4973 independent reflections used in structure solution and refinement (goodness of fit for merging 1.06); 4341 reflections with $F_o^2 > 0$ used in R, which was 0.054 at convergence with most non-hydrogen atoms anisotropic; three hydrogens on bridging methyl group refined, remainder positioned by difference maps or by calculation with C–H = 0.95 Å; refined C–H distances 0.82 (4), 0.94 (4), and 0.88 (4) Å; H–C–H angles 121 (4), 121 (4), and 116 (4)°. The refinement was smooth, and the low values of the final residuals indicates the model is an excellent one. Complete details are given in the supplementary material.

Formation of 3a from 2 and 1. Addition of a benzene-d_6 solution of the alkyl–acyl complex **1** to the ketone complex **2** led to the immediate precipitation of **3a** as a yellow microcrystalline material.

[$Cp_2Zr(\eta^2(C,O)$-$OCMe_2)$][$Cp_2Zr(\eta^2(C,O)$-$OC(Me)CH_2CH_2CMe_3)$](μ-$AlMe_2$)(μ-Cl) (5). The ketone complex **4**[7] and the acyl **1** were dissolved in toluene to give a yellow solution, which was stirred briefly and evacuated to give **5** as a yellow powder (0.276 g, 0.383 mmol, 52%). ^{1}H NMR (C_6D_6): δ 5.86 (s, 5 H), 5.75 (s, 5 H), 5.73 (s, 5 H), 5.69 (s, 5 H), 2.60 (td, ^3J = 12.7 Hz, ^2J = 3.9 Hz, 1 H), 1.75 (s, 3 H), 1.65 (s, 3 H), 1.61 (s, 3 H), 1.39 (td, ^3J = 13.2 Hz, ^2J = 3.9 Hz), 1.27 (td, ^3J = 13.2 Hz, ^2J = 4.6 Hz, 1H), 1.01 (s, 9 H), −0.23 (s, 3 H), −0.28 (s, 3 H). ^{13}C NMR (C_6D_6): δ 110.1, 109.9, 109.7, 109.6, 83.9, 77.9, 42.4, 41.8, 34.5, 33.8, 32.5, 30.6, 30.0.

Acknowledgment. We acknowledge the National Institutes of Health and the National Science Foundation for financial support of this research and the National Science Foundation (Grant No. CHE-83-19039) for financial support of the X-ray facility.

Supplementary Material Available: A complete description of data collection and refinement and tables of crystallographic data, all final positional and thermal parameters, and selected distances and angles (8 pages); a table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Hydrolysis of Tetrachloro(pentamethylcyclopentadienyl)niobium(V). Crystal Structure of $[Nb_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu_2\text{-}O)(\mu\text{-}Cl)](\mu_2\text{-}O)_2(\mu_3\text{-}O)[Nb(\eta^5\text{-}C_5Me_5)Cl]$

Javier de la Mata,† Rosa Fandos,† Manuel Gómez,† Pilar Gómez-Sal,†
Sagrario Martinez-Carrera,‡ and Pascual Royo*,†

Departamento de Química Inorgânica, Facultad de Ciencias-Farmacia, Campus Universitario,
Universidad de Alcalá de Henares, 28871 Alcalá de Henares (Madrid), Spain, and Instituto Rocasolano,
CSIC, Madrid, Spain

Received December 21, 1989

Summary: $NbCp^*Cl_4$ (**1**; $Cp^* = \eta^5$-C_5Me_5) is directly isolated as a crystalline solid by reacting $NbCl_5$ with $SiMe_3(C_5Me_5)$ in dichloromethane–toluene (3:1). Complex **1** reacts with H_2O in the presence of $NHEt_2$ to give the mononuclear hydroxo complex $NbCp^*Cl_3(OH)$ (**2**), which reacts with **1**, losing HCl to give the μ-oxo complex $[NbCp^*Cl_3]_2(\mu$-O) (**3**), also formed by exposure of solid samples of **1** to the ambient atmosphere. **2** also reacts with H_2O in solution to form the μ-oxo hydroxo complex $[NbCp^*Cl_2(OH)]_2(\mu$-O) (**4**), which is also formed from **3** by exposure to air. When the dinuclear complex **4** is heated, it yields the trinuclear niobium oxide cluster $Nb_3Cp^*_3(\mu_2\text{-}O)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)Cl_3$ (**5**). The crystal structure of **5** is reported. The compound crystallizes in the monoclinic space group $P2_1/n$, with $Z = 4$, a = 11.357 (6) Å, b = 19.685 (10) Å, and c = 15.797 (6) Å. Anisotropic refinement of all atoms except hydrogen atoms converged to the residuals R = 0.069 and R_w = 0.030 for 2722 reflections.

The stabilizing[1] effects of the bulky and strong electron donor pentamethylcyclopentadienyl ligand permit us extend the already well-developed chemistry of related early transition metals, whose high oxophilicity[2] gives rise to the reactivity of their derivatives with water and other oxygen sources such as N_2O and CO_2[3] or CO[4] to give complexes containing oxo bridges between two or more metal centers.[5] The hydrolysis of $TaCp^*Cl_4$[6] has been reported to lead to the formation of a mononuclear hydroxo complex and di- and trinuclear (μ-oxo)tantalum derivatives. Here we report a similar hydrolytic behavior for $NbCp^*Cl_4$.

Mono(pentamethylcyclopentadienyl)niobium and -tantalum complexes were first prepared by the reaction of MCl_5 (M = Nb, Ta) with $SnBu^n{}_3(C_5Me_5)$,[7] the niobium derivative being described as an oily residue. The yields have been optimized by using $SiMe_3(C_5Me_5)$,[8] which is a

---

† Universidad de Alcalá de Henares.

‡ Instituto Rocasolano.

(1) Maitlis, P. M. *Coord. Chem. Rev.* **1982**, *43*, 377.

(2) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974.

(3) (a) Bottomley, F.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* 1978, 234. (b) Bottomley, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5239. (c) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

(4) (a) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829. (b) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

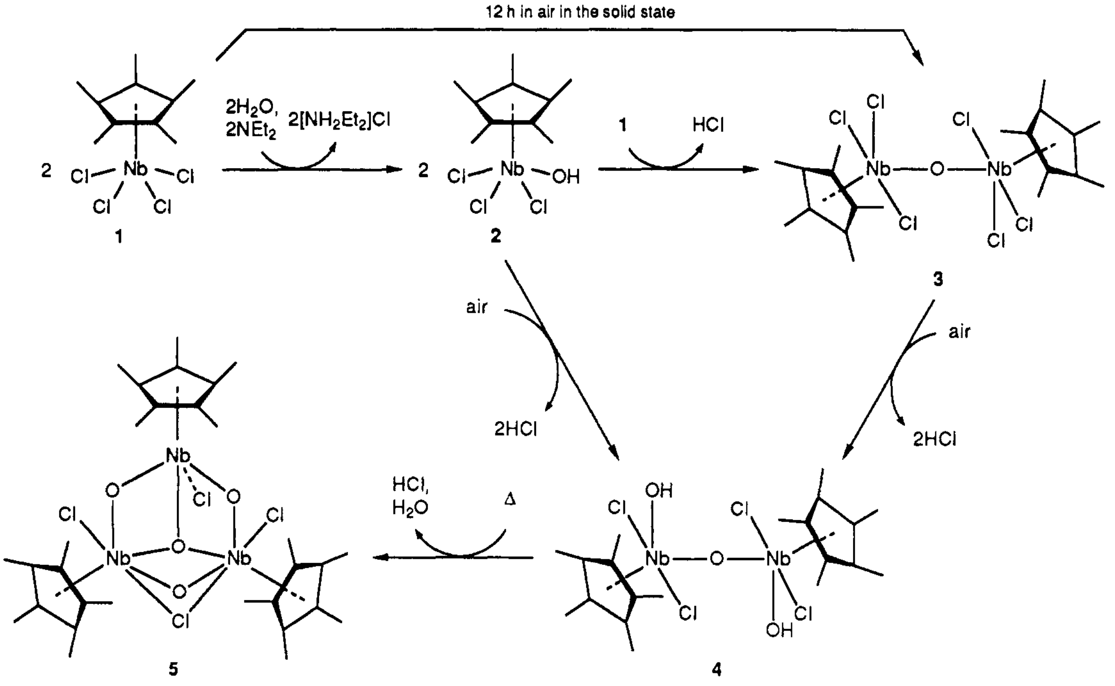
(5) (a) Reid, A. F.; Shannon, J. S.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem.* **1965**, *18*, 173. (b) LePage, Y.; McCowan, J. D.; Hunter, B. K.; Heydig, R. D. *J. Organomet. Chem.* **1980**, *193*, 201. (c) Bleukers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383. (d) Klein, H. P.; Thewalt, W.; Döppert, K.; Sánchez-Delgado, R. *J. Organomet. Chem.* **1982**, *236*, 189. (e) Bortolin, R.; Patel, V.; Munday, I.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 456. (f) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* 1987, 858. (g) Gómez-Sal, M. P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147. (h) Babcock, L. M.; Klemperer, W. G. *Inorg. Chem.* **1989**, *28*, 2033.

(6) (a) Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362. (b) Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *New J. Chem.* **1988**, *12*, 329.

(7) Herrmann, W. A.; Kalcher, W.; Biersack, H.; Bernal, I.; Creswick, M. *Chem. Ber.* **1981**, *114*, 3558.

0276-7333/90/2309-2846$02.50/0

Scheme I



much more convenient reagent to transfer the cyclopentadienyl ring, leading after extraction with toluene to the crystalline niobium derivative. We found that $NbCp^*Cl_4$ (1) can be isolated directly by concentration of the reaction mixture in dichloromethane–toluene (3:1) as a very air- and moisture-sensitive crystalline red solid, for which the same monomeric four-legged piano-stool structure reported for the analogous tantalum complex[9] could be reasonable in solution.

As shown in Scheme I, solid 1 is quantitatively transformed into 3 by exposure to ambient atmosphere for 12 h, and this is the best method to obtain 3.

The reaction of 1 with an equimolar amount of H_2O in the presence of $NHEt_2$ produced the dark green hydroxo derivative 2. When the same reaction is performed with a $Nb/H_2O/NHEt_2$ molar ratio of 2/1/1, the initially formed hydroxo complex 2 is transformed into 3. The formation of 3 is probably due to the reaction of 2 with the present excess of 1, and in fact, when 1 is added to a solution of 2 obtained as indicated by the first reaction, 3 is the unique component in the resulting solution. Complex 4 results from a further hydrolysis of 2 or 3. In fact, 2 is rapidly transformed into 4 in the solid state and bubbling of air through a toluene solution of 2 or 3 produces a complete conversion into orange 4 with evolution of HCl.

3 is stable in air in the solid state, whereas its solutions are extremely air-sensitive so that their NMR spectra always show very small signals due to 4, whose intensity increases with the time of manipulation of the sample. However, 3 is significantly less soluble than 4 and single crystals of it can be obtained by partial evaporation.

Complex 4 is always the final product of hydrolysis even in the presence of an excess of water and is stable under ambient atmosphere in the solid and in solution. All these oxo complexes 2–4 contain the niobium atom in the same pseudo-square-pyramidal environment shown by the starting chloro derivative 1. However, 4 is transformed into the trinuclear yellow complex 5 by heating in vacuo for 6 h at 170 °C.

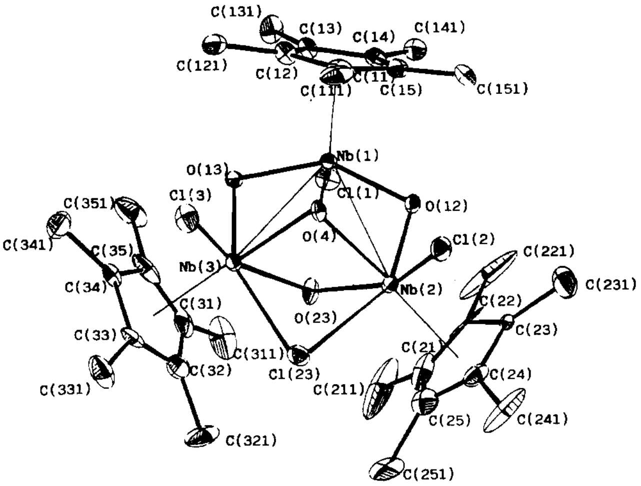


Figure 1. ORTEP view of complex 5 with the atom-labeling scheme.

Complexes 2–5 are moderately soluble in most organic solvents, except in saturated hydrocarbons. The solubility increases with increasing oxygen content. They were analytically and spectroscopically characterized.

Characteristic pentamethylcyclopentadienyl ring ν_{C-C} and stretching ν_{Nb-Cl} absorptions are observed at 1015–1020 and 309–339 cm^{-1}, respectively.

Complexes 3–5 show the Nb–O–Nb IR absorption at 650–590 cm^{-1}, whereas a strong absorption due to ν_{O-H} is observed for 4 at 3569 cm^{-1}, which is shifted for 2 to 3464 cm^{-1}, indicating some type of intra- or intermolecular hydrogen O–H···Cl interaction. This is also shown by the shift observed for ν_{Nb-O}, which appears at 864 cm^{-1} for 2 and at 805 cm^{-1} for 4.

The ^1H NMR spectra of all the complexes 2–4 show the expected singlet for the ring methyl protons, which is shifted to higher field by increasing oxygen substitution. Two singlets at δ 2.07 and 2.06 ppm in $CDCl_3$ with relative

---

(8) (a) Yasuda, H.; Okamoto, T.; Nakamura, A. *Organomet. Synth.* **1988**, *4*, 20. (b) Hidalgo, G.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37.

