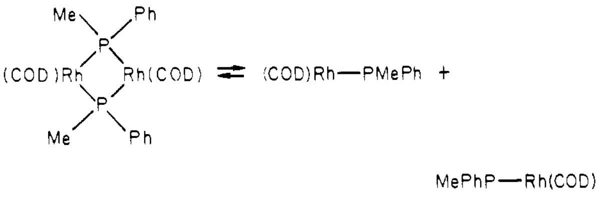
the isomerization is reversible dissociation into monomeric complexes as in eq 7. A more complicated mechanism in-



(7)

volving initial dissociation of only one Rh–P bond followed by association of the resultant free Rh–PMePh ligand with a Rh center of another dimeric complex can also be envisaged. Although the isomerization is relatively slow at 22 °C, requiring ~1 day for equilibrium to be reached, the essential point is that isomerization does occur and the μ-PMePh bridging ligands are clearly not sufficient to retard fragmentation of the binuclear complexes. A similar conclusion was reached in our earlier study of a series of μ-PPh_2-bridged cobalt carbonyl complexes.[18]

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Registry No. **1**, 82829-24-1; $[Rh_2(\mu\text{-PMePh})_2(COD)_2]$, 89908-32-7; $[Rh_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(COD)_2]$, 83681-89-4; $[Rh_2(\mu\text{-Cl})(\mu\text{-PMePh})(COD)_2]$, 89908-33-8; $[Rh_2(\mu\text{-PPh}_2)_2(PEt_3)_4]$, 89908-34-9; $[Rh_2(\mu\text{-Cl})_2(COD)_2]$, 12092-47-6; LiPMePh, 38327-00-3; $LiPPh_2$, 4541-02-0.

Supplementary Material Available: Figure 1, $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2(\mu\text{-PPh}_2)_2(PEt_3)_4]$ in C_6D_6 solution (1 page). Ordering information is given on any current masthead page.

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[18] Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.

Contribution from the Departments of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139,
and Columbia University, New York, New York 10027

Synthesis and Structure of $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl][NbOCl_4(THF)]\cdot THF$[1,2]

Helen C. Aspinall, Michael M. Roberts,
and Stephen J. Lippard*

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High-coordinate early transition metal isocyanide complexes have been of interest to us for several reasons. Because the C≡N—R unit is sterically undemanding, $M(CNR)_xL_{n-x}$ (L = halide, cyanide, etc.; $n > 6$) complexes afford an opportunity to explore relationships among electronic structure, crystal packing forces, and stereoisomerism for this class of compounds.[2,3] The chemistry of these isocyanide complexes has also proved to be quite intriguing, especially the recently discovered dealkylation (eq 1, 2)[4,5] and reductive coupling[6,7] (eq 3, 4) reactions. Although a variety of isocyanide complexes of the group 6 metals now exists, there has been much less work on group 5 isocyanide complexes.[8] Known examples include six-coordinate vanadium compounds,[9] some incompletely characterized niobium and tantalum "insertion products" of RNC into M–halogen bonds,[10] the crystallographically identified compounds $Nb_3Cl_8(CNCMe_3)_5$ and $Nb_2Cl_6(CNCMe_3)_4(\mu\text{-}Me_3CNCCNCMe_3)$,[7] and the bis(cyclopentadienyl) complexes $[(\eta^5\text{-}C_5H_5)_2NbCl(CNR)]$, R = Ph, Cy.[11] In the present note we describe the synthesis and structural characterization of $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl]^+$, a formally eight-coordinate niobium(III) (d^2) cation analogous in some respects to the niobium(III) center in $Nb_2Cl_6(CNCMe_3)_4(\mu\text{-}Me_3CNCCNCMe_3)$.

$$[M(CNR)_7]^{2+} \xrightarrow[\text{alcohol}]{\text{reflux}} [M(CNR)_6(CN)]^+ + \text{other products} \tag{1}$$

