Inorg. Chem. **1995,** *34,* 4253–4255

Structure of Crystalline (C_5Me_5)ReO_3 and Implied Nonexistence of “(C_5Me_5)Tc_2O_3”

Anthony K. Burrell,[†] F. Albert Cotton,*,[‡] Lee M. Daniels,[‡] and Vaclav Petricek[§]

Department of Chemistry, Massey University, Palmerston North, New Zealand, Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843-3255, and Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 00 Prague 6, Czech Republic

Received November 4, 1994[⊗]

The crystal structure of (C_5Me_5)ReO_3 has been solved and refined, despite the fact that the crystals exhibit both twinning and disorder phenomena. The crystals are monoclinic pseudomerohedral twins, made possible because the unique angle ≅ 90° in space group $P2_1/m$ (*c*-axis unique). The metal atom is disordered over two positions, and the crystals are twinned about the [100] plane. The unit cell has the dimensions $a = 5.9330(5)$ Å, $b = 8.672(1)$ Å, $c = 10.590(2)$ Å, $\gamma = 90.01(1)°$, $V = 544.9(1)$ Å^3, and $Z = 2$. The individual molecules of (C_5Me_5)ReO_3 are effectively identical to those previously reported for (C_5Me_4Et)ReO_3 except for the replacement of one Me by Et. All hydrogen atoms were located, and those not disordered about the mirror plane were refined independently. The final residuals are R1 (on F_o) = 0.0257 and wR2 (on F_o^2) = 0.0616, using all data. It is clear that the previously reported compound (C_5Me_5)Tc_2O_3 does not exist. The reported structure, which contains several patently unbelievable features, is shown to be an artifact. It will also be shown that it is extremely unlikely that (C_5Me_5)TcO_3 exists either.

Introduction

A little more than 10 years ago the compound (C_5Me_5)ReO_3 was first reported by two groups[1,2] independently. Both of these groups found it impossible to characterize the compound by X-ray crystallography since the crystals appeared to be twinned.[1,3] One group turned to the (C_5Me_4Et)ReO_3 analog, which formed amenable crystals, in order to acquire metrical structural data on this type of compound.[3] The question of how to solve the structure of Cp*ReO_3 (Cp* = C_5Me_5) appears to have been left in abeyance, although many publications have appeared concerning the chemistry of this particular compound.

We have reexamined the problem of solving the (C_5Me_5)ReO_3 structure correctly for the following reason. The X-ray data that it gives show that it is “isomorphous” with a compound reported to be (C_5Me_5)Tc_2O_3.[4] Since the chemistry of (C_5Me_5)ReO_3, which is extensive,[1,2,5] leaves no doubt that it really is (C_5Me_5)ReO_3 and certainly not “(C_5Me_5)Re_2O_3”, it seemed worth some trouble to demonstrate that the same conclusion could be reached crystallographically. We were not unmindful of the fact that the resolution of the crystallographic problem caused by the twinning of (C_5Me_5)ReO_3 crystals would effectively dispose of the incredible structure reported for “(C_5Me_5)Tc_2O_3”.

Experimental Section

The compound (C_5Me_5)ReO_3 was prepared by a literature method[5e] and purified by silica-gel chromatography.[4] Crystals were grown by slow evaporation of the benzene/diethyl ether eluant.

A representative crystal, selected from a homogeneous crystalline sample, was mounted on a glass fiber and examined at room temperature on an Enraf-Nonius CAD4 diffractometer. The cell dimensions were determined in the usual way and were found to be, as expected, essentially equal to those reported for “(C_5Me_5)Tc_2O_3”. The axial lengths were verified by normal-beam oscillation photographs, but a striking feature in the photographs gave a preliminary indication that the solution and refinement might not be straightforward. In the photograph of the *a* axis, the lower-angle reflections in the $h = 1$ and $h = 2$ layer lines were severely streaked along the layer line. The streaks were also apparent in the photographs of axes *b* and *c*, perpendicular to the layer lines. The effect indicates that while the repeat distance along the *a* direction is regular throughout the crystal, the repeat in either or both of the *b* and *c* directions varies randomly as multiples of the base *b* and *c* distances. A substantial disorder was therefore expected.

