to C_{3v} symmetry. The Cu–As–C(α) angles are each greater than the ideal tetrahedral angle of 109.47°; individual angles vary from 114.4 (5) to 118.2 (5)°, averaging 116.2 [11]°. The C(α)–As–C(α') angles are correspondingly reduced, with a range from 98.6 (7) to 104.7 (6)° and an average value of 102.0 [17]°. Carbon–carbon distances within the phenyl rings average 1.407 [35] Å; individual values are given Table IV.

Conclusions

Tetrameric (triphenylphosphine)copper(I) iodide crystallizes from benzene as $[(AsPh_3)CuI]_4 \cdot C_6H_6$, in which the Cu_4I_4 core has a tetrahedrally distorted cubane-like geometry of approximate T_d symmetry. The far-infrared spectroscopic studies of Teo and Barnes[16] suggest that they studied a $[(AsPh_3)CuI]_4$ complex in which the Cu_4I_4 core had a step structure. It therefore appears that $[(AsPh_3)CuI]_4$ joins $[(PPh_3)AgI]_4$[12] as a second example of a tetrameric (pnicogen ligand)–(coinage metal)–halide complex which exists in both cubane-like and step (or "chair") structures. Further studies are underway in attempting to isolate the step isomer in crystalline form.

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Registry No. $[(AsPh_3)CuI]_4 \cdot C_6H_6$, 69439-90-3.

Supplementary Material Available: A list of data processing formulas and structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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Some New Types of Quadruply Bonded Dirhenium Compounds Containing Bridging Carboxylato Groups

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It has been found that when $Re_2(piv)_4Cl_2$ (piv = the pivalato group, $(CH_3)_3CCO_2$) is heated at temperatures of 220 °C or above, decomposition occurs, and the two chief products, which may be isolated in crystalline form by fractional sublimation, are $Re_2(piv)_2Cl_4$ (**1b**) and $Re_2(piv)_3Cl_3$ (**2**). Both of these compounds have been characterized thoroughly, including X-ray crystallographic structure determination. Compound **1** crystallizes in space group *Cmcm* with a = 14.062 (3) Å, b = 11.935 (8) Å, c = 11.147 (5) Å, V = 1870 (2) Å^3, and Z = 4. The molecule has rigorous *mm* (C_{2v}) symmetry with Re_2Cl_4 lying in one of the mirror planes and the Re–Re bond being bisected by the other. The full symmetry is close to D_{2h}, neglecting the orientations of the methyl groups. Important distances are Re–Re = 2.209 (2) Å, Re–Cl = 2.23 (1), 2.34 (1) Å, and Re–O = 2.02 (1) Å. The molecules are linked into chains by coordination of Cl atoms of one molecule to axial positions on neighboring molecules with Re···Cl = 2.90 (1) Å. The longer intramolecular Re–Cl distances are to the Cl atoms that form these bridges. Compound **2** crystallizes in space group *Cc* with a = 13.877 (4) Å, b = 13.445 (5) Å, c = 13.497 (3) Å, β = 106.56 (2)°, V = 2414 (1) Å^3, and Z = 4. The structure consists of infinite chains of $Re_2(piv)_3Cl_2$ units linked by bridging Cl atoms coordinated in axial positions of adjacent $Re_2(piv)_3Cl_2$ units, at Re···Cl distances of 2.63 and 2.68 Å. Some important distances are Re–Re = 2.229 (2) Å, Re–Cl = 2.28 (1) Å, and Re–O = 2.03 (3) Å.

Introduction

In the course of current studies of the $Re_2(O_2CCMe_3)_4X_2$ (X = Cl, Br) compounds,[1,2] we have observed that these are thermally labile and give rise to mixed pivalato/halo complexes with different compositions. Using the chloro compound, $Re_2(piv)_4Cl_2$, where we introduce the abbreviation piv for $(CH_3)_3CCO_2$, we have examined these thermal transformations in more detail and determined the conditions under which good yields of two new compounds, $Re_2(piv)_2Cl_4$ and $Re_2(piv)_3Cl_3$, can be isolated. We have also thoroughly characterized these compounds, including determination of their crystal structures.

Experimental Section

Preparation of $Re_2(piv)_4Cl_2$. This was done following the method in the literature.[3]

Preparation of 1a and 2. The thermolysis reactions of $Re_2(piv)_4Cl_2$ were carried out in an evacuated 20 × 0.7 cm Pyrex tube which was inserted into a tube furnace with $^1/_2$ its length exposed for condensation

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and resublimation. The tube was fired at the proper temperature to produce the desired species. It was assumed that equilibrium is reached after about 10 h. The tube was then flame-sealed at the midpoint so as to separate residue from products and refired to produce crystals suitable for X-ray diffraction analysis. For production of the desired species it is imperative that the furnace be preheated to one of the three temperatures now to be specified.