M = Mo, W; R = CMe_3

$$2[Mo(CNCMe_3)_7]^{2+} + 2bpy \rightarrow [(Mo(CNCMe_3)_4(bpy))_2(\mu\text{-CN})]^{3+} + \text{other products} \tag{2}$$

$$[M(CNR)_6X]^+ \xrightarrow[\text{THF/H}^+]{\text{Zn}} [M(CNR)_4(RNHC{\equiv}CNHR)X]^+ \tag{3}$$

M = Mo, W; R = alkyl; X = Cl, Br, I, CN

$$Nb_2Cl_6(SMe_2)_3 \xrightarrow{\text{CNR}} Nb_2Cl_6(CNR)_4(\mu\text{-RNC}{\equiv}\text{CNR}) \tag{4}$$

R = CMe_3

Experimental Section

Synthesis of $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl][NbCl_4O(THF)]\cdot THF$. Preparative work was carried out under an atmosphere of nitrogen with use of dried, distilled solvents. The starting material $(\eta^5\text{-}C_5H_5)NbCl_4$ was prepared from $(\eta^5\text{-}C_5H_5)Sn(n\text{-}C_4H_9)_3$[12] by a literature procedure.[13] Sodium amalgam (1%, 2 mL) was added to a mixture of $(\eta^5\text{-}C_5H_5)NbCl_4$ (1 g, 3.33 mmol) and $CNCMe_3$ (1.8 mL, 16.7 mmol) in 40 mL of toluene and 10 mL of THF. The mixture was stirred at room temperature for 20 min. After this time all the sparingly soluble starting material had reacted to give a brown-orange solution, which was filtered through Celite. The filtrate was evaporated in vacuo to give a partly crystallized brown oil. The product was obtained as bright orange needles by two recrystallizations from THF (15 mL) and heptane (~10 mL) at −20 °C. The air-sensitive crystals were washed with heptane and dried in vacuo; yield 0.5 g (32%). Anal. Calcd for $Nb_2Cl_5O_3N_4C_{33}H_{57}$: C, 43.04; H, 6.24; N, 6.08; Cl, 19.25. Found: C, 43.58; H, 6.29; N, 6.37; Cl, 18.99. IR (Nujol): ν_{CN}, 2185 (s, sh), 2146 (vs), 2048 (m, sh) cm^{-1}; other, 1283 (m), 1198 (s), 1065 (m), 1038 (m), 1010 (m), 962 (s, ν_{NbO}) cm^{-1}. NMR ($CDCl_3$): δ 5.02 s (5 H), $\eta^5\text{-}C_5H_5$; 3.96 m (8 H), O–CH_2 (THF); 1.88 m (8 H)

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[1] Part 21 of a continuing series on higher coordinate cyanide and isocyanide complexes.

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*To whom correspondence should be addressed at the Massachusetts Institute of Technology.

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Table I. Experimental Details of the X-ray Diffraction Study of $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl][NbOCl_4(C_5H_8O)]\cdot C_5H_8O$, $Nb_2Cl_5O_3N_4C_{33}H_{57}$

(A) Crystal Parameters[a] at 25 °C

a, Å	12.150 (2)	space group	*Pnma*
b, Å	13.852 (3)	*Z*	4
c, Å	27.394 (6)	ρ(calcd), g cm^{-3}	1.327
V, Å^3	4610.5	ρ(obsd),[b] g cm^{-3}	1.35 (1)
		fw	920.9

(B) Measurement and Treatment of Intensity Data[c]

instrument	Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized
standards	$(2,5,\bar{3})$, $(3,1,9)$, $(3,\bar{2},\overline{12})$ monitored every 9000 s, varied randomly with a net 3% decay
no. of reflcns collected exclusive of syst abs	5861 ($3° \leqslant 2\theta \leqslant 50°$ $(+h,+k,+l)$)
abs cor	
cryst size, mm	0.20 × 0.33 × 0.40
linear abs coeff, cm^{-1}	7.96
transmission factors[d]	0.80–0.92

(C) Final Model in the Least-Squares Refinement[c]

Anisotropic thermal parameters used for all atoms except those of solvent THF and C atoms of the ligand THF

final *R* values[e]: $R_1 = 0.061$; $R_2 = 0.076$

no. of reflcns obsd: 2169 having $I > 2\sigma(I)$

no. of variable parameters: 213

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 25°$. [b] By suspension in a $CHBr_3/CCl_4$/heptane mixture. [c] For procedures used in our laboratory, see ref 9a. [d] Absorption corrections were performed with the Wehe-Busing-Levy ORABS program. [e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w|F_o|^2]^{1/2}$.

