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A Trinuclear Oxoniobium(V) Complex with Ketone Molecules as Ligands, $[NbOCl_3(OCRR')]_3$ with $R = C_6H_5$ and $R' = m\text{-}CH_3C_6H_4$

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Abstract

The title compound and a less stable homolog containing benzophenone have been prepared. X-ray crystallography shows the title compound to be a trimer in which three $NbOCl_3(OCRR')$ units are joined in cyclic fashion so that there is a closed set of $Nb{=}O{\rightarrow}Nb$ bonds. The unusual feature of the compound is the attachment of a ketone molecule to each metal atom. The following average distances were found: Nb=O, 1.767(6); NbO→Nb, 2.091(7); CO→Nb, 2.167(8), Nb–Cl, 2.330(4) Å; C=O–Nb angles were in the range 158°–177°.

Introduction

Metal–metal multiple bonds can be exploited as centers of unusual reactivity [1]. Specifically, the face-sharing bioctahedron compound of niobium $(SMe_2)Cl_2Nb(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)NbCl_2(SMe_2)$, containing a $\sigma^2\pi^2$ Nb=Nb double bond, has been utilized extensively in this Laboratory to exploit various reactivities toward organic functional groups. For example, with RCOONa, where $R = -C_6H_5$ or $-CMe_3$, the niobium dimer gives cationic bi-oxo-capped triangular trinuclear clusters [2] of the general formula $Nb_3O_2(RCOO)_6(THF)_3^+$ and with isocyanides RNC ($R = -CMe_3$, $-CHMe_2$, and c-C_6H_{11}), $Nb_2Cl_6(SMe_2)_3$ forms dinuclear complexes of the type $Nb_2Cl_6(RNC)_6$ in which two isocyanides are coupled through two carbon atoms [3]. The latter reactivity feature led us to the idea of reacting the $Nb_2Cl_6(SMe_2)_3$ starting material with ketones, benzophenone and 3-methylbenzophenone, in the hope of demonstrating yet another Nb=Nb promoted coupling involving two carbonyl groups. This idea was additionally supported by the fact that $\sigma^2\pi^2$ doubly bonded ditungsten(IV) alkoxides, $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$, do couple ketones to afford $W_2Cl_4(\mu\text{-}OR)_2[R_2C(O)C(O)R_2]$ [4].

Under the conditions used, no coupling reaction occurred, but a new, trinuclear niobium compound of composition $Nb_3Cl_9O_3(R_1R_2CO)_3$, where $R_1 = m\text{-}CH_3C_6H_4$ and $R_2 = -C_6H_5$, was formed. In this paper we describe this new niobium trimer which constitutes a rare example of a complex where a ketone, 3-methylbenzophenone, is directly bonded to a metal atom.

Experimental

All manipulations were carried out under an atmosphere of argon. Standard Schlenk and vacuum line techniques were used. Commercial grade solvents were freshly distilled from benzophenone ketyl prior to use. The starting material, $Nb_2Cl_6(SMe_2)_3$, was prepared by literature methods involving the reduction of $NbCl_5$ with sodium amalgam in the presence of dimethylsulfide [5]. Benzophenone and 3-methylbenzophenone were purchased from Fisher Scientific Co. and Lancaster Synthesis Ltd., respectively, and were used without further purification. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer.

Preparation of $[NbCl_3O_2C_{13}H_{10}]_3$ *(1)*

In a 100 ml Schlenk tube equipped with a stirring bar 0.25 g (0.43 mmol) $Nb_2Cl_6(SMe_2)_3$ was dissolved in 12 ml of toluene. The solution was filtered into a Schlenk tube which was then carefully covered with a 15 ml hexane solution of benzophenone (0.18 g, 1.00 mmol). Interdiffusion of the two solutions produced a homogeneous crop of needle-like, light-brown crystals (0.05 g, 15% yield). These crystals diffracted poorly and kept on decomposing on the X-ray diffractometer. However, we were able to collect one incomplete and low intensity data set from which using MULTAN 84 program we identified the major structural feature of the compound, the Nb_3O_3 core. Other crystallographic data were: $a = 9.07(7)$, $b = 21.68(1)$, $c = 12.44(1)$ Å, $\beta = 106.89(1)°$.