(i) Initial firing at 220 °C produced a preponderance of crystalline starting material, $Re_2(piv)_4Cl_2$, at a point on the tube just inside the lip of the tube furnace.

(ii) When the tube was fired at 240 °C, the major product was a pink band, shown by microanalysis to be $Re_2(piv)_3Cl_3$, **2**, just outside of the red-orange $Re_2(piv)_4Cl_2$ band. The residue consisted predominantly of starting material with some white ash. Resublimation at 180 °C produced small but high-quality pink crystals. Anal. Calcd for $Re_2(piv)_3Cl_3$: C, 23.04; H, 3.48. Found: C, 24.0; H, 3.31.

(iii) Firing the tube at 260 °C produced a green band still further away from the lip of the tube furnace. This green solid did not appear crystalline to the naked eye and analyzed as $Re_2(piv)_2(Hpiv)Cl_4$ (**1a**). Anal. Calcd for $C_{15}H_{28}O_6Cl_4Re_2$: C, 22.01; H, 3.45. Found: C, 22.5; H, 3.33.

In order to obtain a crystalline sample, the green solid was resublimed at 160 °C in a sealed tube. This was accompanied by some decomposition, as evidenced by traces of a colorless liquid condensate in the coolest part of the tube (Hpiv?) and a mirror of metal in the hottest part of the tube. Green crystals were formed in the center part of the tube and these analyzed as $Re_2(piv)_2Cl_4$ (**1b**). Anal. Calcd for $C_{10}H_{18}O_4Cl_4Re_2$: C, 16.77; H, 2.53. Found: C, 16.9; H, 2.42.

Conversion of Compound 1a to $Re_2(piv)_3Cl_3$. A few milligrams of compound **1a** was dissolved in 5 mL of diethyl ether in a nitrogen atmosphere, giving a blue solution which was then evaporated in a stream of nitrogen. The solid residue was pink and crystalline and had an absorption spectrum in acetone identical to that of an authentic sample of $Re_2(piv)_3Cl_3$. Evidently, the following reaction occurs and goes to completion because of removal of HCl:

$$Re_2(piv)_2Cl_4 + H(piv) \rightarrow Re_2(piv)_3Cl_3 + HCl \qquad (1)$$

Physical and Analytical Measurements. Elemental analyses were performed by the Center for Trace Characterization, Texas A&M University.

Mass spectra were obtained on a CEC21-110B high-resolution instrument with a 70-eV ionizing electron beam. The sample probe was maintained at 160 °C and the detector at 220 °C. Dr. M. W. Extine kindly supplied the computer program used to calculate the isotope distribution patterns.

X-ray Crystallographic Studies.[4] **$Re_2(piv)_2Cl_4$, 1b.** A green crystal having approximate dimensions of 0.50 × 0.14 × 0.19 mm was attached with epoxy cement to a glass fiber. The ω scans of several intense reflections had peak half-height widths of less than 0.20°. This, combined with a clean extinction under crossed polarizers, indicated the crystal to be of high quality. It was found to belong to the orthorhombic system with the following unit cell dimensions: a = 14.062 (3) Å, b = 11.935 (8) Å, c = 11.147 (5) Å, and V = 1870 (2) Å^3. The observed volume is consistent with expectation for Z = 4. Systematic extinctions of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with space group $Cmcm$, $Cmc2$ (a nonstandard setting of $Ama2$), and $Cmc2_1$, were observed. Data were collected on a Syntex $P\bar{1}$ autodiffractometer at 23° with Mo Kα radiation. The positions of 15 intense reflections were centered and used to derive an orientation matrix. Data were collected with the θ–2θ scan technique in the range $0 < 2\theta < 50°$. The scan range was from 1° above Kα_1 to 1° below Kα_2 with scan rates of 4–24° min^{-1} depending on intensity. The monitoring of three standard reflections showed only random intensity variations during the collection process. The linear absorption coefficient of 138 cm^{-1} necessitated a φ-scan empirical absorption correction using a transmission curve obtained at 10° intervals about $0 < \phi < 360°$ for eight intense reflections which had χ values near 90°. The normalized transmission factors varied from 1.00 to 0.70. Those 382 reflections with $I > 2\sigma(I)$ were used to solve and refine the structure.

