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Organometallic Oxides: Reduction of (Pentamethylcyclopentadienyl)niobium(V) and -tantalum(V) Oxo Complexes

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Hydrolysis of *anti*-$[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$ gave *anti*-$[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (**2**), which was identified by analysis, spectroscopy, and X-ray crystallography. **2** was orthorhombic, space group $F2dd$, with $a = 8.899(1)$ Å, $b = 14.283(2)$ Å, $c = 39.56(1)$ Å, $Z = 8$, and $R = 0.034$. **2** has a structure similar to that of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (**1**). Reduction of **1** or **2** with Na/Hg gave $[(\eta\text{-}C_5Me_5)M]_4O_6$ (**4**) (M = Nb, Ta), for which a rectangular structure is proposed on the basis of spectroscopic and magnetic measurements. For M = Nb, **4** showed temperature-independent paramagnetism with no unpaired electrons in the ground state. Whereas reduction of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$ with zinc gave $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$ as the sole product, reduction of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}A)_2(\mu\text{-}O)$ (A = Cl, OH) gave a mixture of products. Reoxidation of the mixture produced $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\{Zn_4Cl_{10}\}\cdot CH_2Cl_2$ (**3**) in 65% yield. **3** was identified by microanalysis, spectroscopy, and X-ray diffraction. **3** was orthorhombic, space group $P2_12_12$, with $a = 16.513(3)$ Å, $b = 25.729(4)$ Å, $c = 11.234(2)$ Å, $Z = 4$, and $R = 0.053$.

Introduction

We have prepared a number of cyclopentadienylvanadium oxides of general formula $[(\eta\text{-}C_5R_5)V]_m(\mu_x\text{-}O)_n$.[1] Examples are $[(\eta\text{-}C_5H_5)V]_5(\mu_3\text{-}O)_6$[2] and $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$.[3,4] These were usually obtained by oxidation of $(\eta\text{-}C_5R_5)_2V$ or other low-valent vanadium derivatives. Such a method cannot be used to prepare analogous niobium and tantalum oxides because the low-valent cyclopentadienylmetal derivatives either are unknown or are very difficult to prepare. We have therefore turned to reductive aggregation of high-valent cyclopentadienylniobium oxo halides as a route to $[(\eta\text{-}C_5R_5)Nb]_m(\mu_x\text{-}O)_n$. In previous work we have shown that reduction of $[(\eta\text{-}C_5H_5)Nb(H_2O)Cl_3]_2(\mu\text{-}O)$ with aluminum gave $[(\eta\text{-}C_5H_5)NbCl(\mu\text{-}Cl)]_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$[5] and reduction of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$ with zinc gave $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$.[6] We present here the results of reduction of (pentamethylcyclopentadienyl)niobium and -tantalum oxo halides with the powerful reducing agent sodium amalgam. These reductions produce $[(\eta\text{-}C_5Me_5)M]_4O_6$ (M = Nb, Ta).

Results and Discussion

(Pentamethylcyclopentadienyl)niobium(V) and -tantalum(V) Oxo Complexes. Geoffroy and co-workers showed that the hydrolysis of $(\eta\text{-}C_5Me_5)TaCl_4$ occurred stepwise and ultimately gave a high yield of a single oxo complex, $(\eta\text{-}C_5Me_5)_2Ta_2Cl_4(OH)_2O$ (**1**).[7,8] This hydrolysis is a convenient entry into oxo complexes of (pentamethylcyclopentadienyl)tantalum. In using it, we obtained crystals of **1** suitable for X-ray diffraction and were thus able to prove that the compound is *anti*-$[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (structure III of those proposed by Geoffroy and co-workers[8]). The crystal data were identical with those of the same compound obtained by Curtis and co-workers on exposing $(\eta\text{-}C_5Me_5)Ta(CO)_2(THF)$ to the atmosphere.[9]

Hydrolysis of $(\eta\text{-}C_5Me_5)NbCl_4$ did not give a single product but a complicated mixture of mononuclear, dinuclear, and trinuclear products.[10,11] Thus, we used the oxidation of $(\eta\text{-}C_5Me_5)_2NbCl_2$ with O_2 to provide a single-product entry into (pentamethylcyclopentadienyl)niobium oxo complexes. The reaction gave *anti*-$[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$.[6] Hydrolysis of this complex gave *anti*-$[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (**2**), the structure of which was proved to be identical with that of the tantalum analog by X-ray crystallography (see Figure 1 and Table I). We

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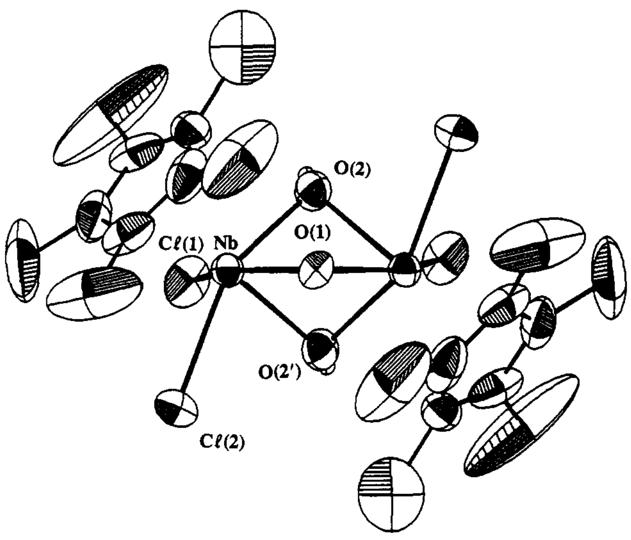


Figure 1. Structure of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$.