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TABLE 1. Crystal Data for $[NbCl_3O_2C_{14}H_{12}]_3$

Formula	$Nb_3Cl_9O_6C_{42}H_{36}$
Formula weight	1234.55
Space group	$P2_1/n$
Systematic absences	$h0l$ $h + l = 2n + 1$ $0k0$ $k = 2n + 1$
a Å	12.214(2)
b Å	13.945(2)
c Å	28.845(8)
β (°)	93.23(2)
V (Å^3)	4905(2)
Z	4
D_{calc} (g/cm^3)	1.672
Crystal size (mm)	0.5 × 0.05 × 0.3 (first crystal) 0.6 × 0.05 × 0.3 (second crystal)
μ(Mo Kα) (cm^{-1})	11.969
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
Orientation reflections, no., range (2θ)	25, ($21.30 \leq 2\theta \leq 36.75$)
Temperature (°C)	25
Scan method	ω
Data collection range, 2θ (°)	4, 45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5320, 3961
No. parameters refined	550
Transmission factors, max., min.	0.9996, 0.9424
R[a]	0.04360
R_w[b]	0.05414
Quality-of-fit indicator[c]	1.489
Largest shift/e.s.d., final cycle	0.04
Largest peak (e/Å^3)	0.674
R_{merge}	0.0457

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Preparation of $[NbCl_3O_2C_{14}H_{12}]_3$ *(2)*

In a 100 ml Schlenk flask equipped with a stirring bar, 0.12 g (0.21 mmol) $Nb_2Cl_6(SMe_2)_3$ was dissolved in 10 ml toluene. The solution was filtered into a Schlenk tube which was then layered with a 10 ml hexane solution of 3-methylbenzophenone (0.22 g, 1.12 mmol). Diffusion of reactant layers produced a red/purple powder identified as the trimeric species, $[NbCl_3O_2C_{14}H_{12}]_3$. Yield: 0.045 g, 26.7%. IR (CsI/Nujol) cm^{-1}: 3043(w), 3042(w), 2982(s), 2945(s), 2940(s), 2908(s), 2869(s), 1590(s, br), 1546(s), 1530(s), 1482(s), 1448(s), 1438(s), 1412(m), 1371(s), 1324(s, br), 1294(s), 1280(s, br), 1259(m), 1214(m), 1183(m), 1178(m), 1168(m), 1155(m), 1142(m), 1105(m), 1088(m), 1075(m), 1038(w), 1022(w), 995(s), 958(w), 940(w), 933(w), 865(m, br), 780(m), 725(m, br), 712(m), 690(m), 675(m), 635(s), 615(m), 600(s), 526(s), 492(s), 486(w), 455(w), 446(w), 430(w), 388(s, br), 345(s, br), 303(m), 250(s).

Crystallographic Study

Crystals of $[NbCl_3O_2C_{14}H_{12}]_3$ were grown by a method similar to the one described above. For crystal formation, an additional solvent layer of a 50/50 mixture of toluene and hexane (10 ml total) was placed between the reactant layers. Slow diffusion caused the formation of long needle-shaped crystals.