(9) (a) Sanner, R. D.; Carter, S. T.; Bruton, W. J., Jr. *J. Organomet. Chem.* **1982**, *240*, 157. (b) Bunker, M. J.; DeCian, A.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1977**, 59.

Table I. Positional Coordinates and Thermal Parameters for 5

atom	x	y	z	U_{eq},[a] Å^2
Nb(1)	0.8914 (1)	0.23594 (9)	0.0050 (1)	291 (6)
Nb(2)	0.6785 (1)	0.18105 (8)	0.0846 (1)	296 (6)
Nb(3)	0.7325 (1)	0.33860 (9)	0.0777 (1)	309 (6)
Cl(1)	0.8474 (4)	0.2377 (3)	−0.1442 (3)	551 (20)
Cl(2)	0.7529 (4)	0.1337 (2)	0.2181 (3)	476 (19)
Cl(3)	0.8270 (4)	0.3743 (2)	0.2102 (3)	547 (21)
Cl(23)	0.5846 (4)	0.2762 (2)	0.1762 (3)	457 (18)
O(12)	0.8081 (9)	0.1508 (5)	0.0206 (7)	361 (44)
O(13)	0.8702 (9)	0.3354 (5)	0.0138 (7)	360 (43)
O(23)	0.662 (1)	0.2627 (6)	0.0102 (7)	465 (48)
O(4)	0.8161 (9)	0.2485 (5)	0.1173 (6)	304 (42)
C(11)	1.055 (1)	0.218 (1)	0.103 (1)	463 (79)
C(12)	1.088 (1)	0.272 (1)	0.054 (1)	391 (71)
C(13)	1.097 (1)	0.2506 (9)	−0.029	324 (65)
C(14)	1.072 (1)	0.178 (1)	−0.023 (1)	471 (78)
C(15)	1.050 (1)	0.159 (1)	0.057 (1)	453 (76)
C(111)	1.044 (1)	0.222 (1)	0.195 (1)	696 (99)
C(121)	1.110 (1)	0.344 (1)	0.084 (1)	585 (88)
C(131)	1.138 (2)	0.289 (1)	−0.098 (1)	738 (103)
C(141)	1.084 (2)	0.133 (1)	−0.098 (1)	780 (117)
C(151)	1.031 (1)	0.091 (1)	0.085 (1)	642 (97)
C(21)	0.502 (3)	0.149 (1)	−0.007 (2)	815 (126)
C(22)	0.585 (2)	0.099 (1)	−0.013 (1)	934 (135)
C(23)	0.596 (1)	0.063 (1)	0.066 (1)	574 (98)
C(24)	0.518 (1)	0.101 (1)	0.115 (1)	545 (89)
C(25)	0.466 (2)	0.152 (1)	0.066 (1)	670 (111)
C(211)	0.458 (4)	0.193 (2)	−0.080 (2)	2554 (277)
C(221)	0.657 (4)	0.068 (2)	−0.086 (3)	3005 (378)
C(231)	0.665 (2)	0.004 (1)	0.096 (2)	1401 (191)
C(241)	0.478 (2)	0.081 (1)	0.200 (1)	1338 (163)
C(251)	0.359 (2)	0.195 (1)	0.083 (3)	1455 (295)
C(31)	0.611 (2)	0.400 (1)	−0.030 (2)	738 (120)
C(32)	0.547 (2)	0.404 (1)	0.039 (1)	663 (106)
C(33)	0.616 (1)	0.444 (1)	0.098 (1)	488 (82)
C(34)	0.720 (1)	0.465 (1)	0.061 (1)	380 (70)
C(35)	0.716 (2)	0.436 (1)	−0.020 (1)	769 (114)
C(311)	0.564 (3)	0.364 (1)	−0.111 (1)	1246 (164)
C(321)	0.426 (2)	0.382 (1)	0.052 (2)	1459 (195)
C(331)	0.578 (2)	0.468 (1)	0.181 (1)	827 (119)
C(341)	0.817 (2)	0.511 (1)	0.099 (1)	860 (120)
C(351)	0.815 (2)	0.454 (1)	−0.076 (2)	1215 (155)

[a] $U_{eq} = {}^1/_3\sum[U_{ij}a_i{}^*a_j{}^*a_ia_j(\cos a_ia_j)] \times 10^4$.

intensity 2:1 are observed for **5**, in which the three Cp rings are not magnetically equivalent, as shown by the X-ray structure discussed below.

The molecular structure of this compound is shown in Figure 1 with the labeling scheme employed. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are presented in Table I. The most representative bond distances and angles are given in Table II.