OCH_2–CH_2 (THF); 1.54 (36 H), $CNCMe_3$.

Collection and Reduction of X-ray Data. The orange crystal used for the diffraction study, mounted in a capillary to avoid loss of solvent, was of approximate dimensions 0.20 mm × 0.33 mm × 0.40 mm bounded by the faces (100), (010), $(0\bar{1}0)$, $(\bar{1}10)$, (011), $(0\bar{1}1)$, $(01\bar{1})$, $(01\bar{2})$, and $(0\bar{1}2)$. Study on the diffractometer showed the crystal to belong to the orthorhombic system, space group *Pnma* (D_{2h}^{16}, No. 62) or $Pn2_1a$ (C_{2v}^{9}, No. 33).[14] Data collection and reduction proceeded by methods standard in our laboratory,[9a] the details of which are presented in Table I.

Determination and Refinement of the Structure. The positions of the niobium atoms were found with use of direct methods. All the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Although the refinement was carried out initially in the non-centric space group $Pn2_1a$, inspection of the positional parameters of these atoms showed them to have a mirror plane of symmetry. There were also high correlation coefficients between the mirror-related atoms at each cycle of refinement. The solution of the structure was therefore completed in space group *Pnma*. Anisotropic thermal parameters were used in the refinement of all atoms except those of the solvent THF and the carbon atoms of the THF ligand. These other atoms were disordered in pairs across the mirror plane and had to be refined with isotropic thermal parameters because of their close proximity to each other. The solvent THF had to be refined as a rigid group with the the thermal parameter of its oxygen atom, O(2), fixed in the final cycle of refinement. The hydrogen atoms were not located in the difference Fourier maps, nor were they placed in their calculated positions. The final difference Fourier map showed peaks <0.7 e/Å^3 situated at 0.56–0.89 Å from the carbon atoms of the THF groups.

Least-squares refinement[15] converged to the *R* indices listed in Table I. Neutral-atom scattering factors and anomalous dispersion corrections were obtained from ref 16. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1.9022/[\sigma^2(F_o) + 0.000625F_o^2]$. Final positional parameters are given in Table II, and details of the molecular geometry are supplied in Table III. A listing of observed and calculated structure factors is provided as Table S1, and Table S2 reports the final thermal parameters for all atoms (both tables in the supplementary material).

Table II. Final Positional Parameters for $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl][NbOCl_4(THF)]\cdot THF$[a]

ATOM	x	y	z
Nb(1)	0.06343(11)	0.2500	-0.37019(5)
Nb(2)	0.23924(9)	0.2500	-0.90034(4)
Cl(1)	0.0363(3)	0.42002(19)	-0.36883(11)
Cl(2)	0.0413(3)	0.2500	-0.92602(16)
Cl(3)	0.0556(4)	0.2500	-0.28314(14)
Cl(4)	0.0190(4)	0.2500	-0.45467(14)
O(1)	-0.1329(10)	0.2500	-0.3629(5)
O(2)	-0.2694(3)	0.2500	0.13335(4)
N(1)	0.2328(6)	0.4309(6)	-0.9813(3)
N(2)	0.1391(7)	0.4229(6)	-0.8281(3)
C(1)	0.2358(8)	0.3668(7)	-0.9553(4)
C(2)	0.1720(8)	0.3636(7)	-0.8526(4)
C(11)	0.2291(9)	0.5239(7)	-1.0082(4)
C(12)	0.1461(12)	0.5108(11)	-1.0508(5)
C(13)	0.3454(11)	0.5445(10)	-1.0259(5)
C(14)	0.1910(12)	0.6019(8)	-0.9727(5)
C(21)	0.1037(10)	0.5054(8)	-0.7994(5)
C(22)	0.2065(14)	0.5373(11)	-0.7678(7)
C(23)	0.0174(15)	0.4735(11)	-0.7651(7)
C(24)	0.0741(20)	0.5871(14)	-0.8354(7)
C(31A)[b]	-0.1836	0.2114	0.2060
C(31B)[b]	-0.2677	0.2061	0.2147
C(32A)[b]	-0.201(3)	0.1752(13)	0.1569(4)
C(32B)[b]	-0.301(3)	0.1711(14)	0.1670(2)
C(61)[b]	-0.212(3)	0.205(2)	-0.3984(12)
C(62)[b]	-0.325(4)	0.24(4)	-0.3828(14)
C(63)[b]	-0.306(2)	0.2934(19)	-0.3415(10)
C(64)[b]	-0.194(3)	0.195(2)	-0.3276(11)
C(71)	0.4265(8)	0.2981(12)	-0.9131(5)
C(72)	0.3949(10)	0.3308(8)	-0.8678(6)
C(73)	0.3766(13)	0.2500	-0.8389(5)
O(3)	0.1998(9)	0.2500	-0.3760(4)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figures 1 and 2 for atom-labeling scheme. [b] These atoms are disordered and have the following population parameters: C(31A), C(32A) = 0.51 (2); C(31B), C(32B) = 0.49 (2); C(61), C(62), C(63), C(64) = 0.50.