The geometric and intensity data were gathered with an automated Enraf-Nonius CAD-4 diffractometer, using a crystal mounted in a glass capillary tube with epoxy cement. Routine unit cell identification and intensity data collection procedures have been described previously. Axial photographs of the principal axes were taken to verify lattice dimensions of the monoclinic cell. During data collection, significant loss of intensity (33%) of the three standard reflections warranted the replacement of the crystal with a second one. A total of 136 reflections were remeasured. Empirical absorption corrections based on azimuthal scans of nine reflections were measured for both crystals and applied to the data sets which were then merged using a SHELX program. The final agreement factor between the two sets was 0.0457, with a total of 5320 unique reflections. Lorentz and polarization corrections were also applied prior to merging the data sets. Systematic absences in the intensity data uniquely determined the space group to be $P2_1/n$. The positions of the three independent niobium atoms were found by applying a direct methods program using the Enraf-Nonius Structure Determination package on a VAX-11/780 computer. The remaining non-hydrogen atoms were located by a series of difference maps and least-squares refinements. The methyl group, C(14c)/C(14c′), was disordered between ring carbons C(12c) and C(4c), and was given half occupancy at each site. No attempt was made to locate and refine the hydrogen atoms. Final anisotropic refinement of all atoms converged to $R = 0.04360$ ($R_w = 0.05414$), and the largest peak in the difference Fourier map following refinement was 0.674 e/Å^3. Additional crystallographic parameters for the data collection and structure refinement are given in Table 1, fractional atomic coordinates in Table 2, and relevant bond distances and angles in Tables 3 and 4, respectively. An ORTEP view of $[NbCl_3O_2C_{14}H_{12}]_3$ is shown in Fig. 1, and defines the atomic numbering scheme used in the Tables. The disordered carbon, C(14c)/C(14c′), is depicted in only one orientation in the ORTEP drawing.

Results and Discussion

The preparation of the title compound (as well as its Ph_2CO homolog) was not a designed synthesis. Beginning with a Nb^{III} compound, $Nb_2Cl_6(Me_2S)_3$, we obtained an oxoniobium(V) product, in modest yield. We believe, but cannot prove, that the source of the oxygen is the ketone since we feel that our techniques for excluding moisture and air were adequate to prevent the formation of more than traces of the product if either of those were the source of the oxygen.

Given that the oxidation, and oxygenation, of the Nb^{III} to NbO^{3+} have occurred, by whatever agency, the structure of the product is not surprising except in two ways. First, the formation of discrete trimeric molecules rather than some other more highly polymeric structure is not something that can be casually explained or anticipated. Second, this substance provides a rare example of a structurally characterized ketone complex. We shall return to a discussion of the latter point as soon as the structure has been described in detail.

