactions. In contrast to the dimeric structures of the Me-L complexes **1** and **6**, the structural analysis confirms the monomeric nature of **8** and the coordination geometry of the complex is best described as a trigonal bipyramidal (Figure 6, selected bond distances and angles in Table 6). The ancillary Me-L ligand assumes an S-shaped conformation and is bound in a meridional fashion with the outer aryloxide donors [O(1) and O(3)] occupying axial positions. The greatest deviation from ideal trigonal-bipyramidal geometry is evident in the axial O(1)−Nb−O(3) bond angle of 166.40(8)°. The equatorial sites comprise two thiolate ligands and the central aryloxide

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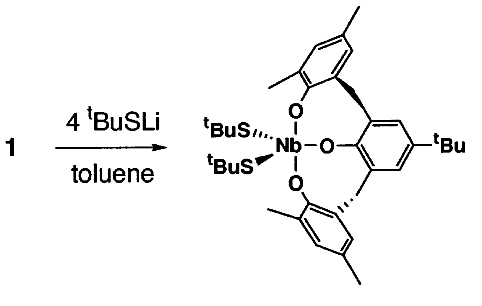
(24) (a) Firth, A. V.; Witt, E.; Stephan, D. W. *Organometallics* **1998**, *17*, 3716−3722. (b) Chisholm, M. H.; Davidson, E. R.; Huffman, J. C.; Quinlan, K. B. *J. Am. Chem. Soc.* **2001**, *123*, 9652−9664.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $Nb(Me\text{-}L)(S^tBu)_2$ (**8**)

Nb−O(1)	1.901(2)	Nb−S(1)	2.357(1)
Nb−O(2)	1.928(2)	Nb−S(2)	2.389(1)
Nb−O(3)	1.910(2)		
S(1)−Nb−S(2)	114.21(3)	S(1)−Nb−O(1)	102.54(6)
S(1)−Nb−O(2)	112.35(6)	S(1)−Nb−O(3)	89.30(6)
S(2)−Nb−O(1)	87.60(6)	S(2)−Nb−O(2)	133.11(6)
S(2)−Nb−O(3)	93.67(6)	O(1)−Nb−O(2)	87.65(8)
O(1)−Nb−O(3)	166.40(8)	O(2)−Nb−O(3)	81.60(8)
Nb−O(1)−C(9)	163.3(2)	Nb−S(1)−C(1)	115.88(11)
Nb−O(2)−C(16)	131.2(2)	Nb−S(2)−C(5)	115.85(11)
Nb−O(3)−C(23)	140.5(2)		

group [O(2)], and the equatorial $NbOS_2$ is planar to within 0.07 Å. The equatorial Nb−O(2) bond of 1.928(2) Å is slightly elongated relative to the axial Nb−O bonds of 1.901(2) and 1.910(2) Å, while the Nb−O(1)−C(9) angle of 163.3(2)° is larger than those at O(2) and O(3) [131.2(2) and 140.5(2)°]. The dihedral angle between the NbO_3 plane and the central aryloxide ring is 60.0°. This twist in the methylene-linked Me-L ligand may be necessary to maintain a trigonal bipyramidal environment for the Nb center. The Nb−S distances of 2.357(1) and 2.389(1) Å compare with the equatorial Nb−S distances in the trigonal bipyramidal complex $(NEt_4)[Nb(S)(S^tBu)_4]$ [ranging from 2.364(6) to 2.407(2) Å].[25]



8, 76%

(6)

The thiolate derivative **8** is fluxional in solution. The ^1H NMR spectra in toluene-d_8 between −80 °C and 80 °C display two methyl and one *tert*-butyl singlets associated with the Me-L ligand, and the two *tert*-butyl mercaptan groups are in a chemically equivalent environment. On the other hand, the methylene protons are seen as two broad signals (δ 3.66 and 4.89) at 10 °C. On cooling of the sample to −20 °C, the methylene protons are observed as a pair of mutually coupled doublets (δ 3.66 and 4.91; $J = 13.4$ Hz), which is consistent with the molecule possessing effective C_2 symmetry with a 2-fold axis (on the NMR time scale) bisecting the S−Nb−S angle. On warming of the sample to 35 °C, these coalesce into one single peak. Line shape analysis for methylene resonances of the Me-L ligand gives the following activation parameters: $\Delta H^{\ddagger} = 51.8$ kJ mol^{-1}; $\Delta S^{\ddagger} = -16.2$ J mol^{-1} K^{-1}.[16] Thus, the activation parameters favor a nondissociative rearrangement for the exchange process, possibly with a somewhat ordered transition state.

Conclusion

In this work, we have provided full details of the preparation and structures of a series of Nb(V) complexes that incorporate the acyclic linked aryloxide trimers R-L^{3-} (R = Me, ^{t}Bu) and de-^{t}Bu-L^{3-}. The chloride complexes **1**, **2**, and **3a** provide useful entry points to new organometallic and coordination complexes of niobium. The chloride ligands in **1** and **2** readily reacted with MeMgI and ^{t}BuSLi, resulting in **6**−**8**. The flexible nature of the R-L ligand is revealed by the crystal structure of the κ^2-bound compounds **4** and **5** and the formation of U-shaped (**1**, **2**, **6**, and **7**) and S-shaped (**3a,b** and **8**) compounds. Studies of the reaction chemistry of transition metal complexes supported by the R-L ligand systems are underway and will be reported in due course.

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Supporting Information Available: Listings of X-ray crystallographic files in CIF format for the complexes of **1**, **2**, **3b**, **4**−**6**, and **8**. This material is available free charge via the Internet at http://pubs.acs.org.

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