Inorg. Chem. **1993,** *32,* 4077–4083

Aliphatic Neodymium Alkoxides with Sterically Demanding Ligands. Preparation and X-ray Crystal Structures of $\mathrm{Nd_2(OCH\text{-}\mathit{i}\text{-}Pr_2)_6L_2}$ (L = THF, py) and $\mathrm{[Nd_2(OCH\text{-}\mathit{i}\text{-}Pr_2)_6(\mu\text{-}DME)]_\infty}$

David M. Barnhart,[1a] **David L. Clark,***[1b] **John C. Huffman,**[1c] **Rebecca L. Vincent,**[1d] **and John G. Watkin***[1d]

Inorganic and Structural Chemistry Group, INC-1, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, and Molecular Structure Center, Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Received April 1, 1993[●]

Reaction of the neodymium tris(silylamide) $\mathrm{Nd[N(SiMe_3)_2]_3}$ with 3 equiv of diisopropylmethanol ($\mathrm{HOCH\text{-}\mathit{i}\text{-}Pr_2}$) in hexane in the presence of THF yields the dimeric Lewis base adduct $\mathrm{Nd_2(OCH\text{-}\mathit{i}\text{-}Pr_2)_6(THF)_2}$ (**1**). The THF ligands are easily replaced with pyridine in hexane solvent at room temperature to yield the pyridine adduct $\mathrm{Nd_2(OCH\text{-}\mathit{i}\text{-}Pr_2)_6(py)_2}$ (**2**). The Nd–O bridges in the dimeric alkoxide unit are found to be quite robust, and reaction of **1** with neat 1,2-dimethoxyethane (DME) at room temperature produces $\mathrm{Nd_2(OCH\text{-}\mathit{i}\text{-}Pr_2)_6(\mu\text{-}DME)}$ (**3**), in which the two oxygen atoms of each DME molecule link adjacent $\mathrm{Nd_2(OCH\text{-}\mathit{i}\text{-}Pr_2)_6}$ units to form an infinite-chain structure. In the solid-state structures of **1–3**, each Nd atom adopts a distorted trigonal bipyramidal geometry, in which the $\mathrm{Nd_2O_6L_2}$ core can be viewed as two $\mathrm{NdO_4L}$ trigonal bipyramids joined along a common axial–equatorial edge with the neutral donor ligand L (THF, py, or $^1/_2$ DME) occupying an axial position. The terminal Nd–O distances of OR ligands average 2.153(4), 2.146(4), and 2.145(6) Å, while bridging Nd–O distances average 2.381(4), 2.383(9), and 2.375(9) Å for **1–3**, respectively. The Nd–O–C angles of the terminal alkoxides are very obtuse and average 164.9(4), 174.9(4), and 171.8(8)°, respectively. The Nd–O distances to the oxygen atom of the neutral THF and DME ligands are 2.552(5) and 2.604(6) Å, while the Nd–N distance for coordinated pyridine is 2.682(5) Å. Crystal data for **1** at −161 °C: monoclinic space group $P2_1/n$, $a = 10.949(1)$ Å, $b = 21.433(3)$ Å, $c = 11.965(1)$ Å, $\beta = 95.63(1)°$, $V = 2794.44$ Å^3, $d_{\mathrm{calc}} = 1.336$ g cm^{-3}, $Z = 2$. Crystal data for **2** at −162 °C: triclinic space group $P\bar{1}$, $a = 12.003(4)$ Å, $b = 12.243(4)$ Å, $c = 11.454(4)$ Å, $\alpha = 109.99(1)°$, $\beta = 108.82(1)°$, $\gamma = 98.76(1)°$, $V = 1430.47$ Å^3, $d_{\mathrm{calc}} = 1.321$ g cm^{-3}, $Z = 1$. Crystal data for **3** at −40 °C: triclinic space group $P\bar{1}$, $a = 10.797(3)$ Å, $b = 10.984(3)$ Å, $c = 12.112(3)$ Å, $\alpha = 109.08(3)°$, $\beta = 100.32(2)°$, $\gamma = 90.80(2)°$, $V = 1331.5$ Å^3, $d_{\mathrm{calc}} = 1.334$ g cm^{-3}, $Z = 1$.

Introduction

Alkoxide and aryloxide ligands of general formula $\mathrm{OR^-}$ have found an extensive use in transition metal inorganic and organometallic chemistry due in part to their variable steric requirements, ability to bridge more than one metal center, and π-buffering capabilities.[2] Recently, an intense interest has been generated in the alkoxide chemistry of yttrium and the lanthanide elements due, in part, to a renewed interest in the preparation of ceramic materials.[3] This renewed interest has generated a reasonable number of publications that have focused primarily on alkoxides of Y, La, and Ce.[4] In spite of the wealth of new information provided by these studies, lanthanide alkoxide chemistry is a relatively young field which remains only poorly understood.[5–34] For example, it is possible to commercially obtain rare earth metal alkoxides formulated as $\mathrm{Ln(OR)_3}$, even though structural and spectroscopic studies from the last decade of research have revealed structurally diverse oligomeric units with

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[●] Abstract published in *Advance ACS Abstracts,* August 15, 1993.

(1) (a) Los Alamos National Laboratory. Present address: Department of Chemistry, University of Washington, BC-10, Seattle, WA 98185. (b) LANL Mail Stop G739, INC-1. (c) Indiana University Molecular Structure Center. (d) LANL Mail Stop C346, INC-1.

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a range of formulas such as $Ln_6(OR)_{17}Cl$,[15] $Ln_5O(OR)_{13}$,[29,30] $Ln_5O(OR)_{13}L_2$,[22] $Ln_3(OR)_9L_2$,[31] $Ln_3(OR)_8ClL_2$,[32,33] $Ln_2(OR)_6L_2$,[34] $Ln_2(OR)_6L$,[35] $Ln_2(OR)_6$,[36-38] *etc.* Only in the case of extremely sterically demanding alkoxide ligands such as OC-*t*-Bu_3 or O-2,6-*t*-$Bu_2C_6H_3$ have monomeric $Ln(OR)_3$ complexes been identified.[23,36,39] The aforementioned studies have demonstrated that the nature of oligomerization is highly dependent on the steric requirements of the alkoxide ligand.