Table I. Important Average Distances (Å) and Angles (deg) in *anti*-$[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$

Nb–Nb	3.027(1)[a]	Nb–OH	2.147(4)
Nb–Cl	2.416(2)	Nb–O	1.942(3)
		Nb–CP[b]	2.168(6)
Nb–O–Nb	102.4(3)	Nb–OH–Nb	89.6(2)

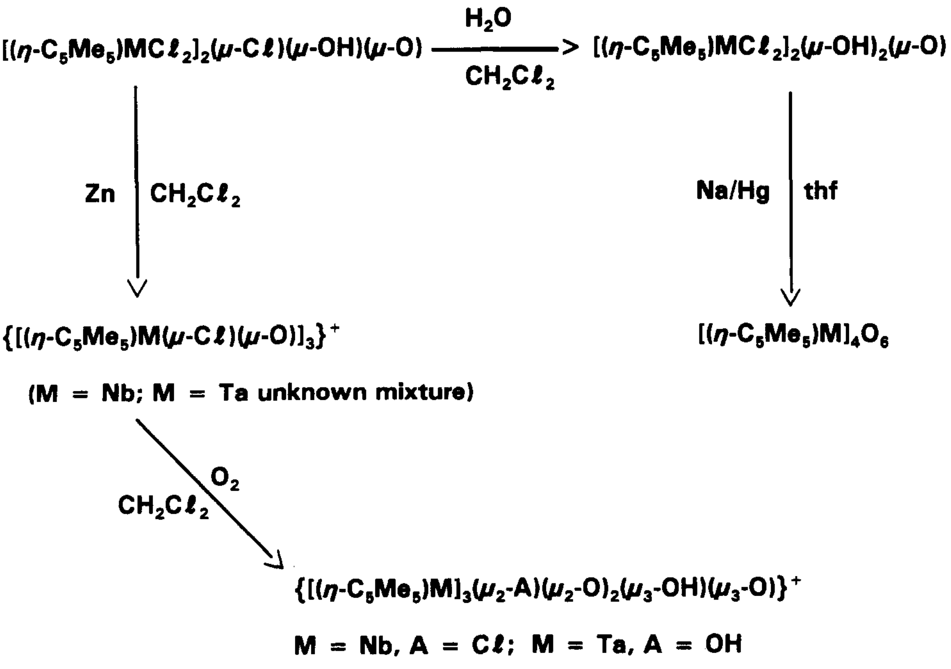
[a] Estimated standard deviations in parentheses. [b] CP is the centroid of the η-C_5Me_5 ligand.

have thus obtained a single starting material, $[(\eta\text{-}C_5Me_5)MCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$, for both Nb and Ta chemistry (see Scheme I).

Attempted Reduction of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}A)_2(\mu\text{-}O)$ (A = Cl, OH) with Zinc: Formation of $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\{Zn_4Cl_{10}\}$. We have found that reduction of dinuclear niobium(V) derivatives such as $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$ with zinc gave $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$. The nature of the niobium(V) starting material was generally immaterial, so long as at least one oxygen atom per niobium was present. The reaction was conveniently followed by the change in color from the orange-red of the Nb(V) compound to the leaf green of $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$.[6] We were surprised to find that an analogous reduction did not proceed with tantalum. On treatment of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}A)_2(\mu\text{-}O)$ (A = Cl, OH), or a mixture of these compounds, with zinc, the yellow color of the Ta(V) compounds slowly changed to pale green, but never to a deeper green. Spectroscopy indicated that a complicated mixture of products was formed, but none of them could be identified. In order to establish whether reduction was taking place at all, the mixture was treated with O_2. This procedure gave diamagnetic $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\{Zn_4Cl_{10}\}$ (**3**), whose structure is discussed below. This salt was also obtained when $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}A)_2(\mu\text{-}O)$ was treated with zinc in air. The formula of the product was established as $\{(\eta\text{-}C_5Me_5)_3Ta_3Cl_3(OH)_2O_3\}_2\{Zn_4Cl_{10}\}$ from the diamagnetism and the Ta:Cl:Zn ratio as defined by the X-ray diffraction experiments. It was clear from the formation of the chlorozincate anion that a reduction had indeed taken place, and the product of reoxidation was very similar to that obtained in the niobium case ($\{[(\eta\text{-}C_5Me_5)NbCl]_3(\mu_2\text{-}Cl)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}^{+}$ [11]), but the reduction was more complicated and the reduced tantalum species remain unknown (see Scheme I).

Structure of $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\{Zn_4Cl_{10}\}$. The structure of the cation of **3** is shown in Figure 2. Important distances and angles are given in Table II. The anion $\{(ZnCl)_4(\mu\text{-}Cl)_6\}^{2-}$ had an adamantane-like structure identical with that reported previously.[6,12] The cation had a structure similar to those of $\{[(\eta\text{-}C_5Me_5)NbCl]_3(\mu\text{-}Cl)(\mu\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}^+$,[6] $\{[(\eta\text{-}C_5Me_5)_3Nb_3(OH)_2Cl](\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}^+$,[11] and $\{[(\eta\text{-}C_5Me_5)_3Ta_3(H_2O)_2Cl](\mu_2\text{-}O)_3(\mu_3\text{-}O)_2\}^+$.[7,8] In all of these compounds the location of the hydrogen atoms, and therefore the assignment of H_2O, OH, and O ligands, is subject to considerable uncertainty. The Ta(2)–O(2) and Ta(3)–O(2) distances (Table II) clearly indicate that O(2) is an oxo, not hydroxo, ligand, but the other distances are