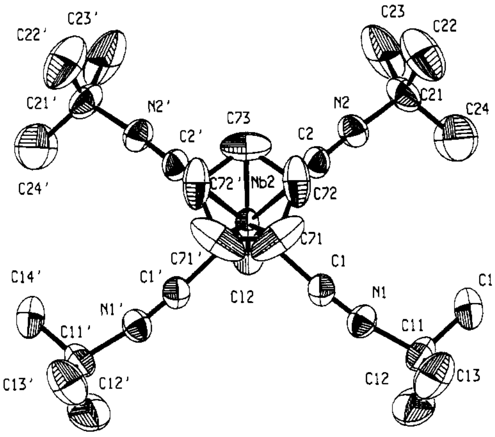

Figure 1. Structure of the $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl]^+$ cation showing the 30% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographically required mirror plane.

Results and Discussion

In the presence of *tert*-butyl isocyanide, sodium amalgam reduces the niobium(V) compound $(\eta^5\text{-}C_5H_5)NbCl_4$ to form the niobium(III) cation $[(\eta^5\text{-}C_5H_5)Nb(CNCMe)_4Cl]^+$. This product may be contrasted with that obtained under more forcing conditions when sodium is used to reduce $(\eta^5\text{-}C_5H_5)NbCl_4$ under 4700 psi of carbon monoxide, namely, $(\eta^5\text{-}C_5H_5)Nb(CO)_4$.[17] The source of the oxygen atom in the niobium(V) counterion, $[NbCl_4O(THF)]^-$, is unknown. Infrared spectra of the crude reaction product prior to recrys-

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(14) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1973; Vol. I, pp 119, 151.

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Table III. Interatomic Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl][NbOCl_4(THF)]\cdot THF^a$