As part of our interest in the application of sterically demanding alkoxide ligands in f-element inorganic chemistry, we report here on the products obtained upon reaction of the neodymium tris(silylamide) $Nd[N(SiMe_3)_2]_3$ with the sterically demanding diisopropylmethanol ligand.

Results and Discussion

Synthesis and Reactivity. Treatment of the neodymium tris(silylamide) $Nd[N(SiMe_3)_2]_3$ with 3 equivalents of 2,4-dimethylpentan-3-ol (diisopropylmethanol) in a hexane solution at room temperature produces a pale blue oil of empirical formula $[Nd(OCH\text{-}i\text{-}Pr_2)_3]_x$, as indicated in eq 1. Due to the effects of the paramagnetic neodymium center on the ^1H and ^{13}C NMR spectra and our inability to obtain a solid material for X-ray diffraction studies, the degree of oligomerization in this oily material remains uncertain. However, reaction of $Nd[N(SiMe_3)_2]_3$ with 3 equiv of diisopropylmethanol in a hexane solution, followed by addition of excess THF (THF = tetrahydrofuran, C_4H_8O), results, after normal workup procedures, in the isolation of a crystalline dimeric alkoxide complex of formula $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (**1**) in good yield as outlined in eq 2.

$$Nd[N(SiMe_3)_2]_3 \xrightarrow[\text{hexane}]{3HOCH\text{-}i\text{-}Pr_2} [Nd(OCH\text{-}i\text{-}Pr_2)_3]_x \text{ “oil”} + 3HN(SiMe_3)_2 \quad (1)$$

$$2Nd[N(SiMe_3)_2]_3 \xrightarrow[\text{hexane/THF}]{6HOCH\text{-}i\text{-}Pr_2} Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2 + 6HN(SiMe_3)_2 \quad (2)$$

Even in the presence of an excess of THF in the solution from which **1** is crystallized, we do not observe the formation in the solid state of any mononuclear products of the type $[Nd(OCH\text{-}i\text{-}Pr_2)_3(THF)_x]$. ^1H NMR spectra of these systems were rather uninformative, due to the presence of paramagnetic neodymium metal centers, and thus we were unable to study detailed behavior with respect to possible monomer formation in solution by NMR. In the case of $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (**1**), two broad ^1H NMR resonances tentatively assigned to α- and β-protons of the THF ligand were observed at δ –6.9 and –4.2 ppm, respectively, but all protons of the diisopropylmethoxide ligands appeared as one very broad resonance ($\Delta\nu_{1/2} \sim 1100$ Hz) centered at δ 0.8 ppm.

The THF adduct $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (**1**) is very soluble in hydrocarbon solvents such as hexane and toluene and reacts readily with an excess of pyridine in hexane solution to give the dimeric pyridine adduct of formula $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$ (**2**) according to eq 3. **2** may also be prepared directly from the reaction of $Nd[N(SiMe_3)_2]_3$ with 3 equiv of diisopropylmethanol in hexane, followed by addition of excess pyridine. We note once again that the use of an excess of Lewis base does not lead to cleavage of the dimeric unit. ^1H NMR spectra of **2** were also uninformative with regard to defining its geometry in solution. A very broad resonance ($\Delta\nu_{1/2} \sim 900$ Hz) centered at δ 1.8 ppm is presumed to correspond to the diisopropylmethoxide ligands, while resonances at δ 1.35, 2.70, and 2.90 ppm in a *ca.* 2:2:1 ratio are assigned as pyridine ligand protons.

$$Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2 \xrightarrow[\text{hexane}]{2py} Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2 + 2THF \quad (3)$$

The alkoxide bridges in these neodymium diisopropylmethoxide complexes appear to be quite robust, as they are not readily cleaved by an excess of Lewis base ligand such as THF or pyridine. In an attempt to produce a monomeric neodymium alkoxide, dimeric $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (**1**) was stirred in neat DME solution (DME = 1,2-dimethoxyethane) at room temperature for 6 h. Crystallization from hexane yielded pale blue crystals which analyzed for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(DME)$ (**3**) as shown in eq 4. As in the previous examples, ^1H NMR spectra were so broad and uninformative that they did not provide an insight into the solution structure of **3**.

$$Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2 \xrightarrow{DME} Nd_2(OCH\text{-}i\text{-}Pr_2)_6(DME) + 2THF \quad (4)$$

Solid State and Molecular Structures. Since ^1H NMR spectroscopy yielded no information with regard to the stereochemistry of **1–3**, single-crystal X-ray diffraction studies were undertaken as described below. Three neodymium diisopropylmethoxide compounds have been examined by single-crystal X-ray diffraction studies during the course of this work: $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (**1**), $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$ (**2**), and $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$ (**3**). In the case of **1** and **2**, the unit cell revealed discrete molecules, whereas in **3** an infinite-chain structure was found. A summary of data collection and crystallographic parameters is given in Table I. Atomic positional parameters are given in Tables II–IV.

(a) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (1). Single crystals of **1** suitable for an X-ray diffraction study were grown from a hexane solution by slow cooling to –40 °C. An X-ray data set was collected at –161 °C. A ball and stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 1. Selected bond distances and bond angles are given in Table V. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell which reside on centers of inversion. Each neodymium atom adopts a somewhat distorted trigonal bipyramidal geometry, in which the centrosymmetric Nd_2O_8 core can be viewed as two NdO_5 trigonal bipyramids joined along a common axial–equatorial edge with the neutral THF ligand occupying an axial position. This structural type has been observed previously in transition metal chemistry in the cases of $Mo_2(O\text{-}i\text{-}Pr)_8$[40] and $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$[41] and has also been found in the actinide complexes $U_2(NEt_2)_8$,[42] $Th_2(OCH\text{-}i\text{-}Pr_2)_8$,[43] and $U_2(O\text{-}i\text{-}Pr)_6[N(SiMe_3)_2]_2$.[44] The three equatorial Nd–O bonds are only slightly distorted from the ideal (120°) trigonal angles, the actual values being 119.97(14), 120.71(15), and 117.57(15)°; hence the trigonal NdO_3 unit is nearly planar. The axial O–Nd–O angle is distorted [160.47(14)°] from the idealized 180°, and this distortion may be due to steric demands in the bridge (Figure 1).

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Table I. Summary of Crystallographic Data[a]

	1	**2**	**3**
empirical formula	$C_{50}H_{106}O_8Nd_2$	$C_{52}H_{100}O_6N_2Nd_2$	$C_{46}H_{100}O_8Nd_2$
color	pale blue	lavender (pink)	pale blue
crystal dimens, mm^{-1}	0.20 × 0.20 × 0.15	0.15 × 0.20 × 0.21	0.2 × 0.13 × 0.08
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	10.949(1)	12.003(4)	10.797(3)
b, Å	21.433(3)	12.243(4)	10.984(3)
c, Å	11.965(1)	11.454(4)	12.112(3)
α, deg		109.99(1)	109.08(3)
β, deg	95.63(1)	108.82(1)	100.32(2)
γ, deg		98.76(1)	90.80(2)
V, Å^3	2794.44	1430.47	1331.5
Z, molecules/cell	2	1	1
fw	1123.86	1137.86	1069.7
d_{calc}, g cm^{-3}	1.3357	1.321	1.334
abs coeff, cm^{-1}	18.871	18.427	19.72
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69
T, °C	−161	−162	−40
2θ range, deg	6.0–45.0	6.0–45.0	2.0–45.0
no. of measd reflns	5291	4039	3693
no. of unique intensities	3642	3732	3470
no. of obsd reflns	2900 ($F > 2.33\sigma(F)$)	3596 ($F > 2.33\sigma(F)$)	3212 ($F > 4\sigma(F)$)
R(*F*)	0.0343	0.0386	0.0556
$R_w(F)$	0.0341	0.0415	0.0743
goodness-of-fit	0.74	1.15	1.81

[a] **1** = $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$; **2** = $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$; **3** = $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Nd(1)	5197.8(3)	633.9(2)	6146.0(3)	13
O(2)	3562(4)	1108(2)	6522(4)	19
C(3)	2384(6)	1323(3)	6721(6)	19
C(4)	1872(6)	1784(3)	5804(6)	22
C(5)	563(6)	1969(4)	5955(7)	32
C(6)	1919(7)	1508(4)	4648(6)	28
C(7)	2393(6)	1593(3)	7917(6)	25
C(8)	3132(7)	2192(4)	8070(7)	35
C(9)	2839(7)	1116(4)	8795(6)	32
O(10)	6706(4)	593(2)	7450(3)	18
C(11)	7343(6)	576(3)	8541(5)	19
C(12)	7569(6)	1226(4)	9022(6)	26
C(13)	6364(7)	1577(4)	9035(7)	36
C(14)	8218(7)	1203(4)	10208(7)	37
C(15)	8501(6)	166(3)	8576(6)	23
C(16)	9522(6)	471(4)	7977(7)	29
C(17)	8199(7)	−484(4)	8101(7)	35
O(18)	5532(4)	391(2)	4247(3)	15
C(19)	6402(5)	759(3)	3720(5)	17
C(20)	5882(6)	961(3)	2543(6)	20
C(21)	4789(7)	1406(4)	2589(7)	34
C(22)	5537(7)	431(4)	1754(6)	28
C(23)	7656(6)	441(3)	3764(6)	21
C(24)	8071(6)	222(4)	4947(6)	27
C(25)	8633(6)	876(4)	3383(6)	28
O(26)	5983(4)	1736(2)	5846(4)	20
C(27)	7255(6)	1922(3)	6063(6)	24
C(28)	7228(7)	2564(4)	6571(7)	36
C(29)	5946(8)	2814(4)	6229(10)	52
C(30)	5308(7)	2295(4)	5540(7)	31

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Fractional Coordinates and Isotropic Thermal Parameters[a] for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Nd(1)	8573.3(3)	−1384.7(3)	8978.4(3)	13
N(2)	6383(5)	−1487(5)	7260(5)	21
C(3)	5552(6)	−1193(7)	7771(7)	28
C(4)	4420(7)	−1163(8)	7006(9)	37
C(5)	4127(7)	−1431(8)	5656(9)	39
C(6)	4941(7)	−1754(7)	5114(7)	34
C(7)	6061(6)	−1781(6)	5934(7)	23
O(8)	10675(4)	−704(3)	10535(4)	16
C(9)	11516(6)	−1381(6)	10897(6)	19
C(10)	11240(6)	−1916(6)	11837(7)	23
C(11)	10026(7)	−2919(7)	11158(7)	29
C(12)	11310(6)	−937(7)	13110(7)	27
C(13)	11567(6)	−2297(6)	9624(7)	23
C(14)	12425(8)	−3045(8)	9986(8)	38
C(15)	11967(7)	−1669(7)	8838(7)	29
O(16)	7450(4)	−1869(4)	9968(4)	20
C(17)	6670(6)	−2131(6)	10596(7)	26
C(18)	7377(7)	−1786(7)	12076(7)	30
C(19)	8176(7)	−474(7)	12821(7)	28
C(20)	6542(8)	−1996(8)	12787(8)	37
C(21)	5840(7)	−3467(7)	9788(7)	30
C(22)	5006(8)	−3724(8)	8349(9)	43
C(23)	6576(8)	−4359(7)	9809(9)	40
O(24)	8648(4)	−2735(4)	7261(4)	18
C(25)	8752(6)	−3689(6)	6223(6)	22
C(26)	8515(6)	−3439(6)	4955(6)	23
C(27)	9438(7)	−2254(7)	5309(7)	34
C(28)	8606(7)	−4469(7)	3807(7)	33
C(29)	7903(7)	−4916(6)	5949(7)	29
C(30)	6563(7)	−4959(7)	5495(8)	35
C(31)	8329(8)	−5173(7)	7206(9)	38