A full hemisphere of data was collected using $\omega-\theta$ scans. The scan widths and 1:1 ratio of ω to 2θ movement were determined by making ω vs θ contour plots of several reflections using the Enraf-Nonius OTPLOT routine.

The only systematic absence found was that for $00l$ ($l = 2n + 1$). The condition $h0l$, $h + l = 2n + 1$ was strongly violated, thereby excluding the space group *Pmnm* as was reported for the Tc compound.

The symmetry of the Patterson map was consistent with either an orthorhombic symmetry or a monoclinic symmetry with all angles equal to 90° and a twinning operation mirror perpendicular to the *a* direction (twinning by pseudomerohedry). In the twinned monoclinic case, the space group is $P2_1/m$ (*c*-axis unique). The Patterson map indicated a heavy-atom position at (0.089, 0.223, 0.250) and the related position at (0.411, 0.223, 0.250), separated by about 1.8 Å. The two heavy atoms were no longer related by symmetry (as was reported for the Tc case); therefore it was possible to refine the relative occupancy of the two disordered Re positions without consideration of any twinning operation. The ratio of the two Re atom occupancies refined to about 60:40. Note that if the ratio were exactly 50:50, the additional symmetry of space group *Pmnm* would indeed be present. One crucial difference between this model and the one for the Tc compound is that the Tc position was reported to be fully occupied (vide infra). A subsequent Fourier synthesis revealed all of the C and O atoms, making it apparent that the alternating, parallel planes of Cp* groups and O_3

---

* Address correspondence to this author.

[†] Massey University.

[‡] Texas A&M University.

[§] Academy of Sciences of the Czech Republic.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) Hugo Klahn-Oliva, A.; Sutton, D. *Organometallics* **1984,** *3,* 1313.

(2) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 383.

(3) Okuda, J.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1988,** *27,* 1254.

(4) Kanellakopulos, B.; Nuber, B.; Raptis, K.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1055.

(5) (a) Herrmann, W. A.; Serrano, R.; Schäfer, A.; Küsthardt, U. *J. Organomet. Chem.* **1984,** *272,* 55. (b) Herrmann, W. A.; Voss, E.; Flöel, M. *J. Organomet. Chem.* **1985,** *297,* C5. (c) Herrmann, W. A. *J. Organomet. Chem.* **1986,** *300,* 111. (d) Herrmann, W. A.; Okuda, J. *J. Mol. Catal.* **1987,** *41,* 109. (e) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Külpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987,** *6,* 1165. (f) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1297.

0020-1669/95/1334-4253$09.00/0

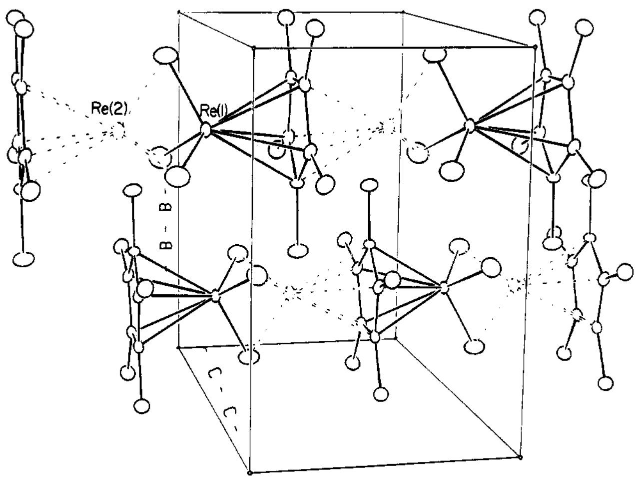

Figure 1. Representation of the disordered model of Cp*ReO_3 and its packing mode. In the final model, the oxygen atoms are not "shared" by the two metal positions as shown here but instead are very slightly separated into two distinct groups.

groups dominate the packing in the crystal. The disorder arises because the distance between the plane of the Cp* group and plane of the O_3 group in one molecule is almost exactly the same as the distance between those groups in adjacent molecules. The situation is indicated in Figure 1, where it is seen that the "piano stools" can have two different orientations depending on whether Re(1) or Re(2) is occupied. It is important to note that, although there are two possible positions for Re in the "chain" of Cp*ReO_3...Cp*ReO_3 along the *a* direction, for a given "chain" only one of the positions is occupied. Therefore the repeat distance in the *a* direction is constant, as evidenced by the axial photographs. The actual disorder arises because of the two different ways the chains can pack together, as evidenced by the streaks along *b* and *c* in the axial photographs.