A three-dimensional Patterson function with mmm sysmmetry was solved in space group $Cmcm$ to give a position for a unique rhenium atom. This was refined and a difference map calculated, whereby the positions of the remaining seven nonhydrogen atoms making up an $Re_2(piv)_2Cl_4$ unit occupying a fourfold position of mm (C_{2v}) symmetry were located. Two cycles of isotropic least-squares refinement gave R_1 = 0.110 and R_2 = 0.122. The absorption corrections were now made, and the residuals dropped to R_1 = 0.086 and R_2 = 0.092. There were, however, certain lacunae in the unit cell, and before attempting anisotropic refinement another difference map was calculated.

This map revealed the presence of two weak peaks lying on the mirror plane at x = 0. These two peaks which were about half the intensity of the carbon atom peaks, plus their two symmetry-related equivalents generated by the mirror at $z = {}^1/_4$, were arranged in an approximate square ~2.1 Å on a side.

The volume occupied by the lacunae containing these four maxima appeared marginally adequate to hold four light atoms, but certainly no more. However, their spatial arrangement made no chemical sense, nor did their apparent contacts with their surroundings, viz., 2.61 Å to Cl(1) and 2.43 Å to C(4). It was also found that attempts to refine them as carbon atoms lead to isotropic thermal parameters in excess of 15 Å^2.

In view of the foregoing facts, and our inability to see any practical alternative, we proceeded with the refinement by simply ignoring these weak peaks. Three cycles of least-squares refinement on all atomic parameters and employing anisotropic thermal parameters for Re, Cl(1), Cl(2), and O produced final agreement indices of R_1 = 0.042 and R_2 = 0.055. The final estimated standard deviation of an observation of unit weight was 1.30. During the final cycle no parameter shifted more than 0.01σ, and a subsequent difference map revealed no peaks of chemical significance.

$Re_2(piv)_3Cl_3$, 2. A pink crystal of $Re_2(piv)_3Cl_3$ having dimensions of 0.03 × 0.10 × 0.17 mm was attached with epoxy cement to a thin glass fiber. The crystal extinguished cleanly under crossed polarizers and exhibited ω scan half-height widths of less than 0.20° on three of the more intense reflections.

Cell constants determined for the monoclinic crystal are a = 13.877 (4) Å, b = 13.445 (5) Å, c = 13.497 (3) Å, β = 106.56 (2)°, and V = 2414 (1) Å^3. The observed volume is consistent with expectation for Z = 4. Systematic extinctions of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, were observed. The space groups $C2$, Cc, and $C2/c$ are consistent with these extinctions. Of the 2683 independent reflections in the range $0 < 2\theta < 50°$, 1631 having $I > 2\sigma(I)$ were used to solve and refine the structure.

The ambiguity in space groups was resolved by solution of a three-dimensional Patterson function, in space group Cc, which revealed the presence of two independent Re atoms. Two cycles of least-squares refinement of the positional parameters of the two metal atoms gave agreement indices of

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.18$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.23$$

Subsequent difference Fourier analysis revealed the positions of the additional 24 independent atoms. The positional and thermal parameters of all atoms were then refined isotropically to convergence. The empirical absorption correction (μ = 109 cm^{-1}) produced a satisfactory drop in the discrepancy indices in the final cycle of isotropic refinement. Normalized transmission factors ranged from 1.00 to 0.69.

Three cycles of least-squares refinement on the positional parameters of all atoms, the anisotropic thermal parameters of the Re, O, and Cl atoms, and the isotropic thermal parameters of C atoms produced final discrepancy indices of R_1 = 0.066 and R_2 = 0.071. The final error in an observation of unit weight was 1.19. A final differences Fourier map revealed no peaks of structural significance. In the final refinement cycle none of the 166 parameters shifted more than 0.17σ. The alternate enantiomorph was also refined to convergence, but this produced no significant reduction (<0.002) in the residuals.

Results and Discussion

We have identified three stable molecules containing the quadruply bonded Re_2 unit coordinated by a mixture of pivalato groups, $(CH_3)_3CCO_2$ (abbreviated piv), and chlorine atoms, namely, $Re_2(piv)_4Cl_2$, $Re_2(piv)_3Cl_3$, and $Re_2(piv)_2Cl_4$, and examined some processes by which they can be interconverted. None of these transformations is a redox reaction; the rhenium remains in the formal oxidation state 3+ throughout.