The structure consists of a cluster containing a triangular core of three niobium atoms, edge bridged by three bridging oxo groups. Two of the niobium atoms are also bridged by a μ-chlorine atom. One other oxygen atom caps the triangular face of niobium atoms in a μ_3-oxide mode. The coordination sphere of each niobium atom is completed by a η^5-C_5Me_5 group and one terminally bonded chlorine atom. Similar triangular niobium clusters have been reported previously,[10-12] but none contain Cp rings.

The cluster core is an isosceles triangle with Nb–Nb distances Nb(1)–Nb(2) = 2.980 (3) Å, Nb(1)–Nb(3) = 2.976 (3) Å, and Nb(2)–Nb(3) = 3.165 (3) Å.

Table II. Selected Bond Distances (Å) and Angles (deg) for 5

Nb(1)–Nb(2)	2.980 (3)	Nb(1)–Nb(3)	2.976 (3)
Nb(2)–Nb(3)	3.165 (3)	Nb(1)–Cl(1)	2.386 (5)
Nb(2)–Cl(2)	2.424 (6)	Nb(3)–Cl(3)	2.424 (6)
Nb(2)–Cl(23)	2.627 (5)	Nb(3)–Cl(23)	2.644 (5)
Nb(1)–O(12)	1.94 (1)	Nb(1)–O(13)	1.97 (1)
Nb(2)–O(12)	1.92 (1)	Nb(3)–O(13)	1.90 (1)
Nb(2)–O(23)	1.99 (1)	Nb(3)–O(23)	1.98 (1)
Nb(1)–O(4)	2.02 (1)	Nb(2)–O(4)	2.10 (1)
Nb(3)–O(4)	2.09 (1)	Nb(1)–C(11)	2.39 (1)
Nb(1)–C(11)	2.39 (1)	Nb(1)–C(12)	2.45 (1)
Nb(1)–C(13)	2.45 (1)	Nb(1)–C(14)	2.40 (1)
Nb(1)–C(15)	2.46 (2)	Nb(2)–C(21)	2.51 (3)
Nb(2)–C(22)	2.45 (3)	Nb(2)–C(23)	2.51 (2)
Nb(2)–C(24)	2.46 (2)	Nb(2)–C(25)	2.49 (2)
Nb(3)–C(31)	2.49 (3)	Nb(3)–C(32)	2.51 (2)
Nb(3)–C(33)	2.50 (2)	Nb(3)–C(34)	2.51 (1)
Nb(3)–C(35)	2.47 (2)		
Nb(1)–Cp(1)[a]	2.18	Nb(3)–Cp(3)	2.24
Nb(2)–Cp(2)	2.27		
O(12)–Nb(1)–O(13)	141.6 (5)	O(13)–Nb(2)–O(23)	89.2 (5)
O(13)–Nb(3)–O(23)	90.2 (5)	Nb(1)–O(12)–Nb(2)	100.8 (5)
Nb(1)–O(13)–Nb(3)	100.1 (5)	Nb(2)–O(23)–Nb(3)	105.3 (6)
O(12)–Nb(1)–Cl(1)	93.2 (4)	Cl(2)–Nb(2)–O(12)	95.4 (4)
O(12)–Nb(1)–Cp(1)	106.9	O(12)–Nb(2)–Cp(2)	103.7
Cl(1)–Nb(1)–Cp(1)	111.5	Cl(2)–Nb(2)–Cp(2)	104.9
Cl(1)–Nb(1)–O(13)	91.9 (4)	Cl(2)–Nb(2)–O(23)	147.4 (4)
O(13)–Nb(1)–Cp(1)	106.9	O(23)–Nb(2)–Cp(2)	105.2
Cl(23)–Nb(2)–O(23)	89.2 (5)	Cl(23)–Nb(2)–O(12)	148.5 (4)
Cl(3)–Nb(3)–O(13)	97.3 (4)	Cl(3)–Nb(3)–O(23)	147.0 (4)
O(23)–Nb(3)–Cp(3)	105.6	O(13)–Nb(3)–Cp(3)	102.5
Cl(3)–Nb(3)–Cp(3)	103.9	Cl(23)–Nb(3)–O(13)	149.0 (4)
Cl(23)–Nb(3)–O(23)	73.8 (4)	Nb(2)–Cl(23)–Nb(3)	73.8 (1)
Nb(1)–O(4)–Nb(2)	92.5 (4)	Nb(2)–O(4)–Nb(3)	97.9 (5)
Nb(1)–O(4)–Nb(3)	92.6 (4)		

[a] Cp(x) is the centroid of the C_5Me_5 ligand.

At least the first two distances are in the same range as those found in niobium(III) triangular clusters[10-12] containing metal–metal bonds, although such a type of interaction cannot be present in our complex.