At this point in the refinement, all of the non-hydrogen atoms were accounted for, but the value of wR2 could not be reduced below about 0.25 (in contrast to an R_{merge} value of 0.0325). The refinement was hampered by severe correlation, and it was not possible to include ansiotropic displacement parameters, so the suspected twinning operation was taken into consideration (about the [100] plane), beginning with the assumption that each twin domain contributed to 50% of each F_o^2. The calculated values of F^2 were now made up of the sum of the F_c^2 values of the individual twin domains, each multiplied by its fractional contribution; i.e. $F_c^2 = k{\cdot}F_c(1)^2 + (1 - k){\cdot}F_c(2)^2$. This method allows the fractional contribution of each twin domain to be included as a refined parameter. This treatment led to a dramatic decrease in the residuals (wR2 below 0.10) and allowed a straightforward completion of the refinement, including anisotropic displacement factors and hydrogen atoms. It should be noted that only when both the disorder **and** the twinning were properly handled could the structure be satisfactorily refined.

When all of the non-hydrogen atoms had been refined with anisotropic displacement parameters, peaks corresponding to the hydrogen atom positions appeared in a difference Fourier map. The hydrogen atoms on the carbon atoms C(11) and C(22) were allowed to refine independently; the hydrogen atoms on C(33) were disordered about the mirror plane passing through the methyl group, and so were included in positions based on a difference electron density synthesis calculated around the circle which represents the loci of possible hydrogen positions. The displacement ellipsoids for the Re and C atoms were reasonable, but those of the O atoms were elongated in the *x* direction (a feature also present in the published Tc structure and indicated in Figure 1). Also the Re−O distances (average 1.83 Å) were longer and the O−Re−O angles (average 96.3°) more acute than those for known complexes containing the *fac*-ReO_3 unit (average 1.72 Å and 106°).[3] These observations suggested that the oxygen positions for the two disordered molecules were not fully overlapped and should be refined independently. In doing so, a similarity restraint was applied to the two independent ReO_3 subunits. The oxygen atoms thus associated with atom Re(2) are indicated as O(1′) and O(2′). The displacement parameters for the oxygen atoms in this final model were now compatible with the rest of the model, and the resulting refined geometries of the ReO_3 units (average Re−O = 1.74(1) Å, average O−Re−O = 105(2)°) are in excellent accord with other such structures containing the same moiety. The final refined occupancy of the major orientation of the molecular unit was 0.616(2), and the twin domain ratio refined to 0.573(2):0.427(2). We were concerned about possible correlation between the disorder ratio and the twin domain ratio, but the least-squares program indicated that the correlation coefficient between these two parameters was less than 0.10. Cases in which a twinning operation is so dramatically combined with disorder are rare and obviously require additional care during refinement.

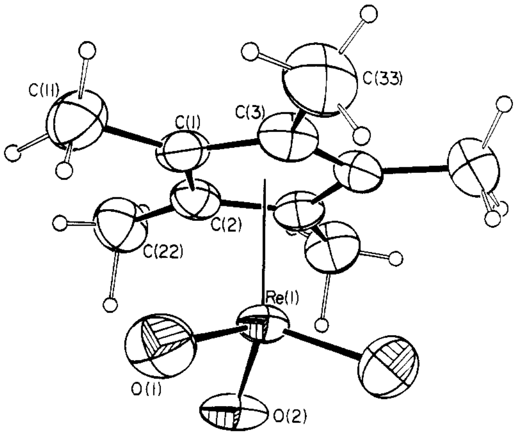

Figure 2. ORTEP drawing of one of the two disordered orientations of Cp*ReO_3. Atoms Re, O(2), C(3), and C(33) lie on a mirror plane; only one of the two orientations of the hydrogen atoms on C(33) is indicated.