The principal reactions occurring when $Re_2(piv)_4Cl_2$ is heated in a sealed tube are (1) pyrolysis of red-brown Re_2-

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Re_2(piv)_2Cl_4$, **1b**[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	0.0000 (0)	0.1009 (1)	0.1509 (1)	2.34 (4)	2.44 (4)	1.69 (4)	0	0	0.05 (7)
Cl(1)	0.0000 (0)	0.2887 (7)	0.1046 (7)	5.7 (5)	2.4 (4)	3.5 (4)	0	0	0.2 (4)
Cl(2)	0.0000 (0)	−0.0909 (7)	0.1086 (6)	4.7 (4)	3.6 (4)	1.3 (2)	0	0	−0.1 (3)
O	0.143 (1)	0.100 (1)	0.150 (1)	3.0 (6)	3.1 (6)	2.3 (5)	−0.2 (7)	0.6 (6)	0.2 (7)
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.189 (2)	0.105 (3)	0.250 (0)	3.2 (6)	C(3)	0.171 (5)	0.480 (8)	0.250 (0)	15.9 (25)
C(2)	0.296 (3)	0.102 (3)	0.250 (0)	4.3 (8)	C(4)	0.171 (4)	0.662 (5)	0.150 (5)	14.8 (18)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

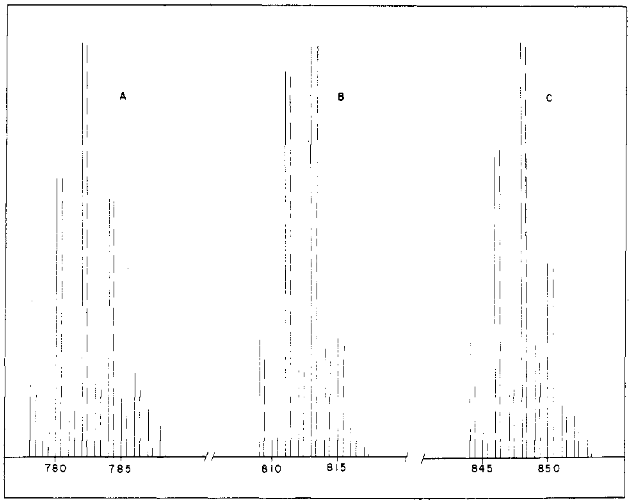

Figure 1. Observed (—) and calculated (– – –) ion multiplets in the mass spectrum of $Re_2(piv)_3Cl_3$. The horizontal axis gives the mass numbers, and the vertical height of each line is proportional to its mass percent of the multiplet. The three multiplets shown correspond to (A) $Re_2(piv)_3Cl_3^+$, (B) $Re_2(piv)_4Cl^+$, and (C) $Re_2(piv)_4Cl_2^+$.

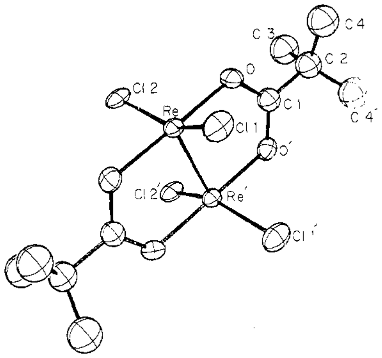

Figure 2. ORTEP drawing of the $Re_2(piv)_2Cl_4$ molecule showing the atomic numbering scheme. Each atom is represented by an ellipsoid of thermal vibration enclosing 40% of its electron density. The *tert*-butyl carbon atoms have been assigned arbitrary radii.

Table II. Bond Distances (Å) and Angles (deg)[a,b] in $Re_2(piv)_2Cl_4$

Re–Re′	2.209 (2)	O–C(1)	1.29 (2)
–Cl(1)	2.229 (8)	C(1)–C(2)	1.52 (4)
–Cl(2)	2.338 (8)	C(2)–C(3)	1.52 (9)
Re–Cl(2)[c]	2.90 (1)	C(2)–C(4)	1.40 (5)
Re–O	2.01 (1)		
Re′–Re–Cl(1)	102.9 (2)	Re–O–C(1)	120 (1)
–Cl(2)	101.6 (2)	O–C(1)–O′	120 (2)
–O	90.2 (3)	O–C(1)–C(2)	120 (1)
Cl(1)–Re–Cl(2)	155.4 (2)	C(1)–C(2)–C(3)	109 (4)
–O	90.3 (4)	–C(4)	109 (3)
Cl(2)–Re–O	89.6 (4)	C(3)–C(2)–C(4)	112 (3)
O–Re–O″	179.1 (7)	C(4)–C(2)–C(4)′	105 (5)

[a] Figures in parentheses are esd's in the least significant digit. [b] Primed atoms are symmetry related to their unprimed counterparts. [c] Intermolecular contact.