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table IV. Fractional Coordinates and Isotropic Thermal Parameters[a] for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Nd(1)	1567(1)	401(1)	1121(1)	16(1)
O(1)	3763(5)	914(5)	702(5)	24(2)
O(2)	2032(5)	2257(5)	2478(5)	24(2)
O(3)	2389(5)	−1233(5)	1474(5)	23(2)
O(4)	607(5)	155(5)	−885(4)	20(2)
C(1)	4714(7)	21(8)	537(8)	27(3)
C(2)	4194(8)	2229(8)	895(8)	32(3)
C(3)	2391(7)	3526(8)	3293(7)	28(3)
C(4)	3381(8)	3491(8)	4365(8)	34(3)
C(5)	4541(9)	2880(10)	3991(9)	48(4)
C(6)	2829(9)	2836(10)	5138(8)	45(4)
C(7)	1243(8)	4231(7)	3619(7)	28(3)
C(8)	1588(10)	5575(9)	4575(9)	49(4)
C(9)	402(10)	4366(10)	2523(9)	44(4)
C(10)	2724(7)	−2321(7)	1789(7)	24(3)
C(11)	3477(8)	−1915(8)	3069(7)	31(3)
C(12)	4712(8)	−1126(9)	3237(9)	41(4)
C(13)	2672(9)	−1140(10)	3966(8)	43(4)
C(14)	3437(7)	−3215(8)	885(7)	27(3)
C(15)	3831(8)	−4385(8)	1222(8)	38(4)
C(16)	2624(10)	−3643(10)	−356(8)	40(4)
C(17)	1327(7)	632(8)	−1565(7)	23(3)
C(18)	797(8)	1827(8)	−1750(7)	24(3)
C(19)	1589(10)	2398(10)	−2432(10)	51(5)
C(20)	723(8)	2867(8)	−578(8)	35(3)
C(21)	1475(8)	−453(8)	−2714(8)	30(3)
C(22)	298(8)	−809(8)	−3674(8)	36(3)
C(23)	1961(8)	−1597(8)	−2431(8)	39(4)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

The terminal Nd–O distances of the alkoxide ligands average 2.153(4) Å and can be compared to average terminal Nd–O distances of 2.05(2), 2.174(2), and 2.148(16) Å seen in $Nd_6(O\text{-}i\text{-}Pr)_{17}Cl$,[15] $\overline{Nd(OC\text{-}t\text{-}Bu_2CH_2P}Me_2)_3$,[7] and $Nd_5O(O\text{-}i\text{-}Pr)_{13}(HO\text{-}i\text{-}Pr)_2$,[22] respectively. The Nd–O–C angles of the terminal alkoxides are very obtuse and average 164.9(4)°. Bridging Nd–O distances are, as expected, somewhat longer than those of the terminal alkoxide ligands and average 2.381(4) Å. The Nd–O distance to the oxygen atom of the THF ligand is 2.552(5) Å, and is almost identical to the 2.56(4) Å found in $(\eta\text{-}C_5H_5)_3Nd(THF)$[45] and 2.575(20) Å (average) in $[(\eta\text{-}C_8H_8)Nd(THF)_2][Nd(\eta\text{-}$

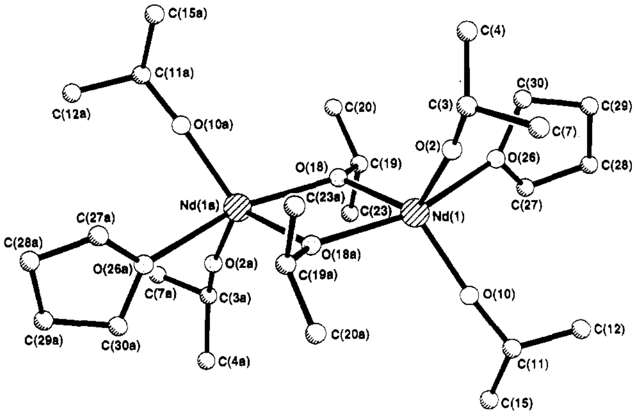

Figure 1. Ball-and-stick drawing of the solid-state molecular structure of $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (**1**). Methyl carbon atoms are omitted for clarity.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$

Nd(1)–O(2)	2.146(4)	O(10)–C(11)	1.419(7)
Nd(1)–O(10)	2.160(4)	O(18)–C(19)	1.430(7)
Nd(1)–O(18A)	2.368(4)	O(26)–C(27)	1.447(8)
Nd(1)–O(18)	2.394(4)	O(26)–C(30)	1.435(9)
Nd(1)–O(26)	2.552(4)	C(3)–C(4)	1.541(10)
O(2)–C(3)	1.411(7)	C(3)–C(7)	1.543(10)

O(2)–Nd(1)–O(10)	117.57(16)	O(18)–Nd(1)–O(26)	89.04(14)
O(2)–Nd(1)–O(18A)	102.06(15)	Nd(1)–O(2)–C(3)	170.2(4)
O(2)–Nd(1)–O(18)	120.71(15)	Nd(1)–O(10)–C(11)	159.6(4)
O(2)–Nd(1)–O(26)	83.71(15)	Nd(1)–O(18)–Nd(1A)	108.09(15)
O(10)–Nd(1)–O(18A)	108.97(15)	Nd(1)–O(18A)–C(19A)	130.6(4)
O(10)–Nd(1)–O(18)	119.97(14)	Nd(1)–O(18)–C(19)	117.9(3)
O(10)–Nd(1)–O(26)	83.96(15)	Nd(1)–O(26)–C(27)	124.1(4)
O(18)–Nd(1)–O(18A)	71.91(15)	Nd(1)–O(26)–C(30)	129.5(4)
O(18A)–Nd(1)–O(26)	160.47(14)		

$C_8H_8)_2]$,[46] while slightly longer than the 2.50 Å (average) in $NdCl_3(THF)_4$.[47]

The overall molecular geometry found in **1** may be contrasted to that of a closely related bismuth alkoxide structure, $\{Bi[OCH(CF_3)_2]_3(THF)\}_2$,[48] in which the metal centers exhibit a distorted octahedral geometry with one missing vertex.