Scheme I



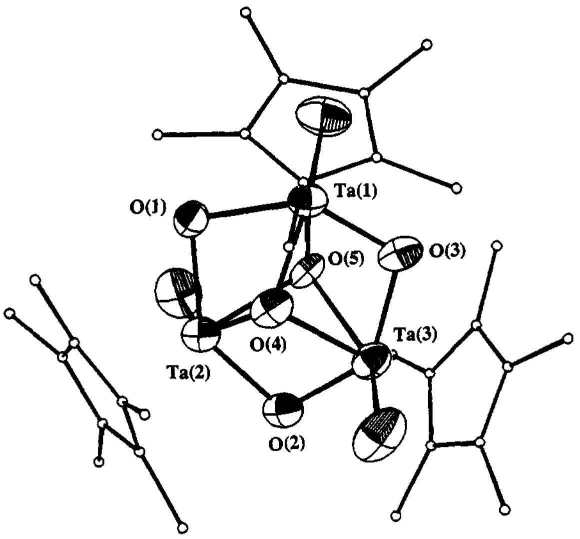


Figure 2. Structure of the $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}^+$ cation of **3**.

ambiguous. The formula has been assigned with regard to the geometry and valency within the cation. The related tantalum[7,8] and niobium[10,11] clusters $[(\eta\text{-}C_5Me_5)MCl]_3(\mu_2\text{-}Cl)(\mu_2\text{-}O)_3(\mu_3\text{-}O)$ differ from **3** in that one of the μ_3-O atoms has become μ_2-O. There is obviously a delicate balance in the energies of these compounds produced by changing the coordination numbers of oxygen and niobium or tantalum.

Reduction of $[(\eta\text{-}C_5Me_5)MCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$: Formation of $[(\eta\text{-}C_5Me_5)M]_4O_6$. Reduction of $[(\eta\text{-}C_5Me_5)MCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (M = Nb, Ta) with sodium amalgam in tetrahydrofuran gave $[(\eta\text{-}C_5Me_5)M]_4O_6$ (**4**) according to eq 1 (see Scheme I). Despite much effort, crystals of

$$2[(\eta\text{-}C_5Me_5)MCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O) + 8Na \rightarrow [(\eta\text{-}C_5Me_5)M]_4O_6 + 8NaCl + 2H_2 \quad (1)$$

4 suitable for X-ray diffraction experiments were never obtained, probably because **4** was highly soluble in all organic solvents. The formula of **4** was established by analytical and spectroscopic methods for both the Nb and Ta analogs (see the Experimental Section). The niobium cluster showed temperature-independent paramagnetism over most of the temperature range studied (see Figure 3). The measured magnetic susceptibility was constant at $(1.3 \pm 0.1) \times 10^{-4}$ cm^3 mol^{-1} from 350 to 50 K. The calculated moment ranged from 0.62 to 0.24 μ_B over that range. The cause of the observed rise in susceptibility below 50 K is uncertain, but it may arise from the presence of a paramagnetic impurity. The moment for $[(\eta\text{-}C_5Me_5)Ta]_4O_6$ was measured at 295 K only and was 0.98 μ_B. There are four electrons in the cluster core, and we conclude that there are no unpaired electrons in the ground state of **4**.

On the evidence, the four structures depicted in Figure 4 may be proposed for $[(\eta\text{-}C_5Me_5)M]_4O_6$. The tetrahedron of metal atoms in structure **4a** may be distorted into a butterfly arrangement, and the rectangles of metal atoms in structures **4b** and **4d** may also be distorted. Such distorted structures would be fluxional. The general arguments given below are intended to establish the basic structure and are not affected by such fluxionality. Linear structures, and other structures involving terminal M═O units, can be eliminated because of the absence of absorption bands assignable to ν(M═O) in the infrared spectra. Structures **4c** and **4d** contain both six- and seven-coordinate metal atoms. Thus, there would be two types of η-C$_5$Me$_5$ ligands, and two sets of resonances would be expected in the ^{1}H and ^{13}C NMR spectra of **4**, in the ratio of 3:1 for structure **4c** and 1:1 for **4d**. Although **4** had a nonzero magnetic moment at room temperature, the ^{1}H spectrum showed a reasonably sharp singlet (Figure 5a), thus eliminating structures **4c** and **4d**. A ^{13}C signal attributable to the methyl carbon atoms, but no signal attributable to the C$_5$ ring carbon atoms, was observed (see Figure 5b). This indicates that there is little transfer of spin density from the cluster core, where the magnetization is located, to the methyl groups of the η-C$_5$Me$_5$ ligands. We have previously observed this phenomenon in paramagnetic clusters such as $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$.[4] Structure **4c** is related to that observed in the clusters $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$,[13] $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$,[14] and $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$,[15] which have the ground state $1a_1^2 1e^2$.[16]

Table II. Important Distances (Å) and Angles (deg) in the $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu\text{-}OH)(\mu\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}^+$ Cation of 3

Ta(1)–Ta(2)[a]	3.199(2)[b]	Ta(2)–O(4)	2.06(2)
Ta(1)–Ta(3)	3.050(2)	Ta(2)–O(5)	2.22(2)
Ta(1)–O(1)	2.09(2)	Ta(2)–Cl(2)	2.380(8)
Ta(1)–O(3)	1.84(2)	Ta(2)–CP(2)	2.11(1)
Ta(1)–O(4)	2.01(2)	Ta(3)–O(2)	1.94(2)
Ta(1)–O(5)	2.17(2)	Ta(3)–O(3)	2.02(2)
Ta(1)–Cl(1)	2.388(9)	Ta(3)–O(4)	2.17(2)
Ta(1)–CP(1)[c]	2.07(2)	Ta(3)–O(5)	2.27(2)
Ta(2)–Ta(3)	3.038(2)	Ta(3)–Cl(3)	2.351(9)
Ta(2)–O(1)	2.13(2)	Ta(3)–CP(3)	2.10(2)
Ta(2)–O(2)	1.94(2)		
O(1)–Ta(1)–O(3)	139.3(8)	O(2)–Ta(3)–O(4)	75.6(8)
O(1)–Ta(1)–O(4)	67.3(7)	O(2)–Ta(3)–O(5)	72.4(7)
O(1)–Ta(1)–O(5)	72.9(7)	O(2)–Ta(3)–O(4)	70.7(8)
O(3)–Ta(1)–O(4)	78.1(8)	O(3)–Ta(3)–O(5)	69.6(7)
O(3)–Ta(1)–O(5)	75.1(8)	O(4)–Ta(3)–O(5)	64.1(6)
O(4)–Ta(1)–O(5)	68.8(7)	Ta(1)–O(1)–Ta(2)	98.6(7)
O(1)–Ta(2)–O(2)	137.1(7)	Ta(2)–O(2)–Ta(3)	102.9(9)
O(12)–Ta(2)–O(4)	65.6(7)	Ta(1)–O(3)–Ta(3)	104.0(10)
O(1)–Ta(2)–O(5)	71.0(6)	Ta(1)–O(4)–Ta(2)	103.7(8)
O(2)–Ta(2)–O(4)	78.5(8)	Ta(1)–O(4)–Ta(3)	93.5(7)
O(2)–Ta(2)–O(5)	73.8(7)	Ta(2)–O(4)–Ta(3)	91.7(8)
O(4)–Ta(2)–O(5)	67.0(6)	Ta(1)–O(5)–Ta(2)	93.6(6)
O(2)–Ta(3)–O(3)	137.2(8)	Ta(1)–O(5)–Ta(3)	86.6(6)