$(piv)_4Cl_2$ to give pink $Re_2(piv)_3Cl_3$, which predominates when the former is heated directly to 240 °C, and (2) conversion of $Re_2(piv)_4Cl_2$ to $Re_2(piv)_2Cl_4$, which first forms as a green solid of apparent composition $Re_2(piv)_2Cl_4{\cdot}Hpiv$. Upon resublimation, this deposits crystals of $Re_2(piv)_2Cl_4$ and releases the pivalic acid to condense in the coolest part of the tube. At lower temperature, the main process is simply sublimation of $Re_2(piv)_4Cl_2$.

The pyrolysis reactions are not stoichiometric, and there are visible byproducts. Mirrorlike deposits in the hotest zones are presumed to be metallic rhenium, but this has not been established conclusively. There are also small amounts of a colorless liquid product, or products, in each case that condense in the coolest region of the pyrolysis tube. We have not attempted to identify these conclusively.

The substance analyzing as $Re_2(piv)_2Cl_4{\cdot}Hpiv$, **1a**, has not been characterized structurally, but the presence of Hpiv in approximately the quantity indicated by the formula is confirmed by the occurrence of reaction 1 as described in the Experimental Section.

The general lability of this entire system of mixed ligand complexes is manifested in the mass spectrum obtained for $Re_2(piv)_3Cl_3$. As shown in Figure 1 the spectrum contains multiplets for $Re_2(piv)_4Cl_2^+$ and $Re_2(piv)_4Cl^+$ as well as one for $Re_2(piv)_3Cl_3^+$, indicating the prompt occurrence of ligand redistribution processes on heating.

Structure of $Re_2(piv)_2Cl_4$, 1b. The atomic positional and thermal parameters for this compound are listed in Table I, and the structure of the $Re_2(piv)_2Cl_4$ molecule is given in Figure 2. The important interatomic distances and angles are listed in Table II.

Presumably the central $Re_2(O_2C-)_2Cl_4$ portion of the molecule would have D_{2h} (*mmm*) symmetry if it were free of the intermolecular interactions (vide infra) that occur in the crystal. The molecule in the crystal has only C_{2v} (*mm*) symmetry, with the two mirror planes being (1) a plane containing the two rhenium atoms and all the chlorine atoms and (2) a plane bisecting the Re–Re′ bond and containing C(1), C(2), and C(3) of the pivalate groups. The Cl(1), Cl(1)′ atoms are thus not equivalent to Cl(2), Cl(2)′, and, in fact, the difference between the two types is pronounced, as evidenced by the considerable difference, 0.11 (2) Å, in the Re–Cl distances, Re–Cl(2) being the longer. This differences arises because Cl(2) and Cl(2)′ participate in intermolecular interactions while Cl(1) and Cl(1)′ do not.

The important intermolecular interaction that occurs is the formation of infinite chains of $Re_2(piv)_2Cl_4$ molecules linked by the Cl(2) atoms, each of which is coordinated, at a distance of 2.90 (1) Å, to the axial position of an adjacnt molecule. The Cl(2) atoms lie almost exactly along the extensions of the Re–Re bonds, the Re–Re···Cl angle being 177.6 (2)°. This chain arrangement is shown in Figure 3.

The structure of $Re_2(piv)_2Cl_4$ can be most naturally compared with that of $Re_2(N_2CPh_3)_2Cl_4$, where N_2CPh_3 is the *N*,*N*′-diphenylbenzamido anion.[5] The latter forms two