(b) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$ (2). Single crystals of **2** suitable for an X-ray diffraction study were grown from a hexane solution by slow cooling to −40 °C. An X-ray data set was collected at −162 °C. A ball and stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 2. Selected bond distances and bond angles are given in Table VI. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with the dimeric unit lying on a crystallographic center of inversion. The overall molecular geometry is strikingly similar to that found in **1**, with each neodymium atom adopting a distorted trigonal bipyramidal geometry. The centrosymmetric $Nd_2O_6N_2$ core can be viewed as two NdO_4N trigonal bipyramids joined along a common axial–equatorial edge with the pyridine ligand occupying an axial position. The three equatorial bonds are once again only slightly distorted from the ideal (120°) trigonal angles, the actual values being 118.61(15), 120.69(16), and 119.02(15)°. The axial O–Nd–N angle is also distorted from 180°, and the value of 163.03(14)° is very similar to the axial O–Nd–O angle of 160.47(14)° in **1**.

Neodymium–oxygen distances to terminal and bridging alkoxide ligands are very similar to those of **1**, averaging 2.146(4) and 2.383(9) Å, respectively. The Nd–O–C angles of the terminal alkoxides are even closer to linearity than those of **1** and average 174.9(4)°. The Nd–N distance to the nitrogen atom of the pyridine ligand is 2.682(5) Å, very similar to the 2.668(5) Å in $(\eta\text{-}C_5H_5)_3Nd(py)$[49] and 2.62 Å in the 1,2-bis(4-pyridyl)ethane ligand of $\{[(C_5H_3S)C(O)CC(O)CF_3]_3Nd(NC_5H_4CH_2CH_2C_5H_4N)\}$.[50]

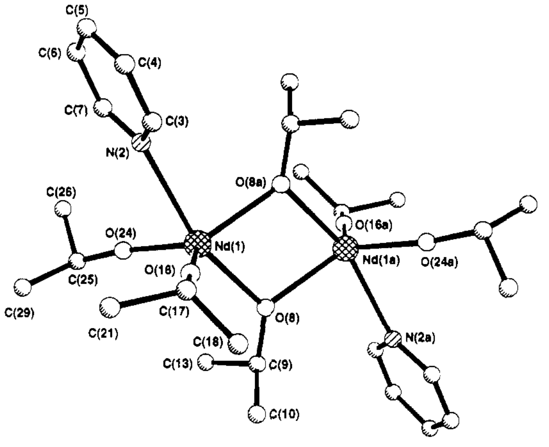

Figure 2. Ball-and-stick drawing of the solid-state molecular structure of $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$ (**2**). Methyl carbon atoms are omitted for clarity.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$

Nd(1)–Nd(1A)	3.817(1)	O(8)–C(9)	1.448(7)
Nd(1)–O(8A)	2.380(4)	O(16)–C(17)	1.414(7)
Nd(1)–O(8)	2.383(4)	O(24)–C(25)	1.408(8)
Nd(1)–O(16)	2.158(4)	N(2)–C(3)	1.345(9)
Nd(1)–O(24)	2.133(4)	N(2)–C(7)	1.338(8)
Nd(1)–N(2)	2.682(5)		

O(8A)–Nd(1)–O(8)	73.48(15)	O(16)–Nd(1)–N(2)	81.26(16)
O(8A)–Nd(1)–O(16)	118.61(15)	O(24)–Nd(1)–N(2)	86.24(16)
O(8)–Nd(1)–O(16)	107.95(14)	Nd(1)–O(8)–Nd(1A)	106.52(15)
O(8)–Nd(1)–O(24)	100.38(14)	Nd(1A)–O(8)–C(9)	130.8(3)
O(8A)–Nd(1)–O(24)	119.02(15)	Nd(1)–O(8)–C(9)	120.8(3)
O(8A)–Nd(1)–N(2)	89.63(14)	Nd(1)–O(16)–C(17)	176.1(4)
O(8)–Nd(1)–N(2)	163.03(14)	Nd(1)–O(24)–C(25)	173.6(4)
O(16)–Nd(1)–O(24)	120.69(16)	Nd(1)–N(2)–C(3)	117.8(4)
Nd(1)–N(2)–C(7)	125.0(4)		

(c) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$ (3). Single crystals of **3** suitable for an X-ray diffraction study were grown from hexane solution at −40 °C. An X-ray data set was collected at −40 °C. A ball and stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 3. Selected bond distances and bond angles are given in Table VII. Compound **3** crystallizes in the monoclinic space group $P\bar{1}$, and the unit cell contains a dimeric $Nd_2(OCH\text{-}i\text{-}Pr_2)_6$ unit which lies on a crystallographic inversion center, along with half of a DME molecule bound to each neodymium atom. Moving into the next unit cell produces the symmetry-generated second half of the DME molecule bonded to another dimeric alkoxide unit. This is repeated throughout the lattice to produce an infinite-chain structure as shown in Figure 4.