Table 1. Crystal Data for Cp*ReO_3

formula	$ReO_3C_{10}H_{15}$
fw	369.42
space group	$P2_1/m$
a, Å	5.9330(5)
b, Å	8.672(1)
c, Å	10.590(2)
γ, deg	90.01(1)
V, Å^3	544.9(1)
Z	2
d_{calcd}, g/cm^3	2.25
μ(Mo Kα), cm^{-1}	111.3
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)
temp, °C	22(1)
transm factors: max, min	0.9977, 0.6285
no. of data/restraints/parameters	1011/15/118
R indices [$I > 2\sigma(I)$][a,b]	R1 = 0.025, wR2 = 0.061
R indices (all data)	R1 = 0.029, wR2 = 0.073

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.616P]$, where $P = (F_o^2 + 2F_c^2)/3$.

The refinement calculations were performed with the SHELXL-93 program[6] running on a DEC 3000-800 AXP workstation. A drawing of the final refined model is shown in Figure 2. A summary of data collection and structure refinement parameters is given in Table 1. Table 2 contains the final refined atomic coordinates, and Table 3 lists major bond distances and angles.

Discussion

The (C_5Me_5)ReO_3 Structure. Clearly, when the modes of both the twinning and disorder that occur in crystals of (C_5Me_5)ReO_3 are recognized and taken into account, the correct molecular structure is obtained and can be refined to normal contemporary standards of accuracy. *Just as clearly*, if the occurrence of these phenomena is overlooked, the data for (C_5-

---

(6) Sheldrick, G. M. SHELXL-93. Institut für Anorganische Chemie, Göttingen, Germany, 1993.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for Cp*ReO_3

	x	y	z	U_{eq}[a]
Re(1)	919(1)	2239(1)	2500	34(1)
O(1)	2047(23)	3097(17)	3849(14)	62(4)
O(2)	2086(31)	416(17)	2500	57(5)
Re(2)	4087(2)	2239(1)	2500	41(1)
O(1′)	2771(55)	3227(34)	3713(29)	97(11)
O(2′)	2948(53)	421(23)	2500	55(8)
C(1)	−2527(12)	2629(6)	1406(4)	40(1)
C(11)	−2566(19)	3169(8)	75(6)	59(2)
C(2)	−2465(13)	1071(5)	1822(5)	39(1)
C(22)	−2535(20)	−359(7)	1054(7)	56(1)
C(3)	−2462(24)	3588(7)	2500	39(2)
C(33)	−2550(34)	5315(9)	2500	67(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Cp*ReO_3[a]

	Distances		
Re(1)−O(1)	1.744(1)	Re(2)−O(1′)	1.73(2)
Re(1)−O(2)	1.73(1)	Re(2)−O(2′)	1.71(2)
Re(1)−C(1)	2.374(6)	Re(2)−C(1)$^{\rm i}$	2.343(7)
Re(1)−C(2)	2.361(7)	Re(2)−C(2)$^{\rm i}$	2.393(7)
Re(1)−C(3)	2.32(1)	Re(2)−C(3)$^{\rm i}$	2.36(1)
	Angles		
O(1)−Re(1)−O(2)	103.7(6)	O(1′)−Re(2)−O(1′)$^{\rm ii}$	96(3)
O(1)−Re(1)−O(1)$^{\rm ii}$	110(1)	O(2′)−Re(2)−O(1′)	106(1)

[a] Symmetry transformations used to generate equivalent atoms: (i) $x + 1, y, z$; (ii) $x, y, -z + {}^1/_2$.

Me$_5$)ReO_3 *could* lead to a structure analogous to that reported for "(C_5Me_5)Tc_2O_3." We have actually carried through a refinement of the "(C_5Me_5)Re_2O_3" model, and find that it works, although the thermal displacement factors for the rhenium atoms become unrealistically large. It should also be pointed out that when this untenable model (in space group *Pmnm*) is adopted for *either* the rhenium or the technetium case, the resulting structures have mean atomic volumes of only about 9 Å^3 per atom. This result is so ludicrous that, by itself, it shows that such a model is unacceptable, for either compound. (The atomic volume of Tc in the metal is 15.3 Å^3.)

There probably exists an interdependence between the disorder and twinning phenomena in crystals of Cp*ReO_3, related to the density of disturbances in the crystals. The twin portions diffract independently, and therefore the observed intensities are sums of generally different intensities. On the other hand, the disordered structure contains in one block two motifs related by the disorder element diffracting coherently, therefore giving rise to the short (metal−metal) Patterson vector. There can exist varying densities of disturbances (disorder) within a block, so that an area containing a high density of disturbances may create the domain wall between the twin portions.

