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Synthesis and Crystal Structure of Mercury-Bridged Transition-Metal Clusters: $Hg[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]_2$ and $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta\text{-}C_5H_5)(CO)_3]$

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The synthesis and crystal structure of $Hg[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]_2$ (II) and $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta\text{-}C_5H_5)(CO)_3]$ (III) are reported. Both compounds are prepared from $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX]$ (X = Br (I) or I) by reaction with $[AsPh_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]$ or $Na[Mo(\eta\text{-}C_5H_5)(CO)_3]$. Crystals of II are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 13.522$ (8) Å, $b = 17.105$ (10) Å, $c = 18.159$ (12) Å, and $\beta = 104.79$ (7)°, while those of III are monoclinic, nonstandard space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 15.377$ (11) Å, $b = 12.714$ (8) Å, $c = 15.917$ (10) Å, and $\beta = 104.12$ (9)°. Each structure was solved from diffractometer data by combined direct and Patterson methods and refined by full-matrix least squares to $R = 0.052$ for 2322 observed reflections for II and $R = 0.064$, $R_w = 0.059$ for 3135 observed reflections for III. In II, the mercury atom, bridging one side of two triangular Ru clusters, is surrounded by four Ru atoms (the Ru–Hg bond distances range from 2.808 to 2.840 Å) where the dihedral angle between the two Ru_2Hg planes is 45°, intermediate between square-planar and tetrahedral geometry. In III the mercury atom is in a nearly trigonal arrangement bridging one side of a triangular Ru cluster and being bonded also to the Mo atom of the $[Mo(\eta\text{-}C_5H_5)(CO)_3]$ group (the Hg atom lies only 0.05 Å above the Ru_2Mo plane; the two Ru–Hg bond distances are 2.811 (2) and 2.812 (2) Å and the Hg–Mo bond is 2.743 (2) Å).

Introduction

We recently reported the synthesis and the crystal structure of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgBr]_2$ (I)[1] (Figure 1). There are two unique features about this transition-metal mercuric halide. First, the mercury is involved in a three-center–two-electron bond, and second, the compound exists as a bromine-bridged dimer in the solid state with the mercury having a distorted-tetrahedral arrangement, in contrast to other transition-metal mercuric compounds, which are monomeric with mercury linearly coordinated.[2] The compound I, however, is monomeric in solution. There are now several other cases that have recently appeared in the literature where mercury has undergone an expansion of its coordination number by delocalized bonding to transition metals.[3,4] In the compound $[MoHgMo(\eta\text{-}C_5H_5)(CO)_3]_4$,[4] which has a metallacubane structure, the mercury is tetrahedrally coordinated to four molybdenum atoms (three Mo atoms at neighboring corners of the cube and one $[Mo(\eta\text{-}C_5H_5)(CO)_3]$ group). In the anionic $[Ge(Co_2(CO)_7)((Co_2CO)_6)(HgCo(CO)_4)]^-$ complex[3] the mercury bridges two cobalt atoms in a three-center–two-electron bond and is bound to a third cobalt atom to give a trigonal-planar geometry around mercury. Both the molybdenum and the cobalt compounds were obtained as minor side products from reactions involving sodium amalgam and metal carbonyls. The reaction of I with various carbonyl metalates represents a possible specific route to mercury-bridged metal clusters which presents an opportunity to study systematically the relationship between structure and bonding in this class of molecules. We report here the initial results of these studies, specifically, the reaction of I with $[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]^-$ and $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$ and the crystal structures of the products obtained.

Results and Discussion

Synthesis of $Hg[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]_2$ and $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3]$. In our initial investigations of the synthesis of the complex I and its iodo analogue we reported 30–40% yields of these compounds from the reaction of PhHgX with $HRu_3(CO)_9(C_2\text{-}t\text{-}Bu)$ or from reaction of HgX_2 with $[AsPh_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]$.[1] In order to study the reaction chemistry of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX]$ (X = Br, I), we wanted to develop a high-yield synthesis of these compounds. We now report a one-pot synthesis of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX]$ (X = Br, I) from $[Ru_3(CO)_{12}]$ where much higher yields of these compounds are realized (eq 1).

$$[Ru_3(CO)_{12}] \xrightarrow[\text{heptane, reflux}]{HC\equiv C\text{-}t\text{-}Bu} [HRu_3(CO)_9(C_2\text{-}t\text{-}Bu)] \xrightarrow[\text{THF, room temp}]{(1)\ KOH,\ (2)\ HgX_2} [(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX] \quad (1)$$

80% overall (X = I)
45% overall (X = Br)

The reaction of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX]$ (X = Br, I) with 1 equiv of $[AsPh_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]$ yields $Hg[Ru_3(CO)_9(C_2\text{-}t\text{-}Br)]_2$ (II) quantitatively (eq 2).

$$[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX] + [AsPh_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)] \xrightarrow[\text{THF}]{\text{room temp}} Hg[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]_2 \quad (2)$$

(X = Br or I)

II, 100%

It should be pointed out that II is also obtained in varying amounts from the reaction of $[AsPh_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]$ with HgX_2 (X = Br, Cl, CN, CH_3COO, SCN) and from the thermolysis of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX]$. Presumably, the formation of II occurs via a redistribution reaction whose equilibrium constant is dependent on X. We are currently investigating this process, and the results of these studies will be reported separately.[5]

The reaction of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$, generated from $[Mo(\eta\text{-}C_5H_5)(CO)_3]_2$ and sodium amalgam, with $[(C_2\text{-}t\text{-}$

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(2) M. J. Mays, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, *6* (1972) (Part 2).

(3) D. N. Duffy, K. M. MacKay, and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 381 (1981).

(4) S. Fadel, J. Deutcher, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **16**, 704 (1977).

(5) It should be noted here that II was erroneously reported in ref 1 as $Hg_2[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9]_2$. This formulation was based on metal analysis by atomic absorption spectroscopy, which was shown to be incorrect due to mutual interferences between Hg and Ru absorptions.

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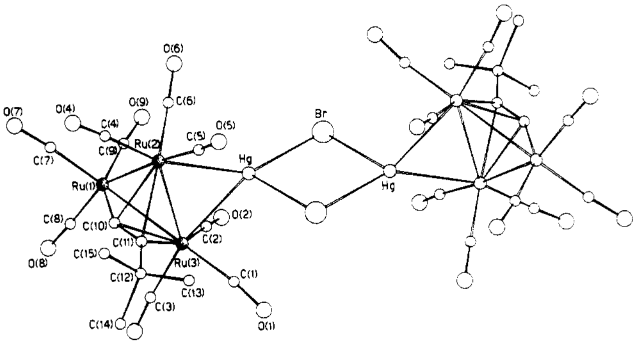

Figure 1. Solid-state structure of $[(C_2\text{-}t\text{-Bu})Ru_3(CO)_9HgBr]_2$ (I).