The geometry and metric parameters within the $Nd_2(OCH\text{-}i\text{-}Pr_2)_6$ moiety are very similar to those already described for **1** and **2** above. Neodymium–oxygen distances for terminal alkoxide ligands average 2.145 Å, while those for bridging ligands average 2.375 Å. The Nd–O distance to the bridging DME ligand is 2.604(6) Å. The O–Nd–O angles of the three equatorial alkoxide ligands [O(2), O(3), O(4)] sum to 358.4°, indicating near planarity, while the axial O(4A)–Nd(1)–O(1) angle is distorted

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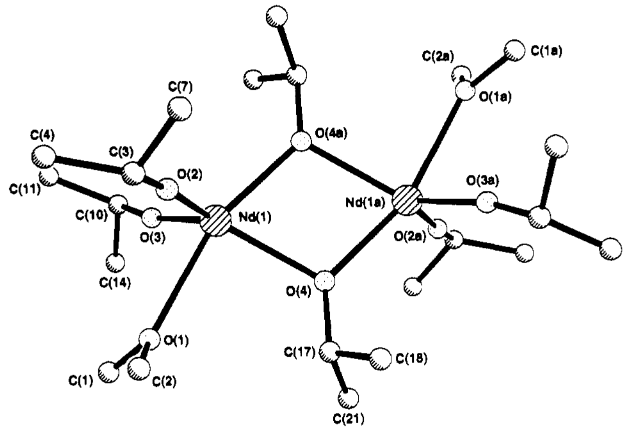


Figure 3. Ball-and-stick drawing of the unit cell contents of the solid-state molecular structure of $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$ (3). Methyl carbon atoms of the diisopropylmethoxide ligands are omitted for clarity.

Table VII. Selected Bond Distances (Å) and Angles (deg) for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$

Nd(1)–O(1)	2.604(6)	O(1)–C(1)	1.425(10)
Nd(1)–O(2)	2.144(4)	O(1)–C(2)	1.441(10)
Nd(1)–O(3)	2.145(6)	O(2)–C(3)	1.420(8)
Nd(1)–O(4)	2.391(5)	O(3)–C(10)	1.402(11)
Nd(1)–O(4A)	2.359(5)	O(4)–C(17)	1.434(11)
Nd(1)–Nd(1A)	3.829(1)		

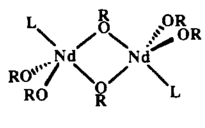
O(1)–Nd(1)–O(2)	81.6(2)	O(4)–Nd(1)–O(4A)	72.6(2)
O(1)–Nd(1)–O(3)	85.4(2)	Nd(1)–O(1)–C(1)	123.7(5)
O(2)–Nd(1)–O(3)	117.8(2)	Nd(1)–O(1)–C(2)	120.2(5)
O(1)–Nd(1)–O(4)	90.1(2)	Nd(1)–O(2)–C(3)	174.3(6)
O(2)–Nd(1)–O(4)	122.4(2)	Nd(1)–O(3)–C(10)	169.3(5)
O(3)–Nd(1)–O(4)	118.2(2)	Nd(1)–O(4)–C(17)	117.7(4)
O(1)–Nd(1)–O(4A)	162.7(2)	Nd(1)–O(4)–Nd(1A)	107.4(2)
O(2)–Nd(1)–O(4A)	108.3(2)	Nd(1A)–O(4)–C(17)	133.0(4)
O(3)–Nd(1)–O(4A)	101.6(2)		

to 162.7(2)°. Terminal alkoxide ligands display almost linear Nd–O–C angles, averaging 171.8°. A comparison of Nd--Nd distances for all three complexes reveals a range of *ca.* 0.04 Å: 3.855(1) Å (**1**), 3.817(1) Å (**2**), 3.829(1) Å (**3**).

Although we have found examples in the literature of 1,4-dioxane behaving as a bridging ligand in an infinite-chain structure, we believe that **3** represents the first structurally characterized example of DME displaying this phenomenon.

Concluding Remarks. We have shown that treatment of $Nd[N(SiMe_3)_2]_3$ with 3 equiv of diisopropylmethanol in a hexane solution at room temperature produces a pale-blue oil of empirical formula $[Nd(OCH\text{-}i\text{-}Pr_2)_3]_x$. While the degree of oligomerization in this oily material remains uncertain, the reaction of $Nd[N(SiMe_3)_2]_3$ with 3 equiv of diisopropylmethanol in hexane in the presence of a Lewis base such as THF or pyridine yields dimeric Lewis base adducts $Nd_2(OCH\text{-}i\text{-}Pr_2)_6L_2$ (L = THF, py) under mild conditions. The Nd–O bridges in the $Nd_2(OCH\text{-}i\text{-}Pr_2)_6$ unit appear to be fairly robust, and reaction of $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ with neat 1,2-dimethoxyethane (DME) at room temperature does not produce a monomeric complex; instead, the dimeric $Nd_2(OCH\text{-}i\text{-}Pr_2)_6$ unit is maintained and $[Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)]_\infty$ (**3**) is produced.

In the solid-state structures of **1**–**3**, each Nd atom adopts a distorted trigonal bipyramidal geometry, in which the centrosymmetric $Nd_2O_6L_2$ core can be viewed as two NdO_4L trigonal bipyramids joined along a common axial–equatorial edge with the neutral donor ligand L (THF, py, or $^1/_2$ DME) occupying an axial position as indicated schematically in **I**. In the case of the adduct formed from the bidentate DME ligand (**3**), oxygen atoms at opposite ends of the DME molecule bridge between adjacent $Nd_2(OCH\text{-}i\text{-}Pr_2)_6$ alkoxide units to form a polymeric, infinite-chain structure in the solid state, and this is indicated schematically in **II**.