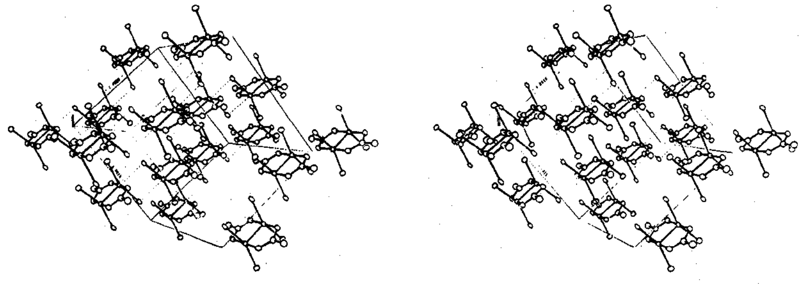

Figure 3. Stereoscopic view of the crystal packing in $Re_2(piv)_2Cl_4$. The *tert*-butyl carbon atoms have been eliminated for clarity. The thermal ellipsoids have been scaled to represent 20% of the electron density.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Re_2Piv_3Cl_3$, 2[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re(1)	0.0000 (0)	0.0075 (1)	0.0000 (0)	2.21 (5)	2.96 (6)	1.65 (3)	0.21 (7)	0.39 (3)	0.09 (6)
Re(2)	0.0105 (1)	−0.0626 (1)	−0.1463 (1)	1.85 (4)	2.65 (5)	1.66 (3)	0.08 (7)	0.43 (3)	0.14 (6)
Cl(1)	0.0202 (7)	0.1158 (8)	0.1684 (6)	4.5 (5)	3.4 (5)	2.4 (3)	0.5 (4)	1.5 (3)	−0.1 (3)
Cl(2)	−0.0710 (8)	−0.1163 (8)	0.0767 (7)	4.3 (5)	4.2 (5)	3.3 (3)	−1.5 (4)	1.6 (3)	0.3 (3)
Cl(3)	−0.0504 (8)	−0.2219 (7)	−0.1332 (7)	3.8 (5)	2.9 (4)	4.3 (4)	−0.4 (4)	1.3 (3)	0.8 (3)
O(1)	−0.145 (2)	0.060 (2)	−0.071 (2)	1.3 (9)	4 (1)	3.2 (9)	−0	0.8 (7)	−1 (1)
O(2)	−0.137 (2)	−0.014 (2)	−0.217 (2)	3 (1)	2 (1)	1.9 (8)	−1 (1)	−0.8 (8)	0.2 (8)
O(3)	0.138 (2)	−0.027 (2)	0.069 (2)	1 (1)	4 (1)	3 (1)	1 (1)	−1.0 (8)	1.5 (9)
O(4)	0.150 (2)	−0.102 (2)	−0.080 (2)	2 (1)	2 (1)	2.8 (9)	1.9 (9)	0.0 (8)	−0.4 (8)
O(5)	0.048 (2)	0.133 (2)	−0.039 (2)	5 (2)	6 (1)	2.0 (9)	−3 (1)	−0 (1)	−2 (1)
O(6)	0.061 (2)	0.070 (2)	−0.189 (2)	4 (1)	3 (1)	2.8 (9)	0 (1)	0.9 (8)	0.0 (9)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	−0.184 (3)	0.040 (2)	−0.175 (2)	2.1 (6)	C(9)	−0.247 (4)	0.201 (4)	−0.248 (3)	5.0 (11)
C(2)	0.190 (3)	−0.073 (3)	0.009 (2)	2.8 (7)	C(10)	0.344 (4)	−0.027 (4)	0.161 (3)	4.7 (10)
C(3)	0.075 (3)	0.142 (3)	−0.125 (3)	4.3 (9)	C(11)	0.327 (5)	−0.192 (5)	0.072 (4)	7.5 (15)
C(4)	−0.273 (3)	0.093 (3)	−0.229 (2)	2.8 (7)	C(12)	0.349 (5)	−0.034 (5)	−0.028 (5)	8.1 (17)
C(5)	0.309 (4)	−0.077 (4)	0.055 (3)	5.1 (11)	C(13)	0.162 (4)	0.224 (4)	−0.236 (4)	5.7 (12)
C(6)	0.108 (3)	0.241 (3)	−0.159 (3)	3.9 (9)	C(14)	0.012 (4)	0.305 (4)	−0.201 (3)	5.5 (11)
C(7)	−0.354 (3)	0.097 (3)	−0.152 (3)	3.6 (8)	C(15)	0.181 (5)	0.290 (5)	−0.059 (4)	7.5 (15)
C(8)	−0.327 (3)	0.032 (3)	−0.334 (3)	3.9 (9)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Bond Distances (Å)[a,b] in $Re_2(piv)_3Cl_3$

Re(1)–Re(2)	2.229 (2)	C(2)–O(3)	1.39 (5)
–Cl(1)	2.632 (10)	–O(4)	1.21 (4)
–Cl(2)	2.272 (10)	–C(5)	1.59 (6)
–O(1)	2.00 (3)	C(3)–O(5)	1.28 (5)
–O(3)	2.03 (3)	–O(6)	1.32 (5)
–O(5)	2.01 (3)	–C(6)	1.52 (6)
Re(2)–Cl(1)′	2.680 (8)	C(4)–C(7)	1.72 (5)
–Cl(3)	2.292 (11)	–C(8)	1.60 (5)
–O(2)	2.01 (3)	–C(9)	1.54 (5)
–O(4)	2.05 (3)	C(5)–C(10)	1.56 (7)
–O(6)	2.09 (3)	–C(11)	1.60 (8)
C(1)–O(1)	1.40 (4)	–C(12)	1.46 (7)
–O(2)	1.21 (4)	C(6)–C(13)	1.47 (6)
–C(4)	1.39 (5)	–C(14)	1.55 (7)
		–C(15)	1.61 (7)

[a] Figures in parentheses are esd's in the least significant digit.
[b] Primed atoms are symmetry related to their unprimed counterparts.