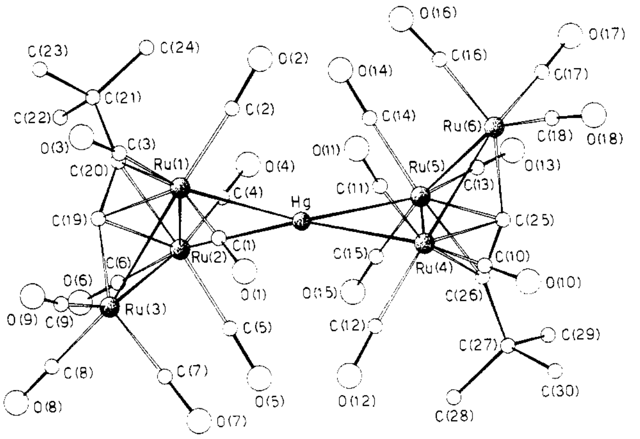

Figure 2. Solid-state structure of $[(C_2\text{-}t\text{-Bu})Ru_3(CO)_9]_2Hg$ (II).

Bu)$Ru_3(CO)_9HgX$] (X = Br, I)] gives $[(C_2\text{-}t\text{-Bu})Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3]$ in moderate yield (eq 3). The

$$Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3] + [(C_2\text{-}t\text{-Bu})Ru_3(CO)_9HgX] \xrightarrow[\text{room temp}]{\text{THF}} [(C_2\text{-}t\text{-Bu})Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3] \quad (3)$$

reaction is accompanied by nonspecific decomposition and by the formation of significant amounts of II and $Hg[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$. Lowering the reaction temperature to 0 °C or reversing the order of addition of reactants did not significantly change the yield of III.

Crystal Structure of $Hg[Ru_3(CO)_9(C_2\text{-}t\text{-Bu})]_2$. The structure of the complex $Hg[Ru_3(CO)_9(C_2\text{-}t\text{-Bu})]_2$ (II) with the atomic numbering system is represented in Figure 2; selected bond distances and angles are given in Table I. The complex can be described as a dimer of two butterfly clusters with the mercury atom sharing a common wingtip. The dihedral angles between the two triangular wings in each butterfly are 124.4 and 126.7°; these values are comparable with those found (127°) in the starting complex I.[1] The coordination geometry around mercury can be described as intermediate between a tetrahedral and a square-planar arrangement. The distortion from these idealized geometries is manifested in the mercury–ruthenium bond angles, which range from 60.4 to 159.4°, and by the dihedral angle between the two Ru_2Hg planes, which is 44.6°. There is a slight asymmetry in the Hg–Ru bonds to each Ru_3 cluster (2.808 (6), 2.840 (6) and 2.819 (6), 2.840 (7) Å, respectively), while in I these bonds are equal and significantly shorter (2.733 (2) and 2.739 (2) Å). The increase in the Hg–Ru bond distances on going from I to II is accompanied by a corresponding decrease in the Ru–Ru bond length at the mercury-bridged side of the Ru_3 cluster (2.855 (3) and 2.847 (3) Å in II and 2.900 (3) Å in I). It is difficult to assess the cause of the asymmetry in the Ru–Hg bonds and the unusual dihedral angle in II, since both intra-

Table I. Selected Bond Distances (Å) and Angles (deg) with Their Estimated Standard Deviations for Complex II

(a) In the Coordination Sphere of the Metal Atoms

Hg–Ru(1)	2.808 (6)	Ru(2)–C(20)	2.27 (4)
Hg–Ru(2)	2.840 (6)	Ru(3)–C(7)	1.85 (4)
Hg–Ru(4)	2.840 (7)	Ru(3)–C(8)	1.89 (4)
Hg–Ru(5)	2.819 (6)	Ru(3)–C(9)	1.83 (5)
Ru(1)–Ru(2)	2.855 (3)	Ru(3)–C(19)	1.98 (3)
Ru(1)–Ru(3)	2.799 (5)	Ru(4)–C(10)	1.84 (4)
Ru(2)–Ru(3)	2.798 (5)	Ru(4)–C(11)	1.90 (4)
Ru(4)–Ru(5)	2.847 (3)	Ru(4)–C(12)	1.95 (4)
Ru(4)–Ru(6)	2.812 (4)	Ru(4)–C(25)	2.17 (3)
Ru(5)–Ru(6)	2.807 (5)	Ru(4)–C(26)	2.24 (3)
Ru(1)–C(1)	1.83 (4)	Ru(5)–C(13)	1.84 (5)
Ru(1)–C(2)	1.90 (3)	Ru(5)–C(14)	1.88 (4)
Ru(1)–C(3)	1.89 (5)	Ru(5)–C(15)	1.90 (3)
Ru(1)–C(19)	2.20 (3)	Ru(5)–C(25)	2.14 (3)
Ru(1)–C(20)	2.31 (4)	Ru(5)–C(26)	2.21 (3)
Ru(2)–C(4)	1.88 (3)	Ru(6)–C(16)	1.83 (5)
Ru(2)–C(5)	1.87 (4)	Ru(6)–C(17)	1.83 (4)
Ru(2)–C(6)	1.87 (4)	Ru(6)–C(18)	1.82 (5)
Ru(2)–C(19)	2.16 (3)	Ru(6)–C(25)	1.96 (3)

Ru(1)–Hg–Ru(2)	60.7 (1)	Ru(3)–Ru(2)–Ru(1)	59.4 (1)
Ru(1)–Hg–Ru(4)	126.6 (1)	Hg–Ru(2)–Ru(1)	59.1 (1)
Ru(1)–Hg–Ru(5)	156.2 (1)	Ru(1)–Ru(3)–Ru(2)	61.3 (1)
Ru(2)–Hg–Ru(4)	159.4 (1)	Ru(5)–Ru(4)–Ru(6)	59.5 (1)
Ru(2)–Hg–Ru(5)	122.1 (1)	Ru(5)–Ru(4)–Hg	59.4 (1)
Ru(4)–Hg–Ru(5)	60.4 (1)	Ru(6)–Ru(4)–Hg	100.7 (1)
Ru(2)–Ru(1)–Ru(3)	59.3 (1)	Ru(6)–Ru(5)–Hg	101.3 (1)
Ru(2)–Ru(1)–Hg	60.2 (1)	Ru(6)–Ru(5)–Ru(4)	59.6 (1)
Ru(3)–Ru(1)–Hg	99.7 (1)	Hg–Ru(5)–Ru(4)	60.1 (1)
Ru(3)–Ru(2)–Hg	98.9 (1)	Ru(4)–Ru(6)–Ru(5)	60.9 (1)