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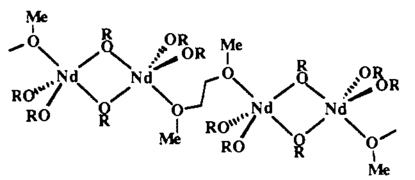

II

The apparent inability of THF, pyridine, or DME ligands to cleave the $Nd_2(OCH\text{-}i\text{-}Pr_2)_6$ unit under mild conditions to give monomeric complexes of general formula $Nd(OR)_3L_x$ is in marked contrast to other $Ln_2(OR)_6$ compounds of yttrium, cerium, and lanthanum (R = $OCPh_3$, $OSiPh_3$), which cleave readily in THF solutions to give monomeric $Ln(OR)_3(THF)_3$ complexes in high yield.[35–38] However, we also note that the yttrium aryloxide complex $[Y(O\text{-}2,6\text{-}Me_2C_6H_3)_3(THF)]_2$ reversibly interconverts between the monomeric trisolvate $Y(O\text{-}2,6\text{-}Me_2C_6H_3)_3(THF)_3$ and dimeric $Y_2(O\text{-}2,6\text{-}Me_2C_6H_3)_6(THF)_2$ with one THF ligand per yttrium center.[34] These differences in reactivity toward Lewis bases may reflect subtle differences in the electronic properties of the alkoxide or aryloxide ligands. Further studies of this concept are in progress.

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox. Sodium bis(trimethylsilyl)amide, $NaN(SiMe_3)_2$, was prepared by a modification of Krüger and Niederprüm.[51] $Nd[N(SiMe_3)_2]_3$ was prepared using the reaction of $NdCl_3$ (Aldrich) with 3 equiv of $Na[N(SiMe_3)_2]$ in THF at room temperature for 48 h.[52] Diisopropylmethanol was purchased from Aldrich, degassed, and used without further purification. Solvents, except for pyridine, were degassed and distilled from Na/K alloy under nitrogen. Pyridine was distilled from CaH_2 under argon. Benzene-d_6 and toluene-d_8 were degassed, dried over Na/K alloy, and then trap-to-trap distilled before use. Solvents were taken into the glovebox, and a small amount was tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22 °C on a Bruker AF 250 spectrometer in benzene-d_6 or toluene-d_8. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in benzene-d_6 or toluene-d_8 set at δ 7.15 or 2.09 ppm, respectively. NMR spectra of paramagnetic neodymium species are highly temperature dependent; thus it is important to note that the temperatures quoted represent average room temperatures and are approximate values. Infrared spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS-40 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Preparations. (a) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (1). To a solution of 1.996 g (3.19 mmol) of $Nd[N(SiMe_3)_2]_3$ in 100 mL of hexane was added dropwise a solution of 1.11 g (9.55 mmol) of diisopropylmethanol in 10 mL of hexane with stirring. The mixture was stirred at room temperature for 1 h, and then 1 mL of THF was added. All solvent was removed *in vacuo* to leave a pale blue solid, which was redissolved in 20 mL of hexane. The solution was then cooled to –40 °C, and pale blue crystals were deposited after 12 h. These were collected by decantation and allowed to dry under a helium atmosphere. Yield: 1.028 g (57%). ^1H NMR (250 MHz, 22 °C, C_6D_6): broad resonances at δ –4.2 and –6.9 ppm, possibly β- and α-THF, respectively; very broad resonance centered at δ 0.8 ppm. IR (KBr, Nujol, cm^{-1}): 1363 (m), 1267 (w), 1238 (w), 1178 (m), 1156 (m), 1142 (s), 1105 (s), 1070 (m), 1034 (s), 1019 (s), 995 (s), 973 (s), 951 (m), 919 (w), 891 (m), 852 (w), 795 (w), 721 (w), 666 (sh, s), 662 (s), 642 (m), 584 (w), 503 (m), 469 (w). Anal. Calcd for $C_{50}H_{106}O_8Nd_2$: C, 53.44; H, 9.51; N, 0.00. Found: C, 52.17; H, 8.51; N, 0.06.

(b) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$ (2). To a solution of 1.998 g (3.19 mmol) of $Nd[N(SiMe_3)_2]_3$ in 100 mL of hexane was added dropwise a solution of 1.11 g (9.55 mmol) of diisopropylmethanol in 10 mL of hexane. The

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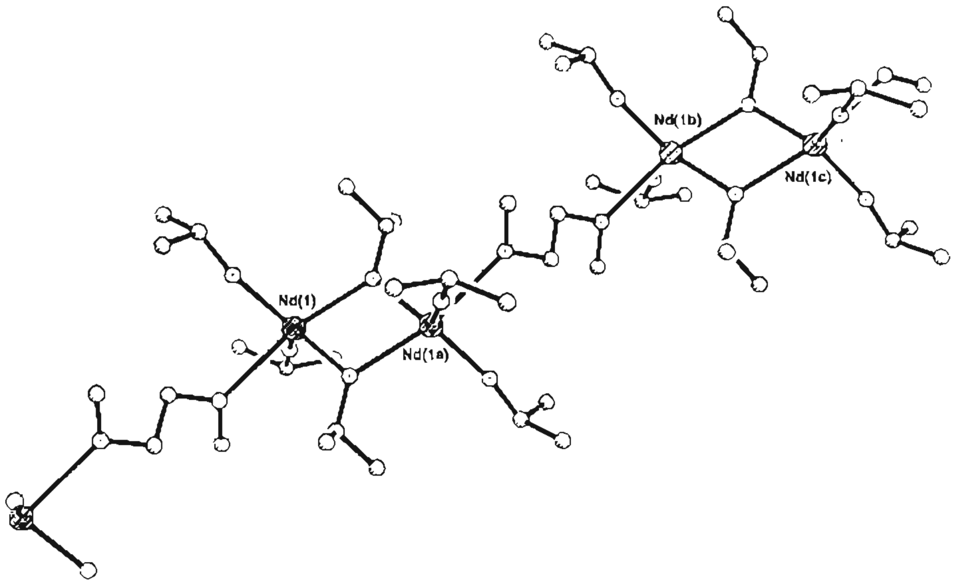

Figure 4. View of a portion of the infinite-chain solid-state structure of $[Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)]_\infty$ (3).