Coordination Sphere			
Nb(1)-O(1)	2.394(12)	Nb(2)-Cl(2)	2.505(4)
Nb(1)-O(3)	1.665(11)	Nb(2)-C(1)	2.210(10)
Nb(1)-Cl(1)	2.378(4)	Nb(2)-C(2)	2.203(9)
Nb(1)-Cl(3)	2.387(4)	Nb(2)-C(71)	2.397(11)
Nb(1)-Cl(4)	2.376(4)	Nb(2)-C(72)	2.371(13)
		Nb(2)-C(73)	2.371(15)
O(1)-Nb(1)-O(3)	179.3(6)	Cl(2)-Nb(2)-C(1)	77.9(3)
O(1)-Nb(1)-Cl(1)	82.0(1)	Cl(2)-Nb(2)-C(2)	79.1(3)
O(1)-Nb(1)-Cl(3)	82.9(3)	C(1)-Nb(2)-C(1)'	94.1(5)
O(1)-Nb(1)-Cl(4)	81.6(3)	C(2)-Nb(2)-C(2)'	91.1(5)
O(3)-Nb(1)-Cl(1)	98.0(1)	C(1)-Nb(2)-C(2)	82.8(4)
O(3)-Nb(1)-Cl(3)	97.7(4)	C(1)-Nb(2)-C(2)'	156.9(4)
O(3)-Nb(1)-Cl(4)	97.7(4)		
Cl(1)-Nb(1)-Cl(1)'	164.0(2)		
Cl(1)-Nb(1)-Cl(3)	88.8(1)		
Cl(1)-Nb(1)-Cl(4)	89.1(1)		
Cl(3)-Nb(1)-Cl(4)	164.6(2)		
Ligand Geometry			
(i) tert-butyl isocyanide groups			
C(1)-N(1)	1.139(13)	C(2)-N(2)	1.133(12)
N(1)-C(11)	1.484(13)	N(2)-C(21)	1.453(14)
C(11)-C(12)	1.553(18)	C(21)-C(22)	1.581(22)
C(11)-C(13)	1.522(18)	C(21)-C(23)	1.476(22)
C(11)-C(14)	1.526(16)	C(21)-C(24)	1.544(22)
Nb(2)-C(1)-N(1)	175.7(8)	Nb(2)-C(2)-N(2)	178.8(8)
C(1)-N(1)-C(11)	171.0(10)	C(2)-N(2)-C(21)	174.3(10)
N(1)-C(11)-C(12)	106.9(9)	N(2)-C(21)-C(22)	106.4(10)
N(1)-C(11)-C(13)	107.1(9)	N(2)-C(21)-C(23)	108.6(10)
N(1)-C(11)-C(14)	107.9(9)	N(2)-C(21)-C(24)	107.5(11)
C(12)-C(11)-C(13)	112.6(10)	C(22)-C(21)-C(23)	107.2(12)
C(12)-C(11)-C(14)	111.4(10)	C(22)-C(21)-C(24)	109.2(12)
C(13)-C(11)-C(14)	110.7(10)	C(23)-C(21)-C(24)	117.4(13)
(ii) Cyclopentadienyl Group			
C(71)-C(71)'	1.33(3)	C(72)-C(73)	1.39(2)
C(71)-C(72)	1.37(2)		
C(71)'-C(71)-C(72)	109.2(8)	C(72)-C(73)-C(72)'	107.3(16)
C(71)-C(72)-C(73)	107.1(11)		
(iii) Disordered THF Group			
O(1)-C(61)	1.50(4)	C(62)-C(63)'	1.40(30)
C(61)-C(62)	1.50(16)	C(63)'-C(64)'	1.42(4)
		C(64)'-O(1)	1.44(3)
Nb(1)-O(1)-C(61)	125.7(15)	C(61)-C(62)-C(63)'	104(7)
Nb(1)-O(1)-C(64)'	124.6(15)	C(62)-C(63)'-C(64)'	116(4)
C(61)-O(1)-C(64)'	109(2)	C(63)'-C(64)'-O(1)	104(2)
O(1)-C(61)-C(62)	106(10)		
Disordered Solvent Geometry			
O(2)-C(32A)	1.48(2)	O(2)-C(32B)	1.48(2)
C(32A)-C(31A)	1.45(1)	C(32B)-C(31B)	1.45(1)
C(31A)-C(31B)'	1.55	C(31B)-C(31A)'	1.55
O(2)-C(32A)-C(31A)	104(1)	O(2)-C(32B)-C(31B)	104(1)
C(32A)-O(2)-C(32B)'	113(1)	C(32B)-O(2)-C(32A)'	113(1)
C(32A)-C(31A)-C(31B)'	108(1)	C(32B)-C(31B)-C(31A)'	107(1)

[a] See footnote *a*, Table II. Values reported have not been corrected for thermal motion.

tallization sometimes failed to show the characteristic Nb–O stretching band at 962 cm^{-1}.[18] Perhaps the anion is originally $[NbCl_6]^-$, which reacts with trace amounts of water in the solvent to produce the oxotetrachloroniobate(V) species.