[a] For numbering scheme see Figure 2. [b] Estimated standard deviations in parentheses. [c] CP is the centroid of the C$_5$ ring of the η-C$_5$Me$_5$ ligand.

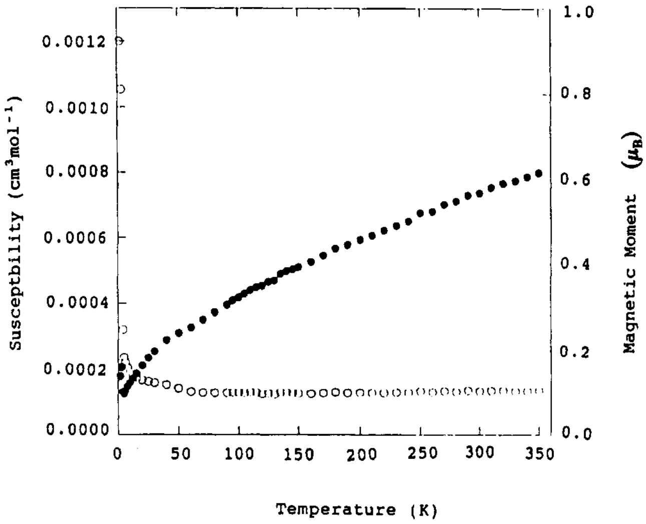


Figure 3. Magnetic behavior of $[(\eta\text{-}C_5Me_5)Nb]_4O_6$.

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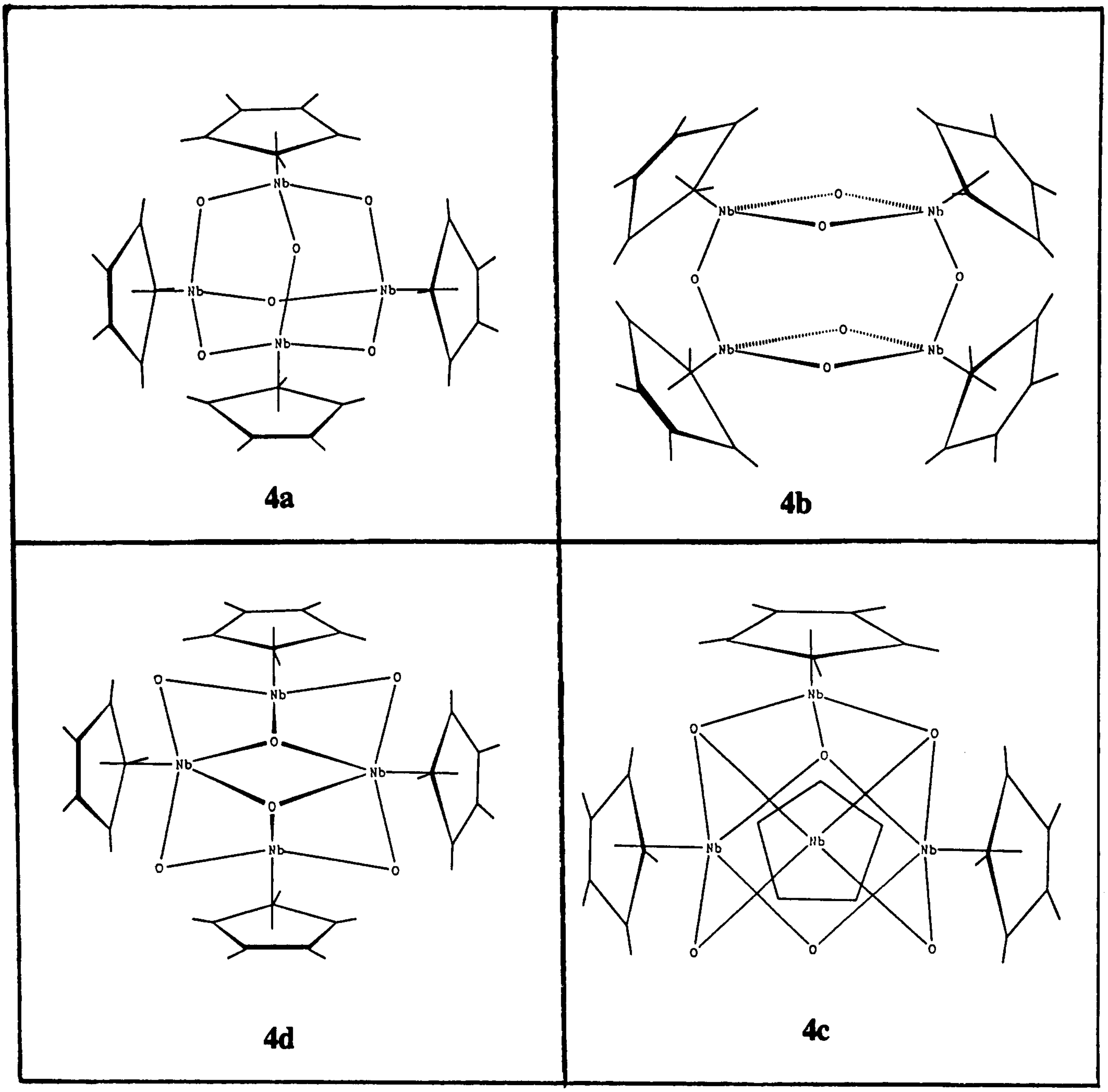

4a **4b** **4d** **4c**

Figure 4. Possible structures for $[(\eta\text{-}C_5Me_5)M]_4O_6$.