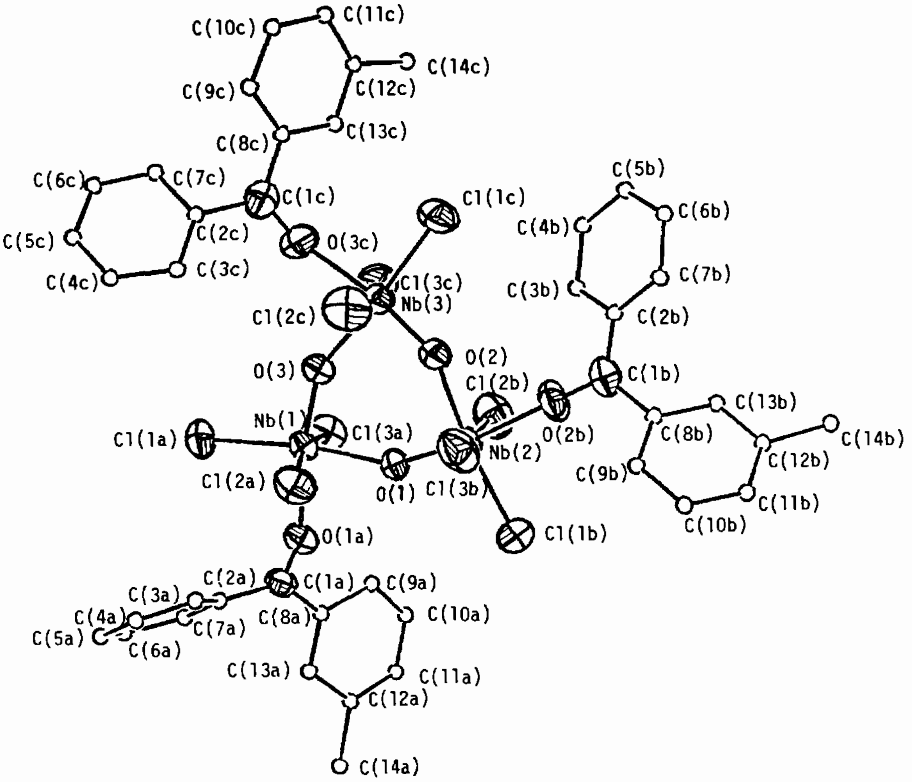

Fig. 1. An ORTEP drawing of the $[NbCl_3O_2C_{14}H_{12}]_3$ molecule which also defines the labeling scheme. The thermal ellipsoids enclose 30% of electron density.

TABLE 2. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters for $[NbCl_3O_2C_{14}H_{12}]_3$

Atom	x	y	z	$B(Å^2)$
Nb(1)	0.48249(6)	0.21888(5)	0.18169(2)	3.66(2)
Nb(2)	0.30397(7)	0.24367(5)	0.07328(3)	4.27(2)
Nb(3)	0.34418(6)	0.00233(5)	0.12894(3)	4.08(2)
Cl(1a)	0.5886(2)	0.1892(2)	0.24921(8)	6.00(6)
Cl(1b)	0.2847(3)	0.3997(2)	0.04513(9)	8.21(8)
Cl(1c)	0.2478(2)	−0.1142(2)	0.08746(9)	6.85(7)
Cl(2a)	0.3342(2)	0.2794(2)	0.21987(8)	5.41(6)
Cl(2b)	0.1450(2)	0.2555(2)	0.11417(9)	6.56(6)
Cl(2c)	0.2098(2)	0.0193(2)	0.1825(1)	6.96(7)
Cl(3a)	0.6302(2)	0.2018(2)	0.13402(8)	5.22(5)
Cl(3b)	0.4355(2)	0.2052(2)	0.02099(9)	6.89(7)
Cl(3c)	0.5096(2)	−0.0304(2)	0.09570(8)	5.74(6)
O(1)	0.3956(4)	0.2656(4)	0.1211(2)	4.0(1)
O(2)	0.3047(4)	0.0999(4)	0.0924(2)	4.3(1)
O(3)	0.4317(4)	0.1014(3)	0.1712(2)	4.1(1)
O(1a)	0.5374(4)	0.3669(4)	0.1835(2)	4.2(1)
O(2b)	0.1916(5)	0.1949(4)	0.0182(2)	5.8(1)
O(3c)	0.4082(5)	−0.1025(4)	0.1794(2)	5.4(1)
C(1a)	0.6025(6)	0.4343(5)	0.1935(3)	3.5(2)
C(2a)	0.6354(6)	0.4516(5)	0.2418(3)	3.7(2)
C(3a)	0.5577(7)	0.4439(6)	0.2753(3)	4.3(2)
C(4a)	0.5863(8)	0.4643(6)	0.3210(3)	5.3(2)
C(5a)	0.6960(8)	0.4850(6)	0.3343(3)	5.7(2)
C(6a)	0.7752(7)	0.4873(6)	0.3018(3)	5.0(2)
C(7a)	0.7456(7)	0.4736(6)	0.2545(3)	4.5(2)
C(8a)	0.6400(7)	0.4931(6)	0.1556(3)	4.5(2)
C(9a)	0.6324(9)	0.4562(7)	0.1095(3)	6.4(3)
C(10a)	0.666(1)	0.5164(8)	0.0739(3)	8.5(3)
C(11a)	0.698(1)	0.6106(8)	0.0834(4)	8.5(3)
C(12a)	0.7016(8)	0.6478(7)	0.1276(3)	6.3(3)
C(13a)	0.6746(7)	0.5882(6)	0.1654(3)	4.9(2)
C(14a)	0.728(1)	0.7551(7)	0.1390(4)	8.4(3)
C(1b)	0.1288(7)	0.1667(6)	−0.0145(3)	4.6(2)
C(2b)	0.1340(7)	0.0681(6)	−0.0303(3)	4.7(2)
C(3b)	0.2342(9)	0.0187(7)	−0.0225(3)	6.0(2)
C(4b)	0.244(1)	−0.0799(7)	−0.0361(3)	7.9(3)
C(5b)	0.150(1)	−0.1228(7)	−0.0564(3)	7.9(3)
C(6b)	0.0514(9)	−0.0760(7)	−0.0648(3)	7.0(3)
C(7b)	0.0412(8)	0.0235(6)	−0.0521(3)	5.6(2)
C(8b)	0.0500(7)	0.2379(6)	−0.0349(3)	5.2(2)
C(9b)	0.0120(8)	0.3107(7)	−0.0061(4)	7.0(3)
C(10b)	−0.0652(9)	0.3778(9)	−0.0257(4)	9.4(4)
C(11b)	−0.0987(9)	0.3698(9)	−0.0728(4)	9.1(3)
C(12b)	−0.0606(8)	0.2976(8)	−0.1018(4)	7.6(3)
C(13b)	0.0142(7)	0.2283(7)	−0.0830(3)	6.1(2)
C(14b)	−0.103(1)	0.279(1)	−0.1541(4)	13.0(5)
C(1c)	0.4303(7)	−0.1744(6)	0.2029(3)	4.4(2)
C(2c)	0.4822(7)	−0.1632(7)	0.2503(3)	5.4(2)
C(3c)	0.4633(9)	−0.0791(8)	0.2738(3)	7.1(3)
C(4c)	0.5211(9)	−0.0766(8)	0.3195(4)	10.1(3)
C(5c)	0.590(1)	−0.150(1)	0.3360(4)	10.6(4)
C(6c)	0.605(1)	−0.230(1)	0.3119(4)	11.1(4)
C(7c)	0.5522(8)	−0.2393(8)	0.2678(3)	8.2(3)
C(8c)	0.4067(7)	−0.2722(6)	0.1833(3)	4.9(2)
C(9c)	0.3736(7)	−0.3458(6)	0.2119(3)	5.2(2)
C(10c)	0.3488(8)	−0.4344(7)	0.1915(4)	7.1(3)
C(11c)	0.3602(8)	−0.4487(7)	0.1447(3)	7.1(3)
C(12c)	0.3937(8)	−0.3735(8)	0.1179(3)	7.2(3)

(continued)

TABLE 2. *(continued)*

Atom	x	y	z	B(Å^2)
C(13c)	0.4189(8)	−0.2833(6)	0.1359(3)	5.5(2)
C(14c)	0.408(2)	−0.373(1)	0.0670(7)	17.9(7)
C(14c′)	0.507(2)	−0.006(2)	0.3450(6)	19.8(8)

[a] e.s.d.s given in parentheses. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. All atoms were refined isotropically.

TABLE 3. Important Bond Distances (Å) for $[NbO_2Cl_3C_{14}H_{12}]_3$[a]

Nb(1)	Cl(1a)	2.319(2)
Nb(1)	Cl(2a)	2.333(2)
Nb(1)	Cl(3a)	2.346(2)
Nb(1)	O(1)	2.099(4)
Nb(1)	O(3)	1.772(4)
Nb(1)	O(1a)	2.170(5)
Nb(2)	Cl(1b)	2.330(2)
Nb(2)	Cl(2b)	2.338(2)
Nb(2)	Cl(3b)	2.331(2)
Nb(2)	O(1)	1.756(4)
Nb(2)	O(2)	2.078(4)
Nb(2)	O(2b)	2.152(5)
Nb(3)	Cl(1c)	2.303(2)
Nb(3)	Cl(2c)	2.333(2)
Nb(3)	Cl(3c)	2.334(2)
Nb(3)	O(2)	1.773(4)
Nb(3)	O(3)	2.097(4)
Nb(3)	O(3c)	2.178(5)
O(1a)	C(1a)	1.254(7)
O(2b)	C(1b)	1.247(8)
O(3c)	C(1c)	1.232(8)
C(1a)	C(2a)	1.451(9)
C(1a)	C(8a)	1.462(9)
C(1b)	C(2b)	1.452(10)
C(1b)	C(8b)	1.482(10)
C(1c)	C(2c)	1.487(9)
C(1c)	C(8c)	1.497(10)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