(b) In the Carbonyl Groups

O(1)–C(1)	1.21 (4)	O(10)–C(10)	1.19 (5)
O(1)–C(2)	1.14 (4)	O(11)–C(11)	1.14 (5)
O(3)–C(3)	1.11 (6)	O(12)–C(12)	1.13 (5)
O(4)–C(4)	1.18 (4)	O(13)–C(13)	1.17 (5)
O(5)–C(5)	1.16 (5)	O(14)–C(14)	1.13 (5)
O(6)–C(6)	1.16 (5)	O(15)–C(15)	1.16 (4)
O(7)–C(7)	1.15 (5)	O(16)–C(16)	1.19 (6)
O(8)–C(8)	1.17 (5)	O(17)–C(17)	1.16 (5)
O(9)–C(9)	1.18 (6)	O(18)–C(18)	1.23 (6)

Ru(1)–C(1)–O(1)	180 (3)	Ru(4)–C(10)–O(10)	173 (3)
Ru(1)–C(2)–O(2)	176 (3)	Ru(4)–C(11)–O(11)	175 (4)
Ru(1)–C(3)–O(3)	175 (4)	Ru(4)–C(12)–O(12)	177 (4)
Ru(2)–C(4)–C(4)	180 (3)	Ru(5)–C(13)–O(13)	178 (4)
Ru(2)–C(5)–O(5)	178 (3)	Ru(5)–C(14)–O(14)	178 (3)
Ru(2)–C(6)–O(6)	178 (3)	Ru(5)–C(15)–O(15)	174 (3)
Ru(3)–C(7)–O(7)	178 (3)	Ru(6)–C(16)–O(16)	175 (4)
Ru(3)–C(8)–O(8)	179 (3)	Ru(6)–C(17)–O(17)	178 (4)
Ru(3)–C(9)–O(9)	173 (4)	Ru(6)–C(18)–O(18)	175 (4)

(c) In the Organic Ligands

C(19)–C(20)	1.32 (4)	C(25)–C(26)	1.27 (4)
C(20)–C(21)	1.51 (5)	C(26)–C(27)	1.54 (5)
C(21)–C(22)	1.57 (6)	C(27)–C(28)	1.50 (6)
C(21)–C(23)	1.59 (5)	C(27)–C(29)	1.54 (6)
C(21)–C(24)	1.47 (5)	C(27)–C(30)	1.62 (6)

Ru(1)–C(19)–Ru(2)	82 (1)	Ru(5)–C(25)–Ru(4)	83 (1)
Ru(1)–C(19)–Ru(3)	84 (1)	Ru(4)–C(25)–Ru(6)	85 (1)
Ru(2)–C(19)–Ru(3)	85 (1)	Ru(5)–C(25)–Ru(6)	86 (1)
Ru(1)–C(20)–Ru(2)	77 (1)	Ru(4)–C(26)–Ru(5)	79 (1)
C(20)–C(19)–Ru(1)	77 (2)	C(26)–C(25)–Ru(4)	76 (2)
C(20)–C(19)–Ru(2)	77 (2)	C(26)–C(25)–Ru(5)	76 (2)
C(20)–C(19)–Ru(3)	156 (3)	C(26)–C(25)–Ru(5)	156 (3)
C(21)–C(20)–Ru(1)	135 (2)	C(27)–C(26)–Ru(4)	133 (2)
C(21)–C(20)–Ru(2)	136 (2)	C(27)–C(26)–Ru(5)	135 (2)
C(21)–C(20)–C(19)	143 (3)	C(27)–C(26)–C(25)	142 (3)
Ru(1)–C(20)–C(19)	68 (2)	Ru(4)–C(26)–C(25)	70 (2)
Ru(2)–C(20)–C(19)	68 (2)	Ru(5)–C(26)–C(25)	70 (2)
C(22)–C(21)–C(23)	112 (3)	C(28)–C(27)–C(29)	112 (3)
C(22)–C(21)–C(24)	112 (3)	C(28)–C(27)–C(30)	107 (3)
C(22)–C(21)–C(20)	106 (3)	C(28)–C(27)–C(26)	114 (3)
C(23)–C(21)–C(24)	110 (3)	C(29)–C(27)–C(30)	111 (4)
C(23)–C(21)–C(20)	105 (3)	C(29)–C(27)–C(26)	108 (3)
C(24)–C(21)–C(20)	112 (3)	C(30)–C(27)–C(26)	104 (3)

Table II. Hg-Ru and Ru-Ru(Bridged Edge Only) Bond Lengths (Å) in Mercury-Bridged Metal Clusters and Related Compounds

compd	Hg-Ru	Ru-Ru	ref
$Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)^-$		2.67	6
$HRu_3(CO)_9(C_2\text{-}t\text{-}Bu)$		2.80	7
$Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)HgX$ (I)	2.74	2.90	1
$[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]_2Hg$ (II)	2.82 (av)	2.85	*a*
$Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)HgMo(\eta^5\text{-}C_5H_5)(CO)_3$ (III)	2.81	2.87	*a*

[a] This work.