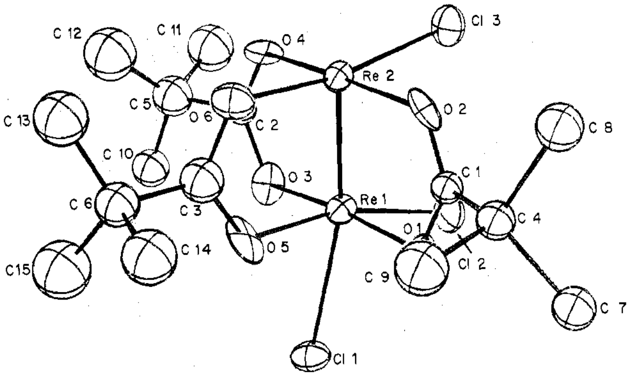

Figure 4. ORTEP drawing of the asymmetric unit of $Re_2(piv)_3Cl_3$ showing the atomic numbering scheme. Each atom is represented by a sphere or ellipsoid of thermal vibration enclosing 50% of its electron density.

crystalline compounds, one of which contains tetrahydrofuran loosely coordinated to one Re atom. In both cases, the molecules have the same transoid structure, that is, a planar Re_2Cl_4 unit with bridging ligands above and below, that is found here in $Re_2(piv)_2Cl_4$. There is also one other comparable structure, namely, that of $Re_2(O_2CPh)_2I_4$.[6] It is noteworthy that in all these transoid structures the Re–Re distances are relatively short. Thus, we have Re–Re distances of 2.209 (2) Å in the present case, 2.198 (1) Å in $Re_2(O_2CPh)_2I_4$, 2.209 (1) Å in $Re_2(N_2CPh_3)_2Cl_4(THF)$, and 2.177 (2) Å in $Re_2(N_2CPh_3)_2Cl_4$, the latter being the shortest known Re–Re distance.

Structure of $Re_2(piv)_3Cl_3$, 2. The atomic coordinates and thermal vibration parameters are listed in Table III, and the interatomic distances and angles are given in Tables IV and V, respectively.

The structure can be described as consisting of parallel infinite chains of $Re_2(piv)_3Cl_2^+$ units linked by bridging Cl^- ions that are shared between the axial positions of successive $Re_2(piv)_3Cl_2^+$ ions in the chains. Figure 4 shows the formula unit, which is the crystallographic asymmetric unit, and the atomic numbering scheme, and Figure 5 shows how the chains are arranged. The chloride bridges, formed by Cl(1), are nearly but not exactly symmetrical. The two Re–Cl distances are 2.63 (1) and 2.680 (8) Å, which differ by only about 3 times the sum of their esds. The two Re–Re–Cl(1) angles are 165.6 (3) and 170.6 (3)°, so that the bridging Cl^- is nearly along the extension of the Re–Re bond axis. The distances

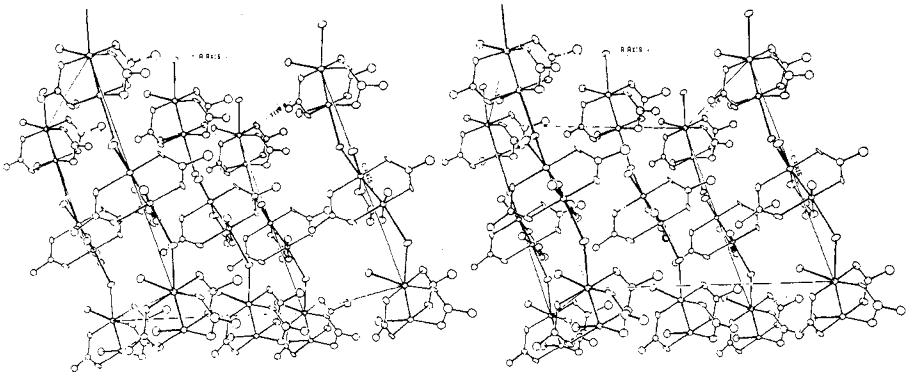

Figure 5. Stereoscopic drawing of the unit cell of $Re_2(piv)_3Cl_3$. The methyl groups of the piv units are omitted for clarity. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 20% of its electron density.