The crystal structure consists of discrete $[(\eta^5\text{-}C_5H_5)Nb(CNCMe_3)_4Cl]^+$ cations (Figure 1), $[NbCl_4O(THF)]^-$ anions (Figure 2), and uncoordinated THF molecules, all of which lie on crystallographically required mirror planes of symmetry. In the cation the mirror plane passes between pairs of coordinated *tert*-butyl isocyanide ligands while, in the anion, two chloride ions sit on the mirror and two straddle it. The $[(\eta^5\text{-}C_5H_5)Nb(CNCMe)_4Cl]^+$ cation has a formal coordination number of 8, making the arbitary assignment that the η^5-cyclopentadienyl group occupies three coordination positions. The Nb–C(C_5H_5) bond lengths, 2.37 (1)–2.40 (1) Å, are comparable to those found in the related molecules $[Nb(\eta^5\text{-}C_5H_5)_2(CH_3)(CS_2)]$ (2.37–2.42 Å)[19] and $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ (2.33–2.44 Å).[20] Although the Nb–CNR bond lengths are near the range found for numerous Mo(II) and W(II) isocyanide complexes,[2,3] the C–Nb–C angles are not acute enough to produce the short nonbonded C···C contacts believed to be important for reductive coupling to occur.[4,21] In accord with this expectation, preliminary studies have shown that, unlike $[Mo(CNCMe_3)_6I]^+$, $[Nb(\eta^5\text{-}C_5H_5)(CNCMe_3)_4Cl]^+$ is not reductively coupled when refluxed with zinc in wet THF.[18] The Nb–Cl bond length, 2.505 (4) Å, is much longer than those in the $[NbCl_4O(THF)]^-$ anion, ~2.38 Å, and is slightly longer than the values of 2.464 (5) and 2.475 (4) Å found for $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$. These values reveal progressive lengthening in the Nb–Cl bond as the metal oxidation state decreases from +5 to +4 to +3.

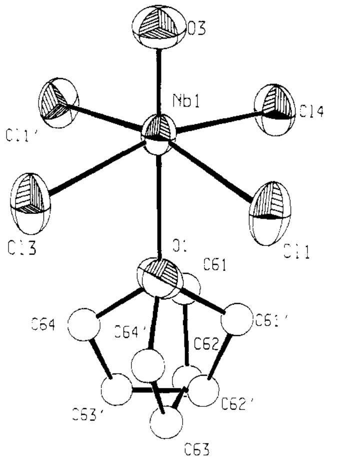

Figure 2. Structure of the $[NbOCl_4(THF)]^-$ ion showing the 20% probability thermal ellipsoids. The carbon atoms of the disordered THF ligand are assigned as spheres with *B* set arbitrarily at 5 Å^2. A mirror plane relates the primed and unprimed atoms.

The $[NbOCl_4(THF)]^-$ anion has the distorted C_{4v} type stereochemistry long known for oxotetrahalometalate anions of the early transition metals.[22] The niobium atom is displaced by 0.33 Å toward the oxo ligand from the best mean plane through the four chlorine atoms. The Nb–O bond length of 1.665 (11) Å is shorter than that found[23] for$[NbOCl_2(C_2H_5O)(bpy)]$, 1.71 (4) Å, and $(Ph_4As)_2[NbO(NCS)_5]$, 1.70 (4) Å, indicating substantial oxygen-to-niobium π bonding.[22] Both the coordinated and the solvate tetrahydrofuran molecules are disordered across the mirror plane at *y* = 0.25. This plane passes through the oxygen atom and the midpoint of the disordered atom pairs C(62), C(62)′ and C(63), C(63)′ (Figure 2). Details of the structural features of these groups, as well as other bond lengths and angles within the ligands, are summarized in Table III.

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Registry No. $[(\eta\text{-}C_5H_5)Nb(CNCMe_3)_4Cl][NbCl_4O(THF)]\cdot THF$, 89890-26-6; $(\eta\text{-}C_5H_5)NbCl_4$, 33114-15-7.

Supplementary Material Available: Tables S1 and S2, reporting final thermal parameters and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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