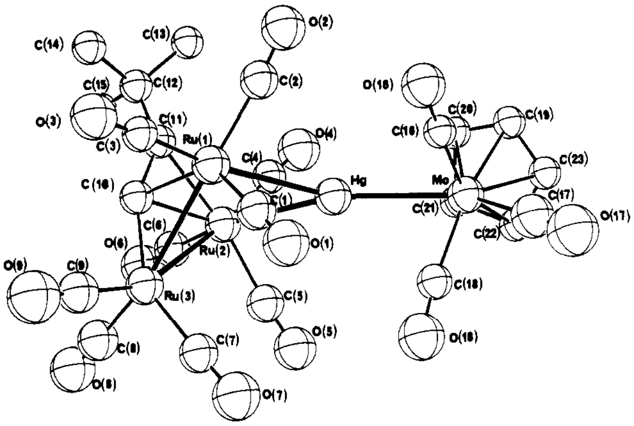

Figure 3. Solid-state structure of $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3$ (III).

molecular steric effects and crystal-packing effects may play an important role. In the two $Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)$ frameworks the Ru atoms define two isosceles triangles (Ru–Ru bonds are 2.855 (3), 2.799 (5), 2.798 (5) and 2.847 (3), 2.812 (4), 2.807 (5) Å, respectively); each Ru atom is bound to three terminal carbonyl groups, and each *tert*-butylacetylene ligand interacts with three Ru atoms via one σ-bond and two π-bonds (this bonding mode is also indicated as $\mu_3\text{-}\eta^2$) and acts as a five-electron donor. The basic structural parameters of these frameworks remain practically unchanged when compared with those found in the hydride $[HRu_3(CO)_9(C_2\text{-}t\text{-}Bu)]$,[7] in the anion $[Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]^-$,[6] and in the dimeric mercurial complex $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgBr]_2$,[1] indicating the remarkable rigidity of this framework.

The significant point of comparison between I and II is the inverse relationship between the Hg–Ru bond length and the Ru–Ru bond lengths at the bridged edge of the Ru_3 triangle, which can be understood in terms of electronegativity effects. An increase in the Ru–Ru bond length at the bridged edge of the Ru_3 triangle is also observed in comparing the structures of $Ru_3(CO)_9((CH_3)_3CC_2)^-$ [6] and $HRu_3(CO)_9[(CH_3)_3CC_2]$[7] (Table II). It appears that the more electronegative bromine atom causes more electron density to be removed from the Ru–Ru bond of the bridged edge of the Ru_3 triangle than does another Ru_3 cluster or hydrogen. The larger size of the mercury atom is not the major factor that determines the Ru–Ru bond length at the bridged edge as can be seen by comparing this bond length in I, II, and $HRu_3(CO)_9((CH_3)_3CC_2)$ (Table II).

Crystal Structure of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3]$. The structure of the complex $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3]$ (III) with the atomic numbering system is represented in Figure 3; selected bond distances and angles are given in Table III. The geometry around mercury in III is trigonal planar, angularly distorted to maintain the 61° bond angle of the Ru–Hg–Ru triangle. The two Mo–Hg–Ru angles are 148 and 150°, respectively, and the mercury atom lies 0.05 Å above the plane defined by the two Ru atoms and the Mo atom. The geometry around the molybdenum atom approximates a square-based pyramid with the cyclopentadienyl group occupying the apical position and is very similar to that found for the molybdenum atoms in many $(\eta^5\text{-}C_5H_5)Mo(CO)_3X$ compounds.[8] The mercury-bridged edge of the Ru_3 triangle is rotated approximately 60° relative to the basal plane of the square-based pyramid defined by the mercury atom and the three carbonyl groups (Figure 3). Here again, as with II, it is difficult to specify whether steric interactions between the carbonyl groups or crystal-packing considerations determine the observed conformation of the transition-metal carbonyl moieties around mercury. The Mo–Hg bond length in III is similar to that observed in other Mo–Hg–Mo systems.[8] We cannot compare Hg–Ru bond lengths in I–III since to our knowledge there is no solid-state structural data available on other Hg–Ru complexes. It is interesting to note, however, that the Ru–Hg and the mer-

Table III. Selected Bond Distances (Å) and Angles (deg) with Their Esd's for Complex III

(a) In the Coordination Sphere of the Metal Atoms			
Hg–Mo	2.743 (2)	Ru(1)–Ru(2)	2.872 (3)
Hg–Ru(1)	2.811 (2)	Ru(1)–Ru(3)	2.812 (3)
Hg–Ru(2)	2.812 (2)	Ru(2)–Ru(3)	2.818 (3)
Ru(1)–C(1)	1.88 (2)	Mo–C(16)	1.97 (2)
Ru(1)–C(2)	1.94 (3)	Mo–C(17)	1.99 (3)
Ru(1)–C(3)	1.96 (2)	Mo–C(18)	2.01 (2)
Ru(2)–C(4)	1.86 (2)	Mo–C(19)	2.36 (3)
Ru(2)–C(5)	1.97 (3)	Mo–C(20)	2.38 (3)
Ru(2)–C(6)	1.96 (2)	Mo–C(21)	2.37 (3)
Ru(3)–C(7)	1.88 (3)	Mo–C(22)	2.33 (3)
Ru(3)–C(8)	1.94 (3)	Mo–C(23)	2.29 (2)
Ru(3)–C(9)	1.90 (3)		
Ru(3)–C(10)	2.00 (2)		
Ru(1)–Hg–Mo	150.1 (1)	Hg–Ru(2)–Ru(1)	59.3 (1)
Ru(2)–Hg–Mo	148.4 (1)	Ru(1)–Ru(2)–Ru(3)	59.2 (1)
Ru(1)–Hg–Ru(2)	61.4 (1)	Ru(2)–Ru(1)–Ru(3)	59.4 (1)
Hg–Ru(1)–Ru(2)	59.3 (1)	Ru(1)–Ru(3)–Ru(2)	61.3 (1)
(b) In the Carbonyl Groups			
C(1)–O(1)	1.14 (2)	C(7)–O(7)	1.18 (2)
C(2)–O(2)	1.12 (3)	C(8)–O(8)	1.12 (3)
C(3)–O(3)	1.10 (2)	C(9)–O(9)	1.13 (3)
C(4)–O(4)	1.17 (2)	C(16)–O(16)	1.22 (3)
C(5)–O(5)	1.14 (3)	C(17)–O(17)	1.15 (3)
C(6)–O(6)	1.11 (2)	C(18)–O(18)	1.15 (3)
Ru(1)–C(1)–O(1)	178 (2)	Ru(3)–C(7)–O(7)	177 (2)
Ru(1)–C(2)–O(2)	174 (2)	Ru(3)–C(8)–O(8)	178 (3)
Ru(1)–C(3)–O(3)	177 (2)	Ru(3)–C(9)–O(9)	179 (2)
Ru(2)–C(4)–O(4)	178 (2)	Mo–C(16)–O(16)	178 (2)
Ru(2)–C(5)–O(5)	174 (2)	Mo–C(17)–O(17)	175 (2)
Ru(2)–C(6)–O(6)	175 (2)	Mo–C(18)–O(18)	174 (2)
(c) In the Organic Ligands			
C(10)–C(11)	1.34 (3)	C(12)–C(14)	1.51 (3)
C(11)–C(12)	1.46 (3)	C(12)–C(15)	1.56 (3)
C(12)–C(13)	1.53 (3)		
C(19)–C(23)	1.32 (4)	C(21)–C(22)	1.43 (4)
C(19)–C(20)	1.25 (4)	C(22)–C(23)	1.40 (4)
C(20)–C(21)	1.54 (4)		
Ru(3)–C(10)–C(11)	155 (2)	C(10)–C(11)–C(12)	140 (2)
Ru(1)–C(10)–Ru(2)	81.5 (7)	C(11)–C(12)–C(13)	114 (2)
Ru(1)–C(11)–Ru(2)	77.8 (7)	C(11)–C(12)–C(14)	110 (2)
		C(11)–C(12)–C(15)	108 (2)
C(19)–C(20)–C(21)	103 (3)	C(22)–C(23)–C(19)	111 (3)
C(20)–C(21)–C(22)	107 (3)	C(23)–C(19)–C(20)	116 (3)
C(21)–C(22)–C(23)	102 (3)		