All these data show that Nb(1) is different from Nb(2) and Nb(3), which are kept together by an extra μ-Cl bridge. This asymmetry is also observed in all the remaining substituents, so that the Nb(1)–Cp(1) distance is significantly shorter than the Nb(2)–Cp(2) and Nb(3)–Cp(3) distances with an average value of 2.262 Å. The Nb(1)–O(4) distance of 2.021 (10) Å is also shorter than the average 2.097 Å for the distances from O(4) to the other two niobium atoms. Also the Nb(1)–Cl(1) distance of 2.386 (5) Å is shorter than the other two, averaging 2.418 (6) Å, which are in the same range as those previously reported.[10-12]

The oxygen and chlorine bridges are reasonably symmetric, the average Nb–Cl bond distance of 2.635 (5) Å being longer than that observed for niobium(III) triangular clusters.

The three niobium atoms define a plane in which O(12) and O(13) are almost coplanar (0.1-Å deviation), whereas O(23) is 1.19 (1) Å out of the plane due to the presence of Cl(23), which is situated 0.616 (5) Å under the plane. As in $[CpTiMe(\mu\text{-}O)]_3$[13] two of the Cp rings are located over and one is situated under this plane in alternating positions with the terminal Cl atoms, one of which, Cl(1), is 2.255 (5) Å over the plane and two (Cl(2), Cl(3)) are 2.267 (5) and 2.256 (5) Å below it. The Nb–C ring distances are again shorter for Nb(1) (between 2.398 (9) and 2.46 (2) Å) than for Nb(2) (between 2.45 (3) and 2.51 (3) Å) and for

---

[10] Cotton, F. A.; Diebold, M. P.; Llusar, R.; Roth, W. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1277.

[11] Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 2833.

[12] Cotton, F. A.; Kibala, P. A.; Roth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 298.

[13] Garcia-Blanco, S.; Gômez-Sal, M. P.; Martinez-Carrera, S.; Mena, M.; Royo, P.; Serrano, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1572.

Table III. Crystal Data, Experimental Data, and Structure Refinement Procedures for 5

	Crystal Data
formula	$C_{30}H_{45}O_4Nb_3Cl_4$
cryst habit	prismatic
cryst size, mm	0.2 × 0.2 × 0.3
symmetry	monoclinic, $P2_1/n$
unit cell determn	least-squares fit from 50 rflns ($\theta < 45°$)
unit cell dimens	
a, b, c, Å	11.357 (6), 19.685 (10), 15.797 (6)
α, β, γ, deg	90.0, 92.70 (2), 90.0
packing	
V, Å^3; Z	3527 (2); 4
D_{calcd}, g cm^{-3}; M_r; $F(000)$	1.67; 890.2; 1792
μ, cm^{-1}	12.5
	Experimental Data
technique	four-circle diffractometer, Enraf-Nonius CAD-4, bisecting geometry, graphite-oriented monochromator, Mo Kα, $\omega/2\theta$ scans, detector apertures 1 × 1, to θ_{max} = 25°
no. of rflns	
indep	6218
obsd	2722 ($3\sigma(I)$ criterion)
range of hkl	−13 to 13, 0–23, 0–18; $((\sin\theta)/\lambda)_{max}$ = 0.9
std rflns	2 rflns every 100 rflns, no variation
max, min transmissn factors	1.245, 0.855

Nb(3) (between 2.47 (2) and 2.51 (2) Å), the range of variation for each Cp being due to the usual thermal motion of the rings, which are, however, η^5 coordinated. The usual C–C ring distances are observed, and only residual van der Waals interactions are present between the different molecules in the crystal.

Experimental Section

Crystallographic Structure Determination for Complex 5. Yellow crystals of **5** suitable for single-crystal x-ray studies were obtained by crystallization at −40 °C from diethyl ether solution. Crystallographic data are collected in Table III. Data were collected at room temperature.

Intensities were corrected for Lorentz and polarization effects in the usual manner. No extinction corrections were made. The structure was solved by a combination of direct methods and Fourier syntheses. The structure was refined (on F) by full-matrix least-squares calculations. Before all the non-hydrogen atoms were refined anisotropically, an empirical absorption correction was made by the Walker and Stuart method.[14] All non-hydrogen atoms were refined anisotropically. In the later stages of the refinement hydrogen atoms were included from geometric calculations, with fixed positions and thermal parameters equivalent to those of the atoms to which they are attached. Final values of R = 0.069 and R_w = 0.030 (weighting scheme: empirical fit as to give no trends in $\langle w\Delta^2F\rangle$ vs $\langle F_0\rangle$ and vs $\langle(\sin\theta)/\lambda\rangle$) were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref 15. Calculations were performed with the X-Ray System 80[16] and the programs MULTAN,[17] DIRDIFF,[18] PARST,[19] and PESOS[20] on a VAX-11750 computer.