Table V. Selected Angles (deg) in $Re_2(piv)_3Cl_3$[a,b]

Re(2)-Re(1)-Cl(1)	165.6 (3)	O(4)-Re(2)-O(6)	85 (1)
-Cl(2)	103.0 (3)	Re(1)-O(1)-C(1)	118 (2)
-O(1)	91.1 (7)	-O(3)-C(2)	115 (2)
-O(3)	90.7 (8)	-O(5)-C(3)	123 (3)
-O(5)	89.8 (7)	Re(2)-O(2)-C(1)	124 (2)
Re(1)-Re(2)-Cl(1)′	170.6 (3)	-O(4)-C(2)	117 (2)
-Cl(3)	102.8 (3)	-O(6)-C(3)	117 (3)
-O(2)	89.2 (7)	O(1)-C(1)-O(2)	118 (3)
-O(4)	91.7 (7)	-C(4)	116 (3)
-O(6)	90.6 (7)	O(3)-C(2)-O(4)	125 (4)
-Cl(1)-Re(2)′	133.9 (4)	-C(5)	115 (3)
Cl(1)-Re(1)-Cl(2)	89.6 (4)	O(5)-C(3)-O(6)	120 (4)
-O(1)	95.6 (7)	-C(6)	125 (4)
-O(3)	81.3 (9)	C(1)-C(4)-C(7)	109 (3)
-O(5)	77.7 (7)	-C(8)	107 (3)
Cl(2)-Re(1)-O(1)	91.1 (8)	-C(9)	110 (3)
-O(3)	94.9 (9)	C(7)-C(4)-C(8)	109 (3)
-O(5)	167.2 (8)	-C(9)	107 (3)
O(1)-Re(1)-O(3)	173 (1)	C(8)-C(4)-C(9)	115 (3)
-O(5)	88 (1)	C(2)-C(5)-C(10)	112 (4)
O(3)-Re(1)-O(5)	85 (1)	-C(11)	102 (4)
Cl(1)′-Re(2)-Cl(3)	86.4 (4)	-C(12)	108 (4)
-O(2)	88.1 (7)	C(10)-C(5)-C(11)	108 (4)
-O(4)	90.1 (7)	-C(12)	115 (5)
-O(6)	80.3 (7)	C(11)-C(5)-C(12)	111 (5)
Cl(3)-Re(2)-O(2)	93.1 (9)	C(3)-C(6)-C(13)	114 (4)
-O(4)	92.3 (9)	-C(14)	107 (4)
-O(6)	166.4 (7)	-C(15)	106 (4)
O(2)-Re(2)-O(4)	174 (1)	C(13)-C(6)-C(14)	112 (4)
-O(6)	89 (1)	-C(15)	110 (4)
		C(14)-C(6)-C(15)	108 (4)

[a] Figures in parentheses are esd's in the least significant digit.
[b] Primed atoms are symmetry related to their unprimed counterparts.

from the rhenium atoms to the bridging chlorine atom are very much longer than those to the other chlorine atoms which occupy two of the eight nonaxial sites. These latter distances are 2.28 ± 0.01 Å. This difference is comparable to that in compound **1b** and in $(NH_4)_2[Re_2(O_2CH)_2Cl_6]$.[7]

Within the $Re_2(piv)_3Cl_2^+$ ion the distance and angles all have normal values. The Re–Re distance of 2.229 (2) Å is quite typical as are the Re–O distances, which average 2.03 ± 0.03 Å. The Re–Re–O angles are all in the range 89–92°, while the Re–Re–Cl angles are, as expected, considerably greater, with a mean value of 102.9 ± 0.1°.

There are now the following different types of $Re_2(O_2CR)_mCl_n$ ($m + n = 6$) compounds that have been structurally characterized.

(1) $Re_2(O_2CR)_4Cl_2$. The first of these to be studied by X-ray crystallography was the benzoate,[8] and the pivalate has now also been done.[1]

(2) $Re_2(O_2CR)_3Cl_3$. This paper presents the first report of the structure of a compound with this composition, namely, the pivalate. One Cl is used to form bridges between $Re_2(O_2CCMe_3)_3Cl_2$ units with local C_{2v} symmetry.

(3) Cisoid $Re_2(O_2CR)_2Cl_4$. Two of these have been reported, both by Koz'min and Surazhskaya, one with R = H[7] and the other with R = CH_3.[9]

(4) Transoid $Re_2(O_2CR)_2Cl_4$. The structure reported here is the first one, although, as already mentioned, several similar molecules, viz., $Re_2(N_2CPh_3)_2Cl_4$ and $Re_2(O_2CPh)_2I_4$, have been described.

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Registry No. 1a, 69351-93-5; **1b**, 69351-92-4; **2**, 69351-94-6; $Re_2(piv)_4Cl_2$, 15654-33-8.

Supplementary Material Available: Tables of structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) The structures of $Re_2(O_2CCMe_3)_4X_2$, X = Cl or Br, have been determined by L. D. Gage and D. M. Collins and will be reported later.
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(4) Methods of collecting data and solving and refining structures have often been described in detail in earlier publications. See, for example: Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176. All computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package.
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