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cury-bridged Ru–Ru bond lengths in III are much closer to the lengths of the same bonds in II than in I. This suggests that the coordination number around mercury and therefore its hybridization is not as important as electronic factors in determining the bond lengths in the Ru_2Hg triangles of I–III (Table II). We are currently extending these studies to the reaction of I with various transition-metal anions in order to test the generality of the trends reported here and the reactivity of these mixed-metal clusters.

Experimental Section

Materials. $Ru_3(CO)_{12}$ was synthesized by known literature procedures from $RuCl_3{\cdot}3H_2O$ (Matthey Bishop). The preparation of $HRu_3(CO)_9(C_2\text{-}t\text{-}Bu)$ and $[As(C_6H_5)_4][(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9]$ has been previously described.[6] $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ was purchased from Strem Chemicals. Tetrahydrofuran (THF, Mallinckrodt) was distilled from sodium benzophenone ketyl. Methylene chloride and heptane (Mallinckrodt) were dried over molecular sieves.

Spectra. ^1H NMR spectra were measured on a Varian EM360 spectrometer, and IR spectra were measured on a Perkin-Elmer IR-20. Mass spectral measurements were performed on an MS-9 spectrometer at the Jet Propulsion Laboratory, Pasadena, CA. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, New York, NY.

Synthesis of $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgX$ (X = Br, I). Ru_3CO_{12} (636 mg, 1.0 mmol) was combined with $(CH_3)_3CC{\equiv}CH$ (Farchan; 0.32 mL, 3 mmol) in heptane (600 mL) in a 1.0-L three-necked flask under a nitrogen atmosphere and refluxed for 1.5 h. The resulting pale yellow solution was evaporated to dryness and the residue taken up in 30 mL of freshly distilled THF. KOH (60 mg, 1.1 mmol) in 5 mL of absolute ethanol was then added dropwise to the THF solution while the system was maintained under an atmosphere of carbon monoxide, and the amber solution was then stirred for 1 h. HgI_2 (2270 mg, 5 mmol) in 10 mL of freshly distilled THF was added, and the reaction mixture was stirred for 0.5 h. The reaction mixture was then evaporated to dryness and extracted with hot hexanes (3 × 60 mL), concentrated to about 50 mL, and cooled to −20 °C overnight. Pure $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgI$ was obtained (770 mg, 80% based on $Ru_3(CO)_{12}$) after reconcentration (20 mL) and cooling. The bromo analogue was obtained in 40% yield overall by this method, but thin-layer chromatography (PR-254G silica gel with 1:4 methylene chloride–hexanes as eluent) was necessary to obtain pure $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgBr$ owing to the formation of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9]_2Hg$ under the reaction conditions.

Synthesis of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9]_2Hg$. To $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgI]$ (93 mg, 0.1 mmol) in 10 mL of freshly distilled tetrahydrofuran was added $[As(C_6H_5)_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]$ (100 mg, 0.1 mmol) in THF (10 mL) under a nitrogen atmosphere. Analytical thin-layer chromatography (silica gel with hexanes as eluent) showed instantaneous, complete conversion to a single fast-moving product, which was isolated by preparative thin-layer chromatography (silica gel, hexanes) to yield 145 mg of $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9]_2Hg$ (90%). Anal. Calcd: C, 24.40; H, 1.22. Found: C, 24.63; H, 1.53. IR (CH_2Cl_2): $\nu(C{=}O)$ 2066 w, 2055 m, 2035 s, 1990 m, br cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.55 (s). Mass spectral data: No parent ion was observed; the highest mass metal cluster fragment observed was m/e = 1216 (based on Ru-101), which corresponds to $Ru_6(CO)_{16}(C_6H_9)_2$ (M^+ − (Hg + 2 CO)). Crystals for the solid-state structure determination were obtained by slow recrystallization from THF at −20 °C.

Synthesis of $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3$. A 0.10 M THF solution of $Na[Mo(CO)_3(C_5H_5)]$[9] was prepared by sodium amalgam reduction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$. A 2.1-mL quantity of this solution (0.2 mmol, $Mo(\eta^5\text{-}C_5H_5)(CO)_3^-$) was added by syringe to a solution of 200 mg of $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgI$ (0.21 mmol) in THF (20 mL) under a nitrogen atmosphere. The solution was immediately evaporated to dryness, the residue was extracted with 5 mL of methylene chloride the extract was concentrated, and then products were separated by preparative thin-layer chromatography (silica gel with 1:4 methylene chloride–hexanes as eluent). Three yellow bands were eluted, and the first and third bands were identified as II and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2Hg$,[2] respectively, from their infrared spectra in methylene chloride. The middle band yielded 50 mg of $(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3$ (18%) after recrystallization from hexane at −20 °C. Anal. Calcd: C, 25.54; H, 1.31. Found: C, 25.87; H, 1.74. IR (CH_2Cl_2) $\nu(C{=}O)$ 2075 w, 2025 s, 1993 s, 1985 s, 1915 m, 1890 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.40 (9, s); 5.29 (5, s). Mass spectrum: $M^+ = m/e$ 1081 (calcd 1081.1 based on ^{101}Ru and ^{95}Mo); M^+ − Hg; M^+ − (Hg + 1–11 CO).