As can be seen in Fig. 1, the trimeric molecule has an essentially regular structure approximating to three-fold symmetry although no symmetry is imposed crystallographically and rigorously speaking there is none. Each metal atom is surrounded by a distorted octahedral array of three Cl atoms, one doubly-bonded oxygen atom and two =O→ donor oxygen atoms, one from an adjacent Nb=O group and one from a ketone molecule. The Nb–Cl distances range from 2.303 to 2.346 Å but there is no pattern to the variation and the grand average value, 2.330(4) Å, seems to be a meaningful number. The Nb=O bonds are all of equal length, within the errors, ranging only from 1.756 to 1.773 Å, with a mean of 1.767(6) Å. The NbO→Nb bonds are also equal within the e.s.d.s, and have a mean value of 2.091(7) Å.

The bonding of the ketone molecules to the metal atoms varies appreciably from site to site as far as the C=O→Nb angles are concerned. These have values of 155°, 167° and 177°, each of which is individually accurate to within much less than 1°, even at the 3σ level. Most likely this variation in angle is due to the operation of different packing forces at the different sites. The CO→Nb distances are in fact equal within the 3σ criterion, with a mean value of 2.167(8) Å, which is slightly longer, by 0.08(1) Å, than the mean NbO→Nb distance. This may well be due to the fact that they are *trans* to the Nb=O bond. The three C=O distances have an average of 1.24(1) Å, which is not significantly different from that characteristic of ketones in general, *ca.* 1.22 Å.

We have made a serious effort to find in the literature prior examples of reported structures of ketone complexes, but have found only one*. Indeed, there are not many examples of well-defined (even if not structurally defined) solid substances containing simple ketones (as contrasted to *o*-quinones, β-diketonate ions, etc.) coordinated to metal atoms. This is not entirely understandable since as liquids ketones (e.g., acetone) are often quite decent solvents for some metal salts and on Gutmann's donor number (*DN*) scale [6], acetone (*DN* = 17) compares favorably with methanol (*DN* = 20), water (*DN* = 18) and acetonitrile (*DN* = 14) which readily form isolable metal complexes. Presumably the *DN* itself fails to capture the essence of what makes a good ligand a good ligand.

Supplementary Material

Tables of structure factors, anisotropic thermal ellipsoids and complete bond lengths and angles are available on request from author S.A.D.

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*See 'Note added in Proof'. We would be grateful to anyone who can bring any others to our attention.

TABLE 4. Important Bond Angles (°) for $[NbO_2Cl_3C_{14}H_{12}]_3$[a]

Cl(1a)	Nb(1)	Cl(2a)	94.54(8)	Cl(1c)	Nb(3)	Cl(2c)	93.33(9)
Cl(1a)	Nb(1)	Cl(3a)	93.63(8)	Cl(1c)	Nb(3)	Cl(3c)	94.46(8)
Cl(1a)	Nb(1)	O(1)	171.8(1)	Cl(1c)	Nb(3)	O(2)	96.7(2)
Cl(1a)	Nb(1)	O(3)	98.8(2)	Cl(1c)	Nb(3)	O(3)	175.5(1)
Cl(1a)	Nb(1)	O(1a)	89.5(1)	Cl(1c)	Nb(3)	O(3c)	91.7(1)
Cl(2a)	Nb(1)	Cl(3a)	163.68(7)	Cl(2c)	Nb(3)	Cl(3c)	162.33(8)
Cl(2a)	Nb(1)	O(1)	85.0(1)	Cl(2c)	Nb(3)	O(2)	98.0(2)
Cl(2a)	Nb(1)	O(3)	98.1(2)	Cl(2c)	Nb(3)	O(3)	84.3(1)
Cl(2a)	Nb(1)	O(1a)	83.8(1)	Cl(2c)	Nb(3)	O(3c)	82.2(2)
Cl(3a)	Nb(1)	O(1)	85.0(1)	Cl(3c)	Nb(3)	O(2)	96.8(2)
Cl(3a)	Nb(1)	O(3)	94.6(2)	Cl(3c)	Nb(3)	O(3)	86.8(1)
Cl(3a)	Nb(1)	O(1a)	82.1(1)	Cl(3c)	Nb(3)	O(3c)	81.8(2)
O(1)	Nb(1)	O(3)	89.4(2)	O(2)	Nb(3)	O(3)	87.4(2)
O(1)	Nb(1)	O(1a)	82.3(2)	O(2)	Nb(3)	O(3c)	171.6(2)
O(3)	Nb(1)	O(1a)	171.3(2)	O(3)	Nb(3)	O(3c)	84.2(2)
Cl(1b)	Nb(2)	Cl(2b)	92.3(1)	Nb(1)	O(1)	Nb(2)	150.7(2)
Cl(1b)	Nb(2)	Cl(3b)	92.8(1)	Nb(2)	O(2)	Nb(3)	153.5(2)
Cl(1b)	Nb(2)	O(1)	99.2(2)	Nb(1)	O(3)	Nb(3)	150.5(2)
Cl(1b)	Nb(2)	O(2)	172.6(1)	Nb(1)	O(1a)	C(1a)	155.4(4)
Cl(1b)	Nb(2)	O(2b)	89.4(2)	Nb(2)	O(2b)	C(1b)	178.2(5)
Cl(2b)	Nb(2)	Cl(3b)	165.50(8)	Nb(3)	O(3c)	C(1c)	166.9(5)
Cl(2b)	Nb(2)	O(1)	95.8(2)	O(1a)	C(1a)	C(2a)	118.9(6)
Cl(2b)	Nb(2)	O(2)	85.7(1)	O(1a)	C(1a)	C(8a)	118.0(6)
Cl(2b)	Nb(2)	O(2b)	83.2(2)	C(2a)	C(1a)	C(8a)	123.1(6)
Cl(3b)	Nb(2)	O(1)	96.8(2)	O(2b)	C(1b)	C(2b)	120.1(7)
Cl(3b)	Nb(2)	O(2)	87.6(1)	O(2b)	C(1b)	C(8b)	116.7(7)
Cl(3b)	Nb(2)	O(2b)	83.3(2)	C(2b)	C(1b)	C(8b)	123.2(7)
O(1)	Nb(2)	O(2)	88.1(2)	O(3c)	C(1c)	C(2c)	119.5(7)
O(1)	Nb(2)	O(2b)	171.4(2)	O(3c)	C(1c)	C(8c)	120.1(6)
O(2)	Nb(2)	O(2b)	83.4(2)	C(2c)	C(1c)	C(8c)	120.4(7)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

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Note Added in Proof

B. M. Foxman, P. T. Klemarczyk, R. E. Liptrot and M. Rosenblum, *J. Organomet. Chem.*, *187* (1980) 253, report $[CpFe(CO)_2(3\text{-Me-cyclohexenone})]^+$. There is also $SnCl_4$-$(4\text{-t-BuC}_6H_4CHO)_2$ reported by S. E. Denmark, B. R. Henke and E. Weber, *J. Am. Chem. Soc.*, *109* (1987) 2512, but this is an aldehyde complex. Several ester complexes are also structurally characterized.