Thus, structure **4c** would be expected to have two unpaired electrons, but as noted above, in fact **4** has no unpaired electrons in the ground state. The only precedents for structure **4d** are the complexes $[M_2Cl_2(S(CH_2)_2NMeCH_2)_2]_2$ (M = Zn,[17] Cd[18]), in which the M–M distances are so long as to preclude any metal–metal interaction. Because of the NMR spectra and magnetic data, we feel that $[(\eta\text{-}C_5Me_5)M]_4O_6$ species do not adopt structure **4c** or **4d**.

The adamantane-like structure **4a** is found in $[(\eta\text{-}C_5Me_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti,[19] V[3,4]). The titanium derivative has no cluster electrons and is diamagnetic. The vanadium derivative, which is the direct analog of $[(\eta\text{-}C_5Me_5)M]_4O_6$, has four cluster electrons and has a magnetic moment of 2.90 μ_B, independent of temperature between 213 and 295 K. Extended Hückel molecular orbital calculations suggested that the ground state of $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$ had the configuration $1a_2{}^2 1e^2$, in agreement with the magnetic results.[4] Thus, if $[(\eta\text{-}C_5Me_5)M]_4O_6$ (M = Nb, Ta) adopted structure **4a**, a similar magnetic moment (probably reduced to a small extent by spin–orbit coupling) would be expected. It therefore appears that $[(\eta\text{-}C_5Me_5)M]_4O_6$ species do not adopt the adamantane-like structure **4a**.

Structure **4b** does not appear to have been observed previously. An extended Hückel molecular orbital cal-

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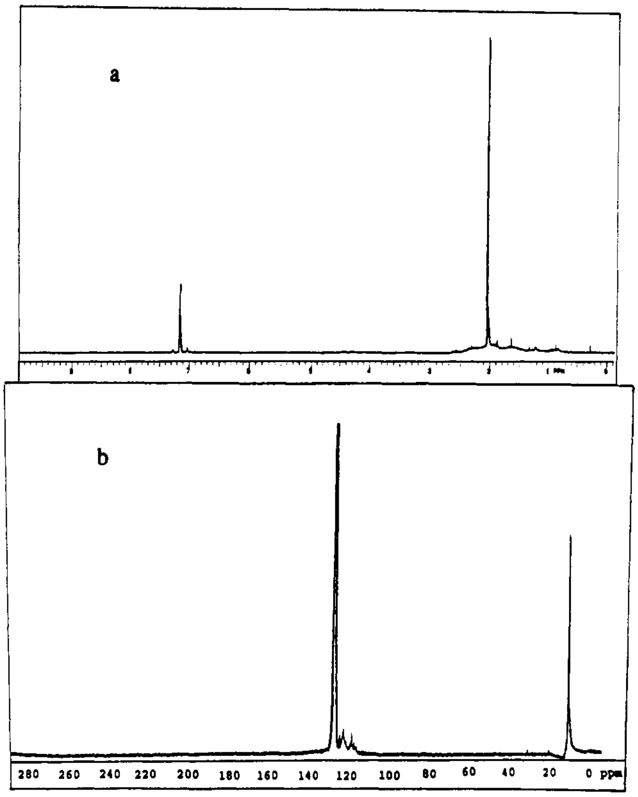

Figure 5. ^1H (a) and ^{13}C (b) NMR spectra for $[(\eta\text{-}C_5Me_5)Nb]_4O_6$.

culation on $[(\eta\text{-}C_5H_5)Nb]_4O_6$ with a rectangle of niobium atoms, the short side (2.85 Å) of which was bridged by two oxygen atoms (Nb–O = 1.94 Å) and the long side (3.15 Å) by one, suggested that the ground state would be diamagnetic. The four cluster electrons would be involved in a direct M–M interaction which would also be antibonding with respect to the M–O π-interaction. The nature of the excited state which mixes with the diamagnetic ground state to produce the temperature-independent paramagnetism of $[(\eta\text{-}C_5Me_5)Nb]_4O_6$ was not apparent from these calculations. Because structure **4b** is in general agreement with all of the data, we tentatively suggest that this is the structure adopted by $[(\eta\text{-}C_5Me_5)M]_4O_6$.

Experimental Section

General Considerations. All manipulations were conducted using a standard double-manifold vacuum line, under argon or under vacuum. Samples were transferred in a dinitrogen-filled glovebag. Solvents were predried over molecular sieves and then distilled over $LiAlH_4$ (Et_2O or THF) or Na (toluene or hexane). Dichloromethane was refluxed over P_2O_5 before distillation. Water was distilled and deoxygenated by freeze–thaw methods. Zinc powder was dried under vacuum before use. The starting materials $(\eta\text{-}C_5Me_5)_2NbCl_2$,[20] $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$,[6] and $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$[8] were prepared by the literature methods cited. Crystals of this last compound were obtained from CH_2Cl_2/Et_2O. All other reagents were used as received.

Instruments used in this work were as follows: Varian XL-200 for ^1H, ^{13}C, and ^{93}Nb NMR spectra, with chemical shifts referenced to the non-deuterated solvent impurity or to $NbCl_5$; Perkin-Elmer 685 for infrared spectra, as KBr pellets or Nujol mulls; Kratos MS50 for mass spectra, using EI or FAB ionization; Faraday method with an Alpha Scientific magnet and Cahn electrobalance for magnetic moments at room temperature. The magnetic susceptibility of $[(\eta\text{-}C_5Me_5)Nb]_4O_6$ was measured over the temperature range 2–350 K using a Quantum Design (MPMS) SQUID magnetometer (field 10 000 Oe). Experimental procedures were as described previously.[21] A correction of -550×10^{-6} cm^3 mol^{-1} was applied for the diamagnetism of the sample. Microanalyses (C, H, and Cl) were performed by Beller Laboratorium, Göttingen, Germany, and molecular weights (by osmometry) by the Mikroanalytisches Laboratorium, Engelskirchen, Germany.

Table III. Crystal and Refinement Data for 2 and 3

	2	3
mol formula	$C_{20}H_{32}Cl_4Nb_2O_3$	$C_{61}H_{96}Cl_{18}O_{10}Ta_6Zn_4$[a]
fw	646.08	2974.85[a]
cryst syst	orthorhombic	orthorhombic
space group	*F2dd*	$P2_12_12$
a, Å	8.899(1)	16.513(3)
b, Å	14.283(2)	25.729(4)
c, Å	39.560(1)	11.234(2)
V, $Å^3$	5028(2)	4772.9(14)
Z	8	2[a]
D(calcd), Mg m^{-3}	1.71	2.05
μ(Mo Kα), cm^{-1}	6.7	47.6
temp, K	295	295
cryst size, mm	0.48 × 0.40 × 0.20	0.68 × 0.20 × 0.15
2θ limits, deg	2–60	2–46
no. of rflns for cell	36	44
2θ limits for cell, deg	40–54	40–44
no. of rflns collcd	1936	3723
no. of unique rflns	1936	3723
no. of obsd rflns	1593	2930
criteria for observn	$I > 1.0\sigma(I)$	$I > 1.0\sigma(I)$
$R(F')$	0.034	0.053
$R_w(F')$	0.048	0.075
GOF	1.66	1.77
no. of refined params	126	231
max Δ/σ	0.01	0.15
max Δ, e $Å^{-3}$	0.60	1.27
N_o/N_v	12.6	12.7
K (weight modifier)	0.0005	0.001

[a] $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\text{-}\{Zn_4Cl_{10}\}\cdot CH_2Cl_2$.

Table IV. Atomic Coordinates and B_{iso} Values for 2

	x	*y*	*z*	B_{iso},[a] $Å^2$
Nb[b]	0.416	0.00079(3)[c]	0.038255(9)	2.51(2)
Cl(1)	0.1565(2)	−0.0121(1)	0.05737(5)	4.92(7)
Cl(2)	0.4720(3)	−0.1508(1)	0.06092(4)	4.75(7)
O(1)	0.5527(6)	0	0	2.7(2)
O(2)	0.3210(5)	0.0888(3)	0.00122(9)	3.4(1)
C(1)	0.511(1)	0.1563(5)	0.0529(2)	5.5(4)
C(2)	0.629(1)	0.1039(6)	0.0544(2)	5.2(3)
C(3)	0.6150(9)	0.0410(5)	0.0795(2)	4.9(3)
C(4)	0.467(1)	0.0612(5)	0.0954(2)	5.2(3)
C(5)	0.407(1)	0.1332(5)	0.0772(2)	5.1(3)
C(11)	0.487(2)	0.2462(7)	0.0306(5)	10.5(4)
C(21)	0.767(2)	0.1204(9)	0.0314(4)	12.0(8)
C(31)	0.733(2)	−0.0240(8)	0.0933(5)	12.7(10)
C(41)	0.414(3)	0.0129(9)	0.1269(2)	12.9(10)
C(51)	0.265(1)	0.177(1)	0.0895(6)	20.2(14)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid multiplied by $8\pi^2$. [b] For the numbering scheme, see Figure 1. [c] Estimated standard deviations in parentheses.

Hydrolysis of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$ To Form $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$. A solution of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)$ (0.20 g, 3.00 mmol) in CH_2Cl_2 (100 cm^3) was stirred under argon for 48 h. The CH_2Cl_2 was commercial grade and was not dried. The resulting yellow solution was concentrated to 40 cm^3 under vacuum and layered

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[20] Bunker, M. J.; de Cian, A.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1977**, 59.

[21] Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1992**, *70*, 2161.