Crystal Structure Determination of II. A very thin yellow-orange, nearly prismatic, crystal of II, having approximate dimensions 0.05 × 0.09 × 0.25 mm, was used for the X-ray data collection. Rotation and Weissenberg photographs indicated monoclinic symmetry and gave preliminary unit cell dimensions. The same crystal was mounted and aligned on an on-line single-crystal automated Siemens AED diffractometer using niobium-filtered Mo Kα radiation (λ = 0.710688 Å) at a takeoff angle of 4°. The settings of 20 reflections with θ in the range 10–12° were determined and used to calculate the refined cell parameters. Crystal data are as follows: $C_{30}H_{18}HgO_{18}Ru_6$, M_r = 1473.47, monoclinic, a = 13.522 (8) Å, b = 17.105 (10) Å, c = 18.159 (12) Å, β = 104.79 (7)°, V = 4061 (4) Å^3, Z = 4, ρ_{calcd} = 2.41 g/cm^3, μ(Mo Kα) = 59.67 cm^{-1}, space group $P2_1/c$ from systematic absences. A complete set of intensity data was collected at room temperature within the angular range $3 \leq \theta \leq 23°$. The θ–2θ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. The scan range was ±0.5° from the peak center. A standard reflection was remeasured after every 20 reflections as a check on crystal and instrument stability; no significant change in the measured intensities of these reflections was observed during data collection. A total of 5631 independent reflections were measured of which 2322 were employed in the analysis having $I \leq 2\sigma(I)$ ($\sigma^2(I)$ = total counts + $(0.05I)^2$); the remaining 3309 were considered unobserved. The large number of unobserved reflections was due primarily to the extremely small crystal size. The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by Wilson's method.

Initial coordinates of the heavy atoms were obtained by combined direct and Patterson methods. A Fourier map, calculated with phases of the heavy atoms, revealed the positions of all other non-hydrogen atoms. Refinement was carried out by full-matrix least-squares[10] methods, first isotropically, and then anisotropically only for the Hg and Ru atoms. No attempt was made to localize the hydrogen atoms, which were placed in their geometrically calculated positions with isotropic thermal parameters (mean values of the thermal parameters of the carbon atoms to which they are bound) in the final structure factor calculation. The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after the variation of $|\Delta F|$ with respect to $|F_o|$ was analyzed. It was not considered worthwhile or necessary to attempt to improve upon the value of R by either a weighting scheme or inclusion of absorption corrections (μr was quite small). The final R value was 5.2% (observed reflections only). The atomic scattering factors (corrected for the anomalous dispersion of Hg and Ru) were taken from ref 11. The final coordinates of the non-hydrogen atoms are given in Table IV. Thermal parameters of the non-hydrogen atoms, calculated coordinates of the hydrogen atoms, and observed and calculated structure factors are available as supplementary material or from the authors on request. All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, Italy.

Crystal Structure Determination of III. A small, 0.25 × 0.25 × 0.40 mm, prismatic yellow crystal of III was mounted on a glass fiber on a eucentric goniometer head. Preliminary unit cell dimensions and space group were determined from precession and Weissenberg photographs. The crystal was transferred to a Picker FACS-1 diffractometer with the b axis of the crystal coincident with the ϕ axis of the diffractometer. Refined cell parameters were obtained by least-squares treatment with 20 reflections ($23° < 2\theta < 35°$), accurately measured with Mo Kα radiation. The crystal data are as follows: $C_{23}H_{14}O_{12}Ru_3HgMo$, M_r = 1073, a = 15.377 (11) Å, b = 12.714 (8) Å, c = 15.917 (10) Å, β = 104.12 (9)°, V = 3018 Å^3, Z = 4, ρ_{calcd} = 2.36 g/cm^3, μ(Mo Kα) = 70.34 cm^{-1}, nonstandard space group $P2_1/n$. A complete data set was collected at room

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Table IV. Fractional Atomic Coordinates ($\times 10^4$) with Their Esd's for the Non-Hydrogen Atoms for Complex II

	x/*a*	*y*/*b*	*z*/*c*		*x*/*a*	*y*/*b*	*z*/*c*
Hg	2443 (1)	2509 (1)	3612 (1)	C(4)	1697 (25)	2055 (19)	5060 (18)
Ru(1)	351 (2)	2462 (2)	2867 (1)	C(5)	1941 (29)	3671 (23)	4646 (21)
Ru(2)	983 (2)	2862 (2)	4444 (1)	C(6)	376 (30)	3195 (23)	5205 (22)
Ru(3)	−280 (2)	3866 (2)	3396 (2)	C(7)	626 (29)	4629 (22)	3253 (21)
Ru(4)	4086 (2)	2721 (1)	2921 (1)	C(8)	−810 (29)	4527 (22)	4033 (21)
Ru(5)	4385 (2)	1888 (2)	4318 (1)	C(9)	−1286 (40)	4087 (29)	2533 (31)
Ru(6)	4933 (2)	1210 (2)	3071 (2)	C(10)	4796 (30)	3029 (22)	2228 (21)
O(1)	1136 (20)	3559 (16)	1830 (15)	C(11)	3053 (32)	2282 (24)	2112 (24)
O(2)	1146 (19)	903 (15)	2456 (14)	C(12)	3523 (30)	3772 (25)	2926 (22)
O(3)	−1602 (24)	2272 (17)	1646 (17)	C(13)	5376 (35)	1320 (26)	4983 (26)
O(4)	2139 (20)	1548 (15)	5445 (14)	C(14)	3454 (28)	1057 (22)	4252 (21)
O(5)	2521 (21)	4183 (17)	4789 (15)	C(15)	4105 (23)	2500 (24)	5117 (18)
O(6)	11 (21)	3387 (16)	5690 (16)	C(16)	3841 (36)	598 (26)	2604 (26)
O(7)	1199 (24)	5109 (19)	3190 (17)	C(17)	5687 (32)	386 (26)	3561 (24)
O(8)	−1133 (22)	4925 (17)	4439 (16)	C(18)	5510 (34)	1181 (26)	2267 (26)
O(9)	−1915 (26)	4160 (19)	1949 (20)	C(19)	−535 (22)	2785 (16)	3685 (16)
O(10)	5349 (21)	3228 (16)	1844 (16)	C(20)	−298 (26)	2043 (21)	3862 (20)
O(11)	2478 (21)	1980 (15)	1622 (15)	C(21)	−736 (24)	1286 (19)	4064 (17)
O(12)	3243 (22)	4396 (18)	2935 (16)	C(22)	−917 (37)	1406 (28)	4875 (27)
O(13)	6008 (23)	971 (17)	5425 (17)	C(23)	−1780 (33)	1171 (26)	3434 (23)
O(14)	2915 (19)	545 (15)	4219 (14)	C(24)	−50 (29)	622 (22)	4047 (21)
O(15)	4002 (19)	2843 (14)	5644 (14)	C(25)	5431 (24)	2168 (18)	3647 (17)
O(16)	3088 (25)	250 (19)	2285 (18)	C(26)	5355 (24)	2801 (18)	3992 (18)
O(17)	6142 (25)	−146 (19)	3875 (18)	C(27)	6001 (30)	3487 (23)	4413 (22)
O(18)	5960 (23)	1185 (18)	1756 (17)	C(28)	5380 (34)	4134 (27)	4633 (25)
C(1)	826 (27)	3122 (21)	2244 (20)	C(29)	6798 (38)	3156 (29)	5102 (28)
C(2)	884 (25)	1493 (20)	2632 (18)	C(30)	6552 (36)	3841 (28)	3790 (26)
C(3)	−869 (36)	2311 (28)	2090 (26)				