Synthesis. Manipulations were performed under an atmosphere of nitrogen or argon with use of Schlenk techniques or in a Vacuum Atmospheres glovebox equipped with a HE-63-P Dri-Train. The following solvents were dried, freshly distilled, and degassed prior to use: dichloromethane (P_2O_5 or $CaCl_2$), diethyl ether (sodium–benzophenone), *n*-hexane (calcium hydride), and toluene (sodium). $NbCl_5$ and $NHEt_2$ were used after purification by sublimation and distillation, respectively. $Me_3Si(C_5Me_5)$ was prepared and isolated as described.[8b]

Infrared spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm^{-1}) as Nujol mulls between polyethylene films. ^{1}H NMR spectra were recorded on a Varian FT 80A instrument with $SiMe_4$ as internal reference. C and H analyses were performed with a Perkin-Elmer 240 B microanalyzer. Cl analyses were carried out by following White's method.[21]

Preparation of NbCp*Cl$_4$ (1). A solution of $Me_3Si(C_5Me_5)$ (3.08 g, 12.14 mmol) in toluene (20 mL) was slowly added to a suspension of $NbCl_5$ (3.28 g, 12.14 mmol) in dichloromethane (60 mL) at 0 °C, over 30 min. The mixture was stirred for 12 h at room temperature. The red solution was filtered, concentrated to ca. 40 mL, and cooled to −40 °C overnight to give a dark red microcrystalline solid of **1**: yield 70% (2.70 g); IR (Nujol mull) 2965 (m), 2915 (m), 2884 (m), 1465 (vs), 1376 (vs), 1302 (w), 1015 (m), 410 (m), 339 (vs) cm^{-1}; ^{1}H NMR (δ (ppm) in $CDCl_3$) 2.50 (s, C_5Me_5); $^{13}C\{^1H\}$ NMR (δ (ppm) in $CDCl_3$) 135.45 (s, C_5Me_5), 15.45 (s, $C_5\mathit{Me}_5$). Anal. Calcd for $NbCl_4C_{10}H_{15}$: C, 32.44; H, 4.05. Found: C, 31.41; H, 3.64.

Preparation of NbCp*Cl$_3$(OH) (2). $NHEt_2$ (0.39 mL, 3.78 mmol) and H_2O (68 μL, 3.78 mmol) were successively added to a suspension of NbCp*Cl$_4$ (1.40 g, 3.78 mmol) in toluene (45 mL), and the mixture was stirred for 12 h. The dark green suspension obtained was filtered, concentrated to ca. 15 mL, and cooled to −40 °C overnight to give dark green microcrystals of **2**: yield 70% (0.93 g); IR (Nujol mull) 3464 (m), 2346 (w), 1578 (m), 1262 (w), 1158 (w), 1072 (m), 1020 (m), 864 (s), 806 (w), 640 (w), 594 (w), 472 (s), 366 (m), 320 (s), 286 (m) cm^{-1}; ^{1}H NMR (δ (ppm) in $CDCl_3$) 2.75 (b, OH), 2.42 (s, C_5Me_5). Anal. Calcd for $NbCl_3OC_{10}H_{16}$: C, 34.15; H, 4.26. Found: C, 34.19; H, 4.30.

Preparation of [NbCp*Cl$_3$]$_2$(μ-O) (3). This complex can be prepared by two different methods.

Method A. When a solid sample of **1** (1.50 g, 2.70 mmol) was exposed to the ambient atmosphere for 12 h, an orange solid was formed and identified as **3**: yield 100% (0.92 g); IR (Nujol mull) 1073 (w), 1017 (m), 825 (w), 646 (s), 603 (w), 593 (s), 383 (m), 331 (s) cm^{-1}; ^{1}H NMR (δ (ppm) in $CDCl_3$) 2.23 (s, C_5Me_5). Anal. Calcd for $Nb_2Cl_6OC_{20}H_{30}$: C, 35.07; Cl, 31.06; H, 4.38. Found: C, 35.27; Cl, 30.10; H, 4.41.

Method B. $NHEt_2$ (0.19 mL, 1.89 mmol) and H_2O (34 μL, 1.89 mmol) were successively added to a suspension of **1** (1.40 g, 3.78 mmol) in toluene (40 mL), and the mixture was stirred for 12 h. The orange solution obtained was filtered, concentrated to ca. 15 mL, and cooled to −40 °C overnight, to give an orange solid identified as **3**. The same compound can also be obtained when equimolar amounts of **2** and **1** are stirred in toluene.

