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STUDIES ON MAIN GROUP METAL-TRANSITION-METAL BONDED COMