Preparation and Crystal Structure of Ru₃(μ-Cl)₂(THF)₂(CO)₈ (THF = Tetrahydrofuran)

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Introduction

Triosmium and triruthenium clusters containing weakly-coordinated ligands are valuable starting materials for the preparation of a wide variety of compounds because of the ease with which these ligands can be displaced by another substrate under mild conditions. Two widely-used complexes of this type are Os₃(CO)₁₀(NCCH₃)₂, which was reported by Tachikawa and Shapley[1] in 1977, and the ruthenium analogue, Ru₃(CO)₁₀-(NCCH₃)₂, reported by Foulds, Johnson, and Lewis[2] in 1985. These compounds are moderately stable and give satisfactory elemental analyses but readily lose acetonitrile in the absence of an excess of this ligand. The osmium complex has been characterized crystallographically,[3] but to our knowledge the structure of the ruthenium compound has not yet been examined. Os₃(CO)₁₁(THF) has been generated in solution[4] but has not been isolated.

There are many crystal structures of coordination complexes of transition metals in moderate to high oxidation states that contain solvents such as water, acetonitrile, or tetrahydrofuran coordinated to the metal. However, surprisingly few low-valent organometallic complexes containing loosely-coordinated solvent molecules have been structurally characterized. Tetrahydrofuran is one of the most commonly used solvents for substitution reactions of metal carbonyls, and species in which a carbonyl has been replaced by THF have often been proposed as intermediates, yet very few of these complexes have ever been isolated and characterized crystallographically. Studies of compounds of this type allow comparisons with similar compounds having more strongly-coordinated ligands and can provide new insights into the changes that take place in a transition metal carbonyl cluster framework when ligands are lost to give reactive unsaturated intermediates.

We wish to report the preparation and crystal structure of a new member of this class of compounds in which tetrahydrofuran is coordinated to a triruthenium carbonyl cluster. In the course of preparing a series of mixed-metal complexes containing ruthenium and indium we were able to isolate an appreciable yield of Ru₃(μ-Cl)₂(THF)₂(CO)₈ (THF = tetrahydrofuran) as a stable crystalline material. To our knowledge, this compound represents the only structurally-characterized example of a ruthenium carbonyl complex containing coordinated tetrahydrofuran.

Experimental Section

General Data. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or under argon in a drybox. Ru₃(CO)₁₂[5] and K₂Ru₄(CO)₁₃[6] were prepared according to literature methods. Indium trichloride was obtained from Johnson

Matthey. Solvents were freshly distilled under an atmosphere of dry nitrogen from sodium (hexane, toluene), sodium benzophenone ketyl (tetrahydrofuran), or calcium hydride (dichloromethane) before use. Infrared spectra were routinely obtained on a Pekin-Elmer 1600 Series Fourier-transform spectrophotometer. ¹H NMR spectra were recorded on an IBM AF-200 (200 MHz) Fourier-transform spectrometer and were calibrated relative to the CHCl₃ resonance.

Preparation of Ru₃(μ–Cl)₂(THF)₂(CO)₈. A solution of K₂Ru₄(CO)₁₃ (1.55 g, 1.76 mmol) in dry tetrahydrofuran (25 mL) was transferred via cannula into a flask containing a stirred solution of indium trichloride (0.3892 g, 1.76 mmol) in tetrahydrofuran (30 mL) at –78 °C. The solution was stirred at this temperature for 30 min and then allowed to warm to 24 °C, where it remained for 48 h. During this period the color of the solution gradually changed from dark red to dark brown. Volatile materials were removed under vacuum to give a dark brown tar. To maximize the yield it is important to minimize the exposure of the material to vacuum at this stage. The tar was then washed with hexane (100 mL). Toluene (100 mL) was added to the remaining brown residue to give an orange solution and insoluble brown powder. The orange solution was filtered via cannula to another flask, and the solvent was removed under vacuum. Orange crystals of Ru₃(μ-Cl)₂(THF)₂(CO)₈ were obtained by recrystallization from a tetrahydrofuran–dichloromethane solvent mixture. Yield: 0.24 g (14% based on ruthenium). ¹H NMR spectrum in CDCl₃: 3.755 (m, 4H), 1.848 (m, 4H) ppm. Infrared spectrum (ν_{CO}, tetrahydrofuran): 2105 (m), 2059 (sh), 2033 (s), 2016 (s), 1987 (w), 1938 (s) cm⁻¹. When a small sample of orange crystals of the complex was ground in a mortar under nitrogen with KBr, the sample took on a light green color. Infrared spectrum (ν_{CO}, KBr disk): 2133 (sh), 2103 (m), 2068 (sh), 2051 (sh), 2027 (sh), 2013 (s), 2002 (sh), 1989 (sh), 1938 (s) cm⁻¹. Crystals that were exposed to dynamic vacuum for 64 h turned a dark greenish brown color. Infrared spectrum (ν_{CO}, KBr disk): 2135 (sh), 2103 (m), 2069 (sh), 2053 (sh), 2013 (s), 2002 (sh), 1989 (sh), 1941 (s), 1803 (w) cm⁻¹. Analysis of the sample after exposure to dynamic vacuum for 2 h (see Results) is as follows. Calc for Ru₃-(μ-Cl)₂(THF)(CO)₈(C₁₂H₈Cl₂O₉Ru₃): C, 21.50; H, 1.20. Found: C, 21.82; H, 1.16. When orange crystals of Ru₃(μ-Cl)₂(THF)₂(CO)₈ were stirred for 2 days in CDCl₃, a yellow precipitate formed. This was separated by filtration, dried under vacuum, and redissolved in dry THF to give a yellow solution. Infrared spectrum (ν_{CO}, tetrahydrofuran): 2133 (m), 2105 (w), 2061 (vs), 2032 (s), 2016 (vs), 1996 (sh), 1986 (sh), 1938 (m) cm⁻¹.

X-ray Crystallography. A suitable crystal was sealed in a thin-walled glass capillary under a nitrogen atmosphere. Data collection was performed on a Siemens Model P4 automated diffractometer using Mo Kα radiation. The unit cell parameters were determined and refined by a least-squares fit of 25 reflections. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on ψ-scans were applied. The space group determination was based upon a check of the Laue symmetry and systematic absences present, which narrowed the possibilities to *C2*, *Cm*, or *C2/m*. The choice of *C2/m* was confirmed by the solution of the structure. The structure was determined by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-Ray Instruments, Inc. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogens were not located. Full details for the structure solution and refinement are available in the supplementary material.

Results and Discussion

Preparation of Ru₃(μ-Cl)₂(THF)₂(CO)₈. Although the rich and varied chemistry of triosmium carbonyl complexes is well-known, it is often the case that the ruthenium analogues of these compounds are either nonexistent or more difficult to obtain. The ruthenium–ruthenium bonds tend to be less robust than their osmium counterparts in compounds of this type, and high reaction temperatures are more apt to lead to fragmentation of the cluster. This degradation of the triruthenium framework can be avoided by the preparation of "lightly stabilized"[1] starting materials in which carbonyl groups have been replaced by other weakly-held ligands. These ligands can then in turn be replaced at ambient temperature by some desired substituent. Another strategy that has met with remarkable success is to use ruthenium carbonyl clusters that are activated by halide ligands. Dissociated halides

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.salts are known to catalyze the substitution of carbonyl groups in $Ru_3(CO)_{12}$,[7] and halide ligands in ruthenium clusters can be displaced by protic solvents to allow further substitution.[8] This rapidly expanding field has been developed by Kaesz and Lavigne and has recently been reviewed by them.[9] The title complex, which has coordinated halides and weakly-held tetrahydrofuran ligands, combines features of both synthetic strategies in the same molecule.

The ruthenium complexes $Ru_3(\mu$-$X)_2(CO)_{10}$ (X = Br, I) have been prepared in approximately 30–40% overall yield via reactions of lithium bromide or sodium iodide, respectively, with $Ru_3(CO)_{12}$ to give $Ru_3(\mu$-$H)(\mu$-$X)(CO)_{10}$ (X = Br, I), followed by addition of the appropriate 3-halopropene.[10] We have fortuitously isolated $Ru_3(\mu$-$Cl)_2(THF)_2(CO)_8$, a formal derivative of the chlorine analogue of these dihalo-bridged compounds in which two of the carbonyls have been replaced by coordinated tetrahydrofurans. This complex has been prepared by the reaction of $Ru_3(CO)_{12}$ with potassium to give $K_2Ru_4(CO)_{13}$,[6] which was isolated and subsequently treated with indium trichloride in THF. The formation of $Ru_3(\mu$-$Cl)_2(THF)_2(CO)_8$ in the latter reaction is clearly the result of partial degradation of the tetranuclear cluster.

The primary feature of interest with regard to the reactivity of the title complex is the lability of the tetrahydrofuran ligands. The compound is moderately stable at 25 °C in the absence of any excess of this solvent; however, 1 equiv of THF can be removed by subjecting the compound to dynamic vacuum for 2 h, as evidenced by the elemental analysis results. The solid-state infrared spectra of samples of the material that have been exposed to dynamic vacuum for varying periods of time show the presence of additional peaks, and there is an accompanying color change from orange to greenish brown. The loss of THF ligands is reversible, and the complex can be regenerated by redissolving the residue in tetrahydrofuran. Although we do not have sufficient information to determine the identity of the compound formed upon loss of THF ligands, it is interesting to note that the loss of carbonyls from similar complexes can cause halide atoms to shift from doubly-bridging to triply-bridging positions. This has been observed for the conversion of $Ru_3(\mu$-$H)(\mu$-$I)(CO)_{10}$ to Ru_3-$(\mu$-$H)(\mu_3$-$I)(CO)_9$[10,11] and $[PPN][Ru_3(\mu$-$Cl)(CO)_{10}]$ to $[PPN]$-$[Ru_3(\mu_3$-$Cl)(CO)_9]$.[8]

The NMR spectrum of the complex in deuterochloroform shows resonances at 3.755 and 1.848 ppm that are shifted slightly downfield from the resonances that we observe at 3.647 and 1.757 ppm for free tetrahydrofuran in $CDCl_3$. Over a period of several hours the solution of the complex in $CDCl_3$ forms a yellow precipitate, and the infrared spectrum of this material when it is redissolved in tetrahydrofuran is substantially different from that of the original THF complex.

Crystal Structure of $Ru_3(\mu$-$Cl)_2(THF)_2(CO)_8$. Crystal data are given in Table I, atomic coordinates can be found in Table II, and lists of bond distances and angles are given in Tables III and IV, respectively. An ORTEP[12] diagram of the nondisordered molecule with 50% probability ellipsoids is shown in Figure 1.

The complex crystallizes in the centrosymmetric monoclinic space group $C2/m$ (No. 12). The asymmetric unit contains halves of each of two molecules that lie on the crystallographic mirror plane at x, 0, z. In both molecules the mirror is perpendicular to the Ru_3 plane and passes through the two chlorines and the

Table I. Crystallographic Data for $Ru_3(\mu$-$Cl)_2(THF)_2(CO)_8$

chem formula	$C_{16}H_{16}Cl_2O_{10}Ru_3$	Z	8
fw	742.42	temp, °C	23
space group	monoclinic, $C2/m$ (No. 12)	λ, Å (Mo Kα)	0.710 73
a, Å	16.518(4)	ρ(calc), g cm^{-3}	2.014
b, Å	19.332(2)	μ(Mo Kα), cm^{-1}	20.89
c, Å	17.363(2)	transm coeff	0.5598–1.0000
β, deg	117.99(1)	R^a	0.0409
V, Å^3	4895.9(14)	$R_w{}^b$	0.0598

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for $Ru_3(\mu$-$Cl)_2(THF)_2(CO)_8$

	x	y	z	U(eq)^a
Ru(1)	3640(1)	0	5778(1)	56(1)
Ru(2)	2125(1)	820(1)	4840(1)	54(1)
Cl(1)	1651(2)	0	3609(2)	58(1)
Cl(2)	1278(2)	0	5292(2)	60(1)
O(2)	723(3)	1354(3)	4011(4)	76(3)
O(11)	5020(5)	−1151(4)	6637(6)	121(5)
O(12)	3079(6)	0	7224(6)	115(6)
O(13)	3900(6)	0	4150(7)	107(6)
O(21)	3256(5)	1683(4)	4288(5)	105(4)
O(22)	2820(5)	1713(4)	6421(5)	114(4)
C(1)	610(6)	2094(4)	4027(8)	93(6)
C(2)	−429(7)	2216(6)	3444(9)	120(7)
C(3)	−846(6)	1517(6)	3300(9)	115(6)
C(4)	−152(6)	1013(5)	3505(8)	102(5)
C(11)	4500(5)	−730(5)	6324(6)	74(4)
C(12)	3273(8)	0	6686(8)	75(6)
C(13)	3766(8)	0	4730(8)	76(6)
C(21)	2817(6)	1357(4)	4488(6)	75(4)
C(22)	2521(5)	1385(5)	5800(6)	75(4)
Ru(3)	3298(1)	0	−237(1)	52(1)
Ru(4)	2500(1)	817(1)	528(1)	56(1)
Cl(3)	3093(2)	0	1762(2)	66(1)
Cl(4)	1200(2)	0	−97(2)	70(1)
O(4)	1722(5)	1324(3)	1171(5)	89(4)
O(31)	3981(6)	−1194(4)	−924(6)	121(5)
O(32)	4968(6)	0	1550(6)	100(5)
O(33)	1461(7)	0	−1913(7)	107(5)
O(41)	1804(5)	1744(4)	−1013(5)	110(4)
O(42)	4157(5)	1698(4)	1291(5)	105(4)
C(5)	1280(19)	992(10)	1596(19)	108(16)
C(6)	816(26)	1532(16)	1876(30)	122(21)
C(7)	1326(31)	2149(12)	1891(29)	118(21)
C(8)	1702(19)	2034(8)	1281(19)	115(18)
C(51)	820(27)	1248(41)	896(31)	344(40)
C(61)	597(40)	1899(38)	1294(26)	156(29)
C(71)	1251(75)	1588(64)	2082(77)	349(95)
C(81)	2132(25)	1527(38)	2022(36)	276(42)
C(31)	3726(6)	−750(5)	−680(6)	77(5)
C(32)	4327(7)	0	904(8)	67(5)
C(33)	2122(8)	0	−1273(7)	69(5)
C(41)	2042(6)	1381(5)	−444(7)	76(5)
C(42)	3521(6)	1361(4)	1019(6)	68(4)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ruthenium and two carbonyls of the $Ru(CO)_4$ unit. As a consequence, each chlorine forms a symmetrical bridge with crystallographically identical Ru–Cl bond lengths. The average length of 2.470(2) Å for the four unique Ru–Cl bonds in the two molecules is virtually the same as the average value of 2.467(3) Å observed in the related complex $Ru_3(\mu$-$Cl)_2(PPh_3)_2(CO)_8$.[13] The latter cluster has the same overall geometry as the title compound, with phosphine ligands in place of the tetrahydrofurans. Likewise, the average Ru–C distances of 1.839(11) and 1.816(12) Å for the carbonyl groups trans to chlorine in the two compounds are also nearly the same; however, the Ru–Ru separations of 3.171(1) and 3.158(1) Å between the chloro-bridged

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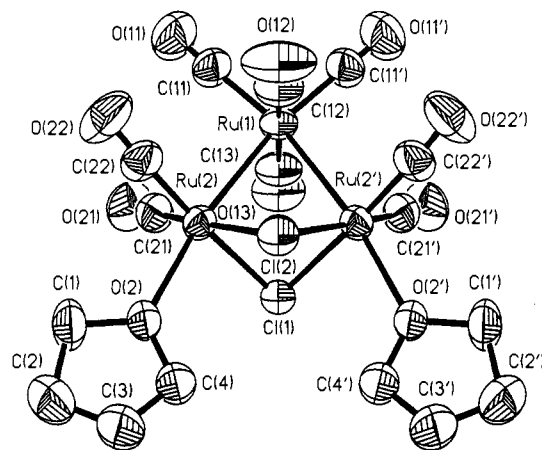(13) Bonnet, J.-J.; Lavigne, G.; Papageorgiou, F. *J. Crystallogr. Spectrosc. Res.* **1986**, *16*, 475.

Table III. Unique Bond Distances (Å) for Ru₃(μ-Cl)₂(THF)₂(CO)₈

Ru(1)–Ru(2)	2.757(1)	Ru(1)–C(11)	1.909(8)
Ru(1)–C(12)	1.937(17)	Ru(1)–C(13)	1.927(16)
Ru(2)–Ru(2′)	3.171(1)	Ru(2)–Cl(1)	2.474(2)
Ru(2)–Cl(2)	2.474(3)	Ru(2)–O(2)	2.317(5)
Ru(2)–C(21)	1.846(11)	Ru(2)–C(22)	1.837(10)
O(11)–C(11)	1.121(11)	O(12)–C(12)	1.120(20)
O(13)–C(13)	1.129(21)	O(21)–C(21)	1.132(14)
O(22)–C(22)	1.145(12)	O(2)–C(1)	1.445(10)
O(2)–C(4)	1.450(10)	C(1)–C(2)	1.548(13)
C(2)–C(3)	1.484(16)	C(3)–C(4)	1.417(14)
Ru(3)–Ru(4)	2.764(1)	Ru(3)–C(31)	1.926(11)
Ru(3)–C(32)	1.913(10)	Ru(3)–C(33)	1.930(10)
Ru(4)–Cl(3)	2.464(2)	Ru(4)–Cl(4)	2.469(2)
Ru(4)–O(4)	2.281(10)	Ru(4)–C(41)	1.847(10)
Ru(4)–C(42)	1.824(8)	Ru(4)–Ru(4′)	3.158(1)
O(31)–C(31)	1.121(14)	O(32)–C(32)	1.123(12)
O(33)–C(33)	1.135(12)	O(41)–C(41)	1.122(13)
O(42)–C(42)	1.134(11)	O(4)–C(5)	1.413(37)
O(4)–C(8)	1.389(18)	C(5)–C(6)	1.503(55)
C(6)–C(7)	1.454(52)	C(7)–C(8)	1.474(71)
O(4)–C(51)	1.342(44)	O(4)–C(81)	1.362(57)
C(51)–C(61)	1.561(102)	C(61)–C(71)	1.418(111)
C(71)–C(81)	1.512(149)		

Table IV. Unique Bond Angles (deg) for Ru₃(μ-Cl)₂(THF)₂(CO)₈

Ru(2)–Ru(1)–C(11)	97.2(2)	Ru(2)–Ru(1)–C(11′)	167.4(2)
Ru(2)–Ru(1)–C(12)	86.4(2)	Ru(2)–Ru(1)–C(13)	85.0(3)
C(11)–Ru(1)–C(12)	92.3(4)	C(11)–Ru(1)–C(13)	94.8(4)
C(12)–Ru(1)–C(13)	169.4(4)	Ru(2)–Ru(1)–Ru(2′)	70.2(1)
C(11)–Ru(1)–C(11′)	95.3(5)	Ru(1)–Ru(2)–Cl(1)	88.5(1)
Ru(1)–Ru(2)–Cl(2)	86.3(1)	Cl(1)–Ru(2)–Cl(2)	82.3(1)
Ru(1)–Ru(2)–O(2)	171.2(1)	Cl(1)–Ru(2)–O(2)	86.0(2)
Cl(2)–Ru(2)–O(2)	86.2(2)	Ru(1)–Ru(2)–C(21)	89.3(3)
Cl(1)–Ru(2)–C(21)	93.9(3)	Cl(2)–Ru(2)–C(21)	174.3(3)
O(2)–Ru(2)–C(21)	97.9(3)	Ru(1)–Ru(2)–C(22)	88.1(2)
Cl(1)–Ru(2)–C(22)	176.3(3)	Cl(2)–Ru(2)–C(22)	96.0(3)
O(2)–Ru(2)–C(22)	97.2(3)	C(21)–Ru(2)–C(22)	87.4(4)
Ru(2)–Cl(1)–Ru(2′)	79.7(1)	Ru(2)–Cl(2)–Ru(2′)	79.7(1)
Ru(2)–O(2)–C(1)	122.0(4)	Ru(2)–O(2)–C(4)	126.5(5)
C(1)–O(2)–C(4)	111.2(6)	O(2)–C(1)–C(2)	104.6(7)
C(1)–C(2)–C(3)	104.8(8)	C(2)–C(3)–C(4)	109.1(9)
O(2)–C(4)–C(3)	107.4(8)	Ru(1)–C(11)–O(11)	178.2(10)
Ru(1)–C(12)–O(12)	178.6(9)	Ru(1)–C(13)–O(13)	175.5(9)
Ru(2)–C(21)–O(21)	178.6(7)	Ru(2)–C(22)–O(22)	175.6(7)
Ru(4)–Ru(3)–C(31)	165.9(3)	Ru(4)–Ru(3)–C(32)	84.0(4)
Ru(4)–Ru(3)–C(33)	87.1(4)	C(31)–Ru(3)–C(32)	95.7(4)
C(31)–Ru(3)–C(33)	91.4(4)	C(32)–Ru(3)–C(33)	169.1(7)
Ru(4)–Ru(3)–Ru(4′)	69.7(1)	C(31)–Ru(3)–Ru(4′)	96.3(3)
C(31)–Ru(3)–C(31′)	97.7(7)	Ru(3)–Ru(4)–Cl(3)	88.1(1)
Ru(3)–Ru(4)–Cl(4)	86.3(1)	Cl(3)–Ru(4)–Cl(4)	83.2(1)
Ru(3)–Ru(4)–O(4)	170.4(2)	Cl(3)–Ru(4)–O(4)	86.3(2)
Cl(4)–Ru(4)–O(4)	85.3(2)	Ru(3)–Ru(4)–C(41)	88.9(4)
Cl(3)–Ru(4)–C(41)	176.3(3)	Cl(4)–Ru(4)–C(41)	94.4(3)
O(4)–Ru(4)–C(41)	96.3(4)	Ru(3)–Ru(4)–C(42)	90.5(3)
Cl(3)–Ru(4)–C(42)	93.5(3)	Cl(4)–Ru(4)–C(42)	175.4(3)
O(4)–Ru(4)–C(42)	97.7(4)	C(41)–Ru(4)–C(42)	88.8(4)
Ru(4)–Cl(3)–Ru(4′)	79.7(1)	Ru(4)–Cl(4)–Ru(4′)	79.5(1)
Ru(4)–O(4)–C(5)	127.4(10)	Ru(4)–O(4)–C(8)	123.2(17)
C(5)–O(4)–C(8)	109.0(20)	Ru(4)–O(4)–C(51)	124.4(28)
Ru(4)–O(4)–C(81)	123.2(22)	C(51)–O(4)–C(81)	108.7(33)
O(4)–C(5)–C(6)	108.6(22)	C(5)–C(6)–C(7)	101.4(40)
C(6)–C(7)–C(8)	107.4(32)	O(4)–C(8)–C(7)	107.1(22)
O(4)–C(51)–C(61)	102.0(46)	C(51)–C(61)–C(71)	81.6(68)
C(61)–C(71)–C(81)	106.8(105)	O(4)–C(81)–C(71)	95.3(50)
Ru(3)–C(31)–O(31)	178.6(9)	Ru(3)–C(32)–O(32)	175.6(14)
Ru(3)–C(33)–O(33)	175.6(14)	Ru(4)–C(41)–O(41)	176.4(8)
Ru(4)–C(42)–O(42)	177.1(10)		

Figure 1. ORTEP drawing of Ru₃(μ-Cl)₂(THF)₂(CO)₈.

tends to correlate with the size of the bridging atom; however, the observed difference between Ru₃(μ-Cl)₂(THF)₂(CO)₈ and Ru₃(μ-Cl)₂(PPh₃)₂(CO)₈, both of which have chlorine bridges, suggests that other ligands on the ruthenium atoms may also play a role. Several relevant comparisons can also be made to the crystal structure of the related complex Ru₃(μ-I)₂(CO)₁₀.[10] This compound exhibits a greater separation of 3.301(1) Å between the iodo-bridged rutheniums, as would be expected from the larger size of iodine relative to chlorine and the lack of a metal–metal bond. The observed shortening of the Ru–C bonds, relative to the other Ru–C bonds in the complex, that was observed for Ru₃(μ-I)₂(CO)₁₀ in positions trans to the halogens is apparent to an even greater extent in Ru₃(μ-Cl)₂(THF)₂(CO)₈ and Ru₃(μ-Cl)₂(PPh₃)₂(CO)₈.

The tetrahydrofuran ligands in Ru₃(μ-Cl)₂(THF)₂(CO)₈ are coordinated to the two chloro-bridged rutheniums in positions trans to the ruthenium–ruthenium bonds. These positions were also adopted by the phosphines in Ru₃(μ-Cl)₂(PPh₃)₂(CO)₈, and this stereochemistry has been shown to be favored for double-bridged triruthenium carbonyl clusters.[15] This arrangement is in contrast to that of the acetonitrile ligands in Os₃(CO)₁₀-(NCCH₃)₂, which are in positions that are cis to the osmium–osmium bonds and perpendicular to the Os₃ plane.[3] The ruthenium–oxygen distances of 2.317(5) and 2.281(10) Å are comparable to the value of 2.268(6) Å observed in Ru₂(μ-O₂-CCF₃)₄(THF)₂.[16] The least-squares plane through the THF ring is oriented such that it is nearly coincident with the Ru₃ plane and bisects the Cl–Ru–Cl and C–Ru–C angles of the ruthenium to which it is attached. This orientation is common to both molecules of the complex; however, in one molecule there is a disorder in the THF coordination such that there is a second position in which the THF plane is roughly perpendicular to the Ru₃ plane. For the "parallel" orientation, the dihedral angle between the THF plane and the Ru₃ plane is 9.2° in one molecule and 6.9° in the other. The dihedral angle for the "perpendicular" orientation is 93.6°. The THF oxygens have planar geometries in all of the configurations, with the sum of the angles between the three substituents equal to 359.7° in the ordered complex and values of 359.6 and 356.3° for the two disordered positions in the other. Another parameter that can be used to describe the coordination of the THF ring can be obtained by calculating the coordinates of the ring centroid and examining the Ru–O–(centroid) angle. This results in values of 173.1° for the ordered complex and 175.3 and 173.6° for the parallel and perpendicular orientations in the disordered complex. This "linear" orientation of the ring centroid relative to the metal–oxygen bond, with trigonal planar geometry for the oxygen, is not what would be

rutheniums in the two molecules of the THF complex are somewhat shorter than the corresponding distance of 3.254(1) Å in the phosphine compound. Formal electron-counting procedures for both complexes give 18-electron counts for these rutheniums in the absence of a metal–metal bond between them.[14] It has been noted previously[13] that in comparisons of similar complexes with other bridging groups the magnitude of the Ru–Ru separation

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predicted by a simple model involving coordination of a single lone pair of electrons from an sp³-hybridized oxygen to give a "bent" alignment of the ring centroid with an ammonia-like trigonal pyramidal geometry at oxygen. However, the orientation observed here is common to other transition metal carbonyl complexes of THF such as $Cr(CO)_5(THF)$[17] and $[Mn(\mu\text{-}Cl)(CO)_3(THF)]_2$.[18] In these compounds the oxygen of the THF is planar and the ring is oriented in a linear fashion relative to the metal–oxygen bond, with the plane of the ring adopting a staggered conformation relative to the four ligands in the cis positions on the octahedrally-coordinated metal. It is interesting to note that there are cases in which tetrahydrofuran is coordinated to a p-block metal in a bent configuration. In the crystal structure of $InCl_3(THF)_2$[19] the sum of the angles about oxygen is 351.2-(7)°, and the In–O–(centroid) angle is 155.8°.

The trans influence exerted by the THF ligands on the Ru–Ru bonds is the most noticeable structural effect observed in $Ru_3(\mu\text{-}Cl)_2(THF)_2(CO)_8$. The two Ru–Ru bond lengths in each

molecule are required by crystallographic symmetry to be identical, with observed values of 2.757(1) Å for the two Ru–Ru bonds in one molecule and 2.764(1) Å for the same bonds in the other. The average value of 2.761 Å is nearly 0.1 Å shorter than the corresponding average lengths of 2.852(1) Å found for $Ru_3(\mu\text{-}Cl)_2(PPh_3)_2(CO)_8$[13] and 2.864(2) Å found for $Ru_3(\mu\text{-}I)_2(CO)_{10}$.[10] This shortening of the metal–metal bonds may be indicative of a strengthening of the cluster framework, which, together with the lability of the THF lignads, indicates that the title complex may prove useful in the synthesis of new triruthenium carbonyl clusters.

Supplementary Material Available: Tables giving full details of the crystal data, data collection, and structure solution parameters (Table S1) and anisotropic thermal parameters (Table S2) (4 pages). Ordering information is given on any current masthead page.

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