Preparation of [NbCp*Cl$_2$(OH)]$_2$(μ-O) (4). A toluene solution of **2** or **3** (1.24 mmol) was stirred in air for 15 min. The orange suspension formed was filtered and the orange solid identified as **4**: yield 90% (0.36 g); IR (Nujol mull) 3569 (s), 2388 (m), 2340 (w), 1157 (w), 1073 (m), 1019 (m), 805 (s), 637 (s), 607 (m), 591 (s), 471 (m) 427 (w), 390 (m), 329 (s), 310 (m) cm^{-1}; ^{1}H NMR (δ (ppm) in $CDCl_3$) 3.83 (s, OH), 2.17 (s, C_5Me_5). Anal. Calcd for $NbCl_4O_3C_{20}H_{32}$: C, 37.04; Cl, 21.92; H, 4.63. Found: C, 36.68; Cl, 21.49; H, 5.17.

Preparation of Nb$_3$Cp*$_3$(μ_2-O)$_3$(μ_3-O)(μ_2-Cl)Cl$_3$ (5). **4** (0.46 g, 0.71 mmol) was heated to 170 °C in vacuo for 6 h. The yellow-orange solid formed was extracted with diethyl ether (2 × 15 mL). The solution was concentrated in vacuo to ca. 10 mL and cooled to −40 °C overnight to give yellow crystals of **5**: yield 55% (0.23 g); IR (Nujol mull) 1260 (s), 1095 (s), 1020 (s), 802 (s), 676 (m), 605 (w), 587 (m), 374 (m), 309 (m) cm^{-1}; ^{1}H NMR (δ (ppm)

---

[14] Walker, N.; Stuart, D. DIFABS. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

[15] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

[16] Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. The X-Ray 80 System; Computer Science Center, University of Maryland: College Park, MD, 1980.

[17] Main, P.; Fiske, S. E.; Hull, S. L.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. MULTAN; Universities of York, England, and Louvain, Belgium, 1980.

[18] Beurskens, P. T.; Bossman, W. P.; Doesburg, H. M.; Gould, R. O.; van der Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. DIRDIF Manual 81, Tech. Report 1981-2; Crystallographic Laboratory: Toernooiveld, The Netherlands, 1981.

[19] Nardelli, M. *Comput. Chem.* **1983**, *7*, 96.

[20] Martinez-Ripoll, M.; Cano, F. H. PESOS; Instituto Rocasolano, CSIC: Madrid, Spain, 1975.

[21] White, D. C. *Mikrochim. Acta* **1961**, 449.

in $CDCl_3$) 2.07 (s, 2 C_5Me_5), 2.06 (s, C_5Me_5); $^{13}C\{^1H\}$ NMR (δ (ppm) in $CDCl_3$) 130.15 (s, 2 C_5Me_5), 129.05 (s, C_5Me_5), 12.42 (s, 2 C_5Me_5), 11.77 (s, C_5Me_5). Anal. Calcd for $Nb_3Cl_4O_4C_{30}H_{45}$: C, 40.45; H, 5.05. Found: C, 39.85; H, 5.43.

Acknowledgment. We thank the CICYT for supporting this work (Grant No. PB 86-0093) and the Universidad de Alcalá de Henares for a fellowship to J.d.l.M.

Supplementary Material Available: Listings of positional and thermal parameters, bond distances and angles, least-squares planes, and interatomic and intermolecular contacts (23 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Additions and Corrections

R. R. Schrock,* R. T. DePue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. DiMare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Krüger, and P. Betz: Further Studies of Imido Alkylidene Complexes of Tungsten, Well-Characterized Olefin Metathesis Catalysts with Controllable Activity. **1990**, *9*, 2262.

In the first line of the fourth paragraph in column 2 of page 2271, the notation for compound **2** should be deleted. In the first paragraph of column 2 on page 2272, the paragraph head should read W(C-*t*-Bu)(NHAr′)(dme)Cl_2.

Takakazu Yamamoto,* Kenji Sano, Kohtaro Osakada,* Sanshiro Komiya, Akio Yamamoto,* Yoshihiko Kushi, and Toshiji Tada: Comparative Studies on Reactions of α,β- and β,γ-Unsaturated Amides and Acids with Nickel(0), Palladium(0), and Platinum(0) Complexes. Preparation of New Five- and Six-Membered Nickel- and Palladium-Containing Cyclic Amide and Ester Complexes. **1990**, *9*, 2396.

In the fifth paragraph of column 2 on page 2402, the eighth line should read "...(28%) of **7**."