mixture was stirred at room temperature for 1 h, and then 1 mL of pyridine was added. All solvent was removed *in vacuo* to leave a pale blue solid, which was redissolved in 20 mL of hexane. The solution was then cooled to −40 °C, and pale blue crystals were deposited after 12 h. These were collected by decantation and allowed to dry under an atmosphere of He. Yield: 1.336 g (74%). ^{1}H NMR (250 MHz, 22 °C, C_6D_6): broad resonances observed at δ 1.35, 1.98, 2.70, and 2.90 ppm; very broad resonance centered at δ 1.8 ppm. IR (KBr, Nujol, cm^{-1}): 1594 (m), 1442 (s), 1362 (sh, m), 1216 (m), 1177 (m), 1156 (m), 1141 (s), 1107 (s), 1068 (m), 1033 (s), 1020 (s), 993 (m), 973 (s), 952 (m), 919 (w), 905 (w), 854 (w), 825 (w), 799 (w), 749 (m), 702 (m), 664 (m), 642 (w), 617 (w), 510 (m), 469 (w), 451 (w). Anal. Calcd for $C_{52}H_{100}N_2O_6Nd_2$: C, 54.89; H, 8.86; N, 2.46. Found: C, 53.88; H, 9.17; N, 2.17.

(c) $[Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)]_\infty$ (3). A 0.498-g (0.44-mmol) sample of $[Nd(OCH\text{-}i\text{-}Pr_2)_3(THF)]_2$ (1) was dissolved in 20 mL of neat dimethoxyethane, and the solution was stirred at room temperature for 6 h. All solvent was removed *in vacuo* to leave a pale blue solid, which was dissolved in 20 mL of hexane. The solution was then cooled to −40 °C, and pale blue crystals were deposited after 12 h. These were decanted free from solvent and allowed to dry under a helium atmosphere. Yield: 0.372 g (74%). ^{1}H NMR (250 MHz, 22 °C, C_6D_6): room-temperature spectrum is very uninformative. IR (KBr, Nujol, cm^{-1}): 1365 (sh, m), 1342 (sh, w), 1178 (w), 1157 (sh, w), 1141 (m), 1105 (s), 1070 (w), 1032 (sh, s), 1019 (s), 994 (m), 976 (w), 952 (w), 728 (w), 664 (m), 643 (w). Anal. Calcd for $C_{46}H_{100}O_8Nd_2$: C, 51.65; H, 9.42; N, 0.00. Found: C, 51.57; H, 8.81; N, 0.03.

Crystallographic Studies. A summary of crystallographic data can be found in Table I. General operating procedures have been described elsewhere.[53] The diffractometer utilized for data collection for 1 and 2 was designed and constructed locally at the IUMSC. The diffractometer consisted of a Picker four-circle goniostat, equipped with a Furnas monochromator (HOG crystal), and Picker X-ray generator, interfaced to a Z80 microprocessor and controlled by an RS232 Serial port on an IBM PC microcomputer. Motors are Slo-Syn stepping motors, and a special top/bottom–left/right slit assembly is used to align the crystal. All computations were performed on IBM-compatible microcomputer systems.

(a) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$ (1). A small fragment measuring 0.20 × 0.20 × 0.15 mm was cleaved from a larger crystal and affixed to the end of a glass fiber using silicone grease. The crystal was then transferred to the goniostat using standard inert-atmosphere handling techniques employed by the IUMSC, and it was cooled to −161 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$. Subsequent solution and refinement confirmed this choice. Data were collected using a continuous θ–2θ scan with fixed background counts at each extreme of the scan. All data were corrected for Lorentz and polarization terms and equivalent data averaged to a unique set of intensities and associated σ's in the usual manner.

The structure was easily solved by direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least-squares procedures. All hydrogen atoms were clearly visible in a difference Fourier map phased on the non-hydrogen atoms and were included in the final least-squares calculations. Final refinement using 2900 unique observed [$F > 2.33\sigma(F)$] reflections converged at $R = 0.0343$, $R_w = 0.0341$. A final difference Fourier map was featureless, the largest peak being 0.82 e/Å^3, located at the metal site.

(b) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$ (2). A small, well-formed crystal measuring 0.15 × 0.20 × 0.21 mm was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat using standard inert-atmosphere handling techniques employed by the IUMSC, and it was cooled to −162 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space failed to reveal any symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the centrosymmetric choice of $P\bar{1}$. Data were collected using a standard moving crystal–moving detector technique with fixed background counts at each extreme of the scan. Equivalent data were averaged after correction for Lorentz and polarization terms.

The structure was readily solved by direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were located and refined. Final refinement using 3596 unique observed [$F > 2.33\sigma(F)$] reflections converged at $R = 0.0386$, $R_w = 0.0415$. The dimeric species lies at a crystallographic center of inversion. A final difference Fourier map was a featureless, the largest peak being 0.45 e/Å^3.

(c) $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$ (3). A small, pale blue, oblong crystal measuring 0.20 × 0.13 × 0.08 mm was selected under the microscope under an argon purge. It was affixed to the end of a glass fiber using silicone grease and transferred to the goniometer head of an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, where it was cooled to −40 °C for characterization and data collection. Unit cell parameters were determined from the least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 accurately centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans was applied. The structure was readily solved by Patterson methods and subsequent difference Fourier maps. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 3212 unique observed [$F > 4.0\sigma(F)$] reflections converged at $R = 0.056$, $R_w = 0.074$ {where $w = [\sigma^2(F) + 0.0016F^2]^{-1}$}. All calculations for 3 were performed using the SHELXTL

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(53) Chisholm, M. H.; Folting, K. Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc., 1990). A final difference Fourier map contained some residual electron density around the neodymium metal atom, the largest peak being 3.33 e/Å^3, approximately 1.0 Å from Nd(1).

Acknowledgment. We wish to thank Drs. A. P. Sattelberger and J. L. Atwood for helpful discussions. We acknowledge Los Alamos National Laboratory and the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-36, for financial support.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, and bond angles for $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(THF)_2$, $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(py)_2$, and $Nd_2(OCH\text{-}i\text{-}Pr_2)_6(\mu\text{-}DME)$ (6 pages). Ordering information is given on any current masthead page. Structure factor tables are available from the authors upon request.