The Nonexistence of (C_5Me_5)Tc_2O_3. It is clear from the immediately preceding two paragraphs that the alleged (C_5Me_5)Tc_2O_3 is a myth. Its existence is unbelievable for crystallographic reasons alone. The reported structure is an artifact of a failure to recognize that both twinning and disorder were present in the crystal used to collect data.

There remains, however, one crystallographic detail that is not explained by the postulate that the original authors had in their hands (C_5Me_5)TcO_3 and simply misinterpreted their crystallographic data. The model we have refined for (C_5Me_5)ReO_3 requires partial occupancy of each metal atom position, whereas the Tc atoms of "(C_5Me_5)Tc_2O_3" were refined, with acceptable thermal displacement parameters, at full occupancy. Does this undermine our dismissal of "(C_5Me_5)Tc_2O_3" as a mythical compound? And what about other properties reported to support the alleged "(C_5Me_5)Tc_2O_3"? We shall now show that there is a simple way to explain *everything*.

Has Cp*TcO_3 Ever Been Made? While the crystallographic data alone make the existence of "(C_5Me_5)Tc_2O_3" untenable, the entire body of data reported in ref 4 are subject to only one interpretation: *Cp*TcO_3 was not the compound examined (and may not exist at all) while Cp*ReO_3 was the compound described.* The accidental contamination of a sample of a Tc compound with the analogous Re compound is easily conceivable in a laboratory where both metals are routinely studied. It should be noted that at least two independent groups,[7] beginning with Tc starting materials of known purity, have never been able to reproduce either the reported Tc compound or even Cp*TcO_3. It is also to be noted that even the original authors[4] of the Cp*Tc_2O_3 paper were never able to reproduce the material. While it is possible to control the oxidation of Cp*Re(CO)$_3$ so as to stop at Cp*ReO_3, it appears that so far, at least, the oxidation of Cp*Tc(CO)$_3$ cannot be prevented from going all the way to TcO_4^-.

With the above proposition in mind, we note that the reported synthesis used conditions that are known to produce Cp*ReO_3, that the supposed Tc polymer was eluted from a column with benzene/ether, and that the yield of the compound was only 16%. At this point the Cp*ReO_3 was effectively separated from the bulk solution, and the analytical and diffraction studies were performed on these crystals. Since the atomic weight of ^{99}Tc is close to half that of natural-abundance Re, the analytical results expected for Cp*Tc_2O_3 are necessarily close to those for Cp*ReO_3. Likewise, the parent ion observed in the mass spectrum was simply that of Cp*ReO_3 (the difference of approximately 12 amu could be overlooked at low resolution). It has already been pointed out that the reported Tc−O stretching vibrations are characteristic of terminal oxo ligands,[8] but perhaps the most convincing evidence that the compound was indeed the known Re compound is that the reported values (909 and 880 cm^{-1}) are *exactly* the same ($\pm$1 cm^{-1}) as those reported for Cp*ReO_3![1]

We were able to obtain the deposited structure factors for the Tc compound and carry out a successful refinement using our model for Cp*ReO_3. The important difference in the models is that the sites that were formerly refined as fully-occupied Tc ($Z = 43$) sites were refined as half-occupied Re ($Z = 75$) sites. Simply stated, half a rhenium atom mimics a technetium atom. The ratio of the site occupancies refined to 50:50, as expected since the additional symmetry relating to the two positions was implied by the additional absences observed in the data set. Following refinement of the "Cp*Tc_2O_3" data with this correct (Cp*ReO_3) model, peaks corresponding to the hydrogen atoms were seen in a difference map, further convincing us that the crystals that produced the intensity data were indeed Cp*ReO_3.

Acknowledgment. We are grateful to the National Science Foundation for support. V.P. thanks the Grant Agency of the Czech Republic for additional support, Grant 202/93/1154.

Supporting Information Available: Full listings of crystallographic data, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

IC941273W

---

(7) Sattelberger, A. P.; Alberto, R. Personal communications.

(8) Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgärtner, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 189.