Table V. Fractional Atomic Coordinates ($\times 10^4$) of the Non-Hydrogen Atoms with Their Esd's for Complex III

	x/*a*	*y*/*b*	*z*/*c*		*x*/*a*	*y*/*b*	*z*/*c*
Hg	2773 (1)	1698 (1)	9892 (1)	O(8)	4977 (13)	4407 (15)	13372 (13)
Mo	2883 (1)	64 (2)	8782 (1)	C(9)	4024 (17)	5734 (22)	11257 (17)
Ru(1)	2380 (1)	3810 (1)	10168 (1)	O(9)	4091 (13)	6608 (17)	11122 (13)
Ru(2)	3001 (1)	2409 (1)	11605 (1)	C(10)	2661 (14)	4097 (17)	11567 (13)
Ru(3)	3909 (1)	4307 (2)	11485 (1)	C(11)	1864 (14)	3612 (17)	11392 (14)
C(1)	3096 (15)	3883 (19)	9376 (15)	C(12)	1006 (14)	3688 (17)	11599 (14)
O(1)	3569 (12)	3934 (14)	8908 (12)	C(13)	352 (20)	2827 (23)	11195 (20)
C(2)	1298 (17)	3295 (20)	9397 (16)	C(14)	579 (16)	4746 (19)	11314 (16)
O(2)	635 (12)	3079 (14)	8942 (12)	C(15)	1169 (18)	3614 (22)	12609 (18)
C(3)	2068 (15)	5258 (19)	9946 (15)	C(16)	2062 (15)	1162 (18)	8145 (14)
O(3)	1916 (11)	6126 (15)	9826 (11)	O(16)	1570 (12)	1840 (14)	7721 (12)
C(4)	2257 (16)	1261 (19)	11528 (15)	C(17)	3251 (18)	89 (22)	7718 (19)
O(4)	1808 (13)	502 (16)	11489 (12)	O(17)	3518 (13)	176 (16)	7092 (14)
C(5)	4150 (18)	1756 (21)	11667 (17)	C(18)	4020 (16)	722 (19)	9181 (16)
O(5)	4809 (12)	1331 (15)	11636 (12)	O(18)	4756 (13)	1074 (15)	9359 (12)
C(6)	3245 (18)	2415 (22)	12854 (18)	C(19)	1719 (20)	−1279 (25)	8681 (20)
O(6)	3433 (13)	2478 (16)	13594 (13)	C(20)	1784 (21)	−853 (26)	9402 (21)
C(7)	4851 (16)	3942 (20)	11000 (16)	C(21)	2747 (21)	−1132 (27)	9897 (20)
O(7)	5426 (12)	3663 (15)	10680 (12)	C(22)	3164 (22)	−1653 (27)	9299 (22)
C(8)	4594 (18)	4389 (22)	12674 (18)	C(23)	2471 (21)	−1675 (26)	8544 (21)

temperature in the angular range 3° ≤ 2θ ≤ 47° with use of zirconium-filtered Mo Kα radiation, a takeoff angle of 4°, and the θ–2θ scan technique. A 20-s peak scan, variable 2θ scan range, 10-s stationary-counter background counts were obtained. Three standard reflections were monitored after every 50 reflections as a check on crystal and instrument stability; no significant change in these check reflections was observed. A total of 4332 independent reflections were measured, of which 3135 with $I \geq 2\sigma(I)$, where $\sigma^2(I)$ = total counts + $(0.03I)^2$, were considered to be observed. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. Because the value of μr was large, a numerical absorption correction, based on the shape of the crystal, was applied to each reflection during all least-squares refinements, after initial heavy-atom positioning.

Approximate positional parameters for the five metal atoms were obtained by combined direct and Patterson methods. A difference Fourier map with phases from the metal atoms gave several additional carbon and oxygen atom positions, but subsequent difference Fourier synthesis to locate the remaining non-hydrogen atoms gave ambiguous results. This ambiguity was due primarily to the large absorption correction required and the fact that over 90% of the scattering intensity was due to only 5 atoms out of 54 atoms total. Careful anisotropic refinement of five metal atoms and several well-positioned carbon and oxygen atoms, along with difference Fourier synthesis, revealed the remaining non-hydrogen atoms. Refinement was carried out by full-matrix least-squares techniques,[10] with anisotropic metal atoms and isotropic carbon and oxygen atoms. No attempt was made to locate hydrogens. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$; unit weights were used initially but replaced by $w = 1/\sigma^2(F)$ for the final stages of refinement. The final R value was 0.064 while R_w was 0.059 (observed reflections only). The atomic scattering factors for the neutral atoms, corrected for anomalous dispersion for Ru, Hg, and Mo, were taken from ref 11. The final coordinates of all non-hydrogen atoms are given in Table V. Thermal parameters of the non-hydrogen atoms, and observed and calculated structure factors are available as supplementary material or from the authors on request. All calculations were carried out on a Cyber 760 computer at the California State University Data Center, Los Angeles, CA.

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Registry No. I, 74436-25-2; II, 84802-26-6; III, 84802-27-7; $[(C_2\text{-}t\text{-Bu})Ru_3(CO)_9HgI]_2$, 84802-25-5; $Ru_3(CO)_{12}$, 15243-33-1; $(CH_3)_3CC{\equiv}CH$, 917-92-0; HgI_2, 7774-29-0; $[As(C_6H_5)_4][Ru_3(CO)_9(C_2\text{-}t\text{-Bu})]$, 76741-75-8; $Na[Mo(CO)_3(C_5H_5)]$, 12107-35-6; $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2Hg$, 12194-13-7.

Supplementary Material Available: Listings of calculated coordinates of the hydrogen atoms for complex II and thermal parameters and observed and calculated structure factor amplitudes of complex II and complex III (30 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Tetramercury Bis(hexafluoroarsenate), $Hg_4(AsF_6)_2$

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The preparation of $Hg_4(AsF_6)_2$ from Hg and AsF_5 in SO_2 solution is described. An X-ray crystallographic determination has shown that crystals of $Hg_4(AsF_6)_2$ are monoclinic, space group $P2_1/c$, with $a = 5.489$ (2) Å, $b = 11.633$ (4) Å, $c = 9.850$ (6) Å, $\beta = 92.20$ (4)°, $V = 628.5$ (5) Å^3, and $d_{calcd} = 6.24$ g cm^{-3} for $Z = 2$. To a first approximation the compound may be described as consisting of almost linear Hg_4^{2+} ions and octahedral AsF_6^- ions. However, there are relatively short interactions between the Hg_4^{2+} ions such that they form nonlinear chains running through the crystal.

Introduction

Oxidation of liquid mercury with a limited amount of arsenic pentafluoride in solution in liquid sulfur dioxide at room temperature leads to the formation of a deep red solution in equilibrium with the insoluble golden yellow metallic compound $Hg_{3-\delta}AsF_6$.[1] The deep red solution contains the Hg_4^{2+} and Hg_3^{2+} cations.[2] The overall reaction between the stoichiometric amounts of reactants needed to give the Hg_4^{2+} ion may be represented by

$$4Hg + 3AsF_5 \rightarrow Hg_4(AsF_6)_2 + AsF_3$$

However, it is probably not possible to obtain pure solutions of $Hg_4(AsF_6)_2$, which always appears to be in equilibrium with the insoluble compound $Hg_{3-\delta}AsF_6$ and $Hg_3(AsF_6)_2$ in solution

$$3Hg_4^{2+} + 2AsF_6^- \rightarrow 2Hg_3^{2+} + 2Hg_{3-\delta}AsF_6(s)$$

On crystallization, the deep red solution yielded crystals of $Hg_3(AsF_6)_2$ and red-black crystals of $Hg_4(AsF_6)_2$. The preparation and crystal structure of $Hg_3(AsF_6)_2$ have been previously described,[2] and a preliminary communication on the preparation, structure, and NMR and UV spectra of $Hg_4(AsF_6)_2$ has been published.[3] In this paper we give a full account of the determination of the structure of $Hg_4(AsF_6)_2$.

Experimental Section

Reactions were carried out under vacuum in flame-sealed double-bulb ampules fitted with medium glass frits. Sulfur dioxide (Matheson) was repeatedly distilled from, and stored over, phosphoric oxide before use. Arsenic pentafluoride was prepared directly from the elements.

Preparation of $Hg_4(AsF_6)_2$. Arsenic pentafluoride (2.96 g, 17.4 mmol) was condensed onto elemental mercury (4.658 g, 23.2 mmol) in ~10 mL of liquid sulfur dioxide at −196 °C, and the mixture was allowed to warm up to room temperature. A deep red solution containing the insoluble gold crystalline compound $Hg_{3-\delta}AsF_6$ was obtained after stirring for a few hours. The red solution was filtered, and the solvent was slowly distilled off under reduced pressure over a period of 1 week to give a mixture of yellow crystals $Hg_3(AsF_6)_2$ and red-black needle-shaped crystals $Hg_4(AsF_6)_2$.

X-ray Crystallography. The dark red needles of $Hg_4(AsF_6)_2$ were separated from the yellow crystals of $Hg_3(AsF_6)_2$ and were sealed in dry Lindemann capillaries under a dry nitrogen atmosphere in a dry box equipped with a microscope. Although visually the crystals appeared to be well-formed needles, many were not single. Preliminary precession photographs were used to give cell and symmetry information, and the following crystal data were then established with use of Mo K$\bar{\alpha}$ radiation on a Syntex P2$_1$ diffractometer (graphite monochromator).

Crystal Data for $Hg_4(AsF_6)_2$: fw = 1179.8; monoclinic; space group $P2_1/c$; $a = 5.489$ (2) Å, $b = 11.633$ (4) Å, $c = 9.850$ (6) Å, $\beta = 92.20$ (4)°, $V = 628.5$ (5) Å^3, and $d_{calcd} = 6.24$ g cm^{-3} for $Z = 2$; Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å); μ(Mo K$\bar{\alpha}$) = 553 cm^{-1}.

The crystal used throughout was a thin needle defined by the forms {011} and the approximate faces (301) and ($\bar{3}$01), which were respectively 0.0033, 0.014, and 0.014 cm from an origin within the crystal. Unit cell dimensions for this crystal were obtained by using a least-squares fit of 2θ, ω, and χ for 14 high-angle ($23 < 2\theta < 30°$) reflections on the diffractometer. Intensity data were measured by using θ–2θ scans over a scan range (Kα_1 − 1.2°) to (Kα_2 + 1.2°) with variable scan rates of 2.0–29.3° min^{-1} dependent on the intensity of a 2-s prescan. Stationary-background counts were recorded at each end of the scan, each for one-fourth of the scan time. Two standard reflections, which were monitored after every 48 reflections collected, showed no significant variations over the period of the data collection. A total of 1834 reflections (including standards) in the quadrants ($h,k,\pm l$) with $2\theta < 55°$ was eventually collected.

Lorentz and polarization corrections were applied to all reflections. At a later stage in the refinement several calculations of the absorption corrections were made so that the crystal shape and size were optimized. For the crystal dimensions above, the calculations using the program ABSORB[4] and a 10 × 7 × 7 Gaussian grid gave a range of A^* values from 26.42 to 9.93. After removing systematically absent and zero F_o data and averaging several equivalent reflections ($R_{merge} = 0.039$), we obtained a final data set of 1207 reflections; of these, 629 were considered observed ($I/\sigma(I) > 3.0$).

Solution and Refinement of the Structure. With $Z = 2$ in the space group $P2_1/c$, the Hg_4^{2+} cation has crystallographic imposed inversion symmetry. The positions of the heavy atoms in the unit cell were found by inspection of the three-dimensional Patterson function. Least-

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