Table V. Atomic Coordinates and B_{iso} Values for 3

	x	y	z	B_{iso},[a] Å^2
Ta(1)[b]	0.92648(8)[c]	0.28398(5)	0.0977(1)	3.10(5)
Ta(2)	1.02971(7)	0.21683(5)	0.2832(1)	3.05(5)
Ta(3)	0.97744(8)	0.32738(5)	0.3390(1)	3.37(6)
O(1)	0.973(1)	0.2089(7)	0.114(2)	3.1(8)
O(2)	1.043(1)	0.2710(7)	0.402(2)	3.2(8)
O(3)	0.921(1)	0.3449(8)	0.184(2)	4.1(10)
O(4)	0.923(1)	0.2574(7)	0.266(2)	3.7(9)
O(5)	1.044(1)	0.2906(7)	0.183(1)	2.8(8)
Cl(1)	1.0200(6)	0.3039(4)	−0.0579(7)	5.4(4)
Cl(2)	1.1590(5)	0.2100(4)	0.1910(8)	5.1(4)
Cl(3)	0.8685(6)	0.3222(4)	0.4732(9)	6.0(5)
Zn(1)	0.5199(3)	0.4287(1)	0.1833(3)	4.9(2)
Zn(2)	0.6161(3)	0.5141(1)	0.4277(4)	4.9(2)
Cl(1A)	0.6305(6)	0.4434(4)	0.3021(9)	5.7(4)
Cl(2A)	0.5	0.5	0.534(1)	5.8(7)
Cl(3A)	0.5	0.5	0.063(1)	7.0(9)
Cl(4A)	0.5487(7)	0.3578(4)	0.084(1)	7.6(6)
Cl(5A)	0.7252(7)	0.5259(5)	0.537(1)	7.2(6)
Cl(6A)	0.4075(7)	0.4172(4)	0.296(1)	6.7(5)
Cl(1S)[d]	0.620(3)	0.021(2)	0.139(2)	13.7(32)
Cl(2S)[d]	0.747(3)	0.018(12)	0.052(4)	12.9(29)
C(1)	0.837(1)	0.3176(6)	−0.048(2)	4.4(7)
C(2)	0.797(1)	0.3212(7)	0.062(2)	6.3(9)
C(3)	0.782(1)	0.2707(8)	0.103(2)	7.1(11)
C(4)	0.813(1)	0.2359(6)	0.019(2)	5.0(8)
C(5)	0.847(1)	0.2649(7)	−0.074(2)	5.4(8)
C(6)	0.856(2)	0.3622(8)	−0.129(3)	13.1(21)
C(7)	0.767(2)	0.3703(9)	0.119(3)	16.2(27)
C(8)	0.734(2)	0.256(1)	0.211(2)	23.0(41)
C(9)	0.804(2)	0.1779(6)	0.021(3)	11.8(18)
C(10)	0.879(2)	0.243(1)	−0.189(2)	12.4(19)
C(11)	1.016(1)	0.1720(5)	0.467(1)	4.4(7)
C(12)	1.0837(9)	0.1511(6)	0.410(1)	5.8(8)
C(13)	1.057(1)	0.1241(6)	0.309(1)	5.4(8)
C(14)	0.973(1)	0.1283(6)	0.304(1)	3.7(6)
C(15)	0.9471(9)	0.1579(6)	0.402(1)	4.5(7)
C(16)	1.016(1)	0.1995(8)	0.585(1)	7.3(10)
C(17)	1.1689(9)	0.152(1)	0.456(2)	9.3(14)
C(18)	1.109(1)	0.091(1)	0.229(2)	8.3(12)
C(19)	0.918(1)	0.1008(9)	0.217(2)	8.6(12)
C(20)	0.8608(9)	0.168(1)	0.437(2)	11.7(18)
C(21)	1.004(1)	0.4004(7)	0.463(1)	6.7(10)
C(22)	0.985(1)	0.4196(7)	0.350(2)	5.9(8)
C(23)	1.047(1)	0.4051(7)	0.272(1)	6.1(9)
C(24)	1.104(1)	0.3770(7)	0.336(2)	5.9(9)
C(25)	1.078(1)	0.3741(7)	0.455(2)	7.4(11)
C(26)	0.958(2)	0.411(1)	0.576(2)	12.7(19)
C(27)	0.915(2)	0.455(1)	0.321(2)	8.6(13)
C(28)	1.055(2)	0.422(1)	0.144(1)	10.3(16)
C(29)	1.184(1)	0.358(1)	0.290(2)	11.1(17)
C(30)	1.125(2)	0.352(1)	0.557(2)	16.4(27)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid multiplied by $8\pi^2$. [b] For the numbering scheme, see Figure 2. [c] Estimated standard deviations in parentheses. [d] CH_2Cl_2, Cl occupancy 0.5.

with ether (20 cm^3). After 48 h yellow crystals were obtained: yield 0.16 g, 84%. Anal. Found: C, 36.4; H, 4.8; Cl, 21.2. Calcd for $C_{20}H_{32}Cl_4Nb_2O_3$: C, 37.1; H, 4.9; Cl, 21.9. Molecular weight (osmometry, CH_2Cl_2 solution): found, 590; calcd, 648. ^{1}H NMR ($CDCl_3$, 200 MHz): 3.85 (s, 2H, O*H*), 2.18 ppm (s, 30H, $C_5(CH_3)_5$). Infrared (Nujol mull): 3570 cm^{-1} (s, br, ν(O–H)). Mass spectrum (EI, 70 eV; *m/e*, assignment, % intensity): 611, $(C_5Me_5)_2Nb_2Cl_3(OH)_2O^+$, 3; 576, $(C_5Me_5)_2Nb_2Cl_2(OH)_2O$, 2; 511, $(C_5Me_5)Nb_2Cl_4(OH)_2O$, 5. The compound was also characterized by X-ray crystallography (see Tables III and IV).

Reaction of a Mixture of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ and $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ with Zinc: Formation of $\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\{Zn_4Cl_{10}\}$. An approximately 1:4 mixture of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ and $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (1.25 g) in CH_2Cl_2 (100 cm^3) was stirred with zinc powder (0.40 g) in air for 4 days. The resultant pale green solution was filtered and the filtrate concentrated to 30 cm^3 under vacuum and then layered with ether (20 cm^3). After this mixture was set aside at room temperature for 48 h, a pale green precipitate was obtained. This was collected by filtration and recrystallized from CH_2Cl_2/ether. Anal. Found: C, 23.8; H, 3.15; Cl, 21.1. Calcd for $C_{61}H_{96}Cl_{18}O_{10}Ta_6Zn_4$ ($\{[(\eta\text{-}C_5Me_5)TaCl]_3(\mu_2\text{-}OH)(\mu_2\text{-}O)_2(\mu_3\text{-}OH)(\mu_3\text{-}O)\}_2\{Zn_4Cl_{10}\}\cdot CH_2Cl_2$): C, 24.6; H, 3.3; Cl, 21.4. ^{1}H NMR (200 MHz, $CDCl_3$ solution): 3.25 (2H, O*H*), 2.20 (30H, $C_5(CH_3)_5$ on Ta(1) and Ta(2) (see Figure 2)), 2.30 ppm (15H, $C_5(CH_3)_5$ on Ta(3)). Infrared (KBr disk): 3400–3700 cm^{-1} (m, vbr, ν(O–H)). Mass spectrum (FAB; *m/e*, assignment, % intensity): 1100, $(C_5Me_5)_3Ta_3Cl_2(OH)_2O_3^+$, 12; 1000, $(C_5Me_5)_2Ta_3Cl_3(OH)_2O_3^+$, 53. The compound was diamagnetic (Faraday method, 295 K). The compound was also characterized by X-ray crystallography (see Tables III and V).

Reduction of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ with Sodium Amalgam: Formation of $[(\eta\text{-}C_5Me_5)Nb]_4O_6$. A solution of $[(\eta\text{-}C_5Me_5)NbCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (1.25 g, 1.88 mmol) in THF (150 cm^3) was stirred with sodium amalgam (4.7 cm^3, 9.4 mmol of Na) for 2 h. The color of the solution changed from orange-red through green to brown. The solution was removed from the amalgam with a syringe, and the solvent was completely removed under vacuum. The resultant brown solid was extracted with toluene (100 cm^3); the extract was reduced to 40 cm^3 under vacuum and then layered with hexane (30 cm^3). The mixed solvents were reduced to a volume of 40 cm^3; then the solution was set aside at −40 °C for 6 days. The brown precipitate which formed was collected by filtration, washed with cold hexane (30 cm^3), and dried under vacuum: yield 60% according to eq 1. Anal. Found: C, 47.7 (4, 0.4); H, 5.9 (4, 0.1); Cl, <0.5; Nb, 35.4 (3, 12, by atomic absorption). The first digit in parentheses is the number of determinations, and the second is the maximum deviation from the mean. Calcd. for $C_{40}H_{60}Nb_4O_6$: C, 47.6; H, 5.95; Cl, 0; Nb, 36.9. Molecular weight (by osmometry in benzene): found, 945; calcd for $(C_5Me_5)_4Nb_4O_6$, 1007.6. ^{1}H NMR (200 MHz, C_6D_6 solution): 1.97 ppm (s, $C_5(CH_3)_5$). ^{13}C NMR (C_6D_6 solution): 10.95 ppm (s, $C_5(CH_3)_5$); no signal for $C_5(CH_3)_5$ was observed. Infrared (Nujol mull): 670 and 590 cm^{-1} (intense, broad), assigned to vibrations of the Nb_4O_6 core; no absorptions which could be assigned to ν(O—H) or ν(Nb═O) were observed. Mass spectrum (FAB Magic Bullet ($HSCH_2(CH(OH))_2CH_2SH$) as matrix; *m/e*, assignment, % intensity): 1025, $[M + OH]^+$, 27; 1024, $[M + O]^+$, 65; 1008, M^+, 23; 889 $[M + OH - C_5Me_5]^+$ 55; 873, $[M - C_5Me_5]^+$, 13. Magnetic moment: 0.57 μ_B at 300 K (see Figure 3). ESR (C_6H_6 solution): no signal at 298 K.

Reduction of $[(\eta\text{-}C_5Me_5)TaCl_2]_2(\mu\text{-}OH)_2(\mu\text{-}O)$ with Sodium Amalgam: Formation of $[(\eta\text{-}C_5Me_5)Ta]_4O_6$. By a procedure exactly analogous to that for the niobium analog, $[(\eta\text{-}C_5Me_5)Ta]_4O_6$ was obtained in 65% yield. Anal. Found: C, 34.7; H, 4.6; Cl, 0.7; Ta (by atomic absorption), 51.5. Calcd for $C_{40}H_{60}O_6Ta_4$: C, 35.3; H, 4.4; Cl, 0; Ta, 53.2. Molecular weight: found, 1290; calcd for $(C_5Me_5)_4Ta_4O_6$ 1360. ^{1}H NMR: 2.04 ppm (s). ^{13}C NMR: 11 ppm (v br, $C_5(CH_3)_5$). Infrared: 680 and 580 cm^{-1} (medium intensity). Mass spectrum (FAB; *m/e* assignment, % intensity): 1377, $[M + OH]^+$, 13; 1361, $[M + H]^+$, 12; 1241 $[M + O - C_5Me]^+$, 17; 1225, $[M - C_5Me_5]^+$, 17; 1091, $[M - 2C_5Me_5]^+$, 15. Magnetic moment (Faraday method): 0.98 μ_B at 295 K.

X-ray Crystallography. X-ray diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer. The radiation was Mo Kα (λ = 0.710 69 Å). Data were collected using the $\omega/2\theta$ scan method. Refinement used the NRCVAX suite of programs.[22] The weighting scheme was of the form $w = 1/(\sigma(F)^2 + kF^2)$. Scattering factors for the neutral atoms, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the program. Crystal and refinement data for 2 and 3 are collected in Table III. In the final refinements, hydrogen atoms were included as fixed contributors with C–H = 0.96 Å and an isotropic U value equal to 0.01 Å^2 plus U for the carbon atom to which they were attached.

The determination of the structure of 2 was uneventful. The hydroxyl hydrogen atom was observed in a difference Fourier synthesis. Its position was not refined. The determination of

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(22) Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

the structure of 3 was complicated by the presence of a disordered molecule of CH_2Cl_2 in the lattice but was otherwise routine. Crystal data for 2 and 3 are given in Table III, atomic positions in Tables IV and V, and selected distances and angles in Tables I and II. Other details are available as supplementary material.

The extended Hückel molecular orbital calculations used the program of Hoffmann and co-workers,[23] with the niobium coefficients taken from the literature.[24]

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Supplementary Material Available: Figures showing full numbering schemes and tables of hydrogen atom positions, anisotropic and isotropic thermal parameters, comprehensive distances and angles, and mean planes for 2 and 3 (14 pages). Ordering information is given on any current masthead page.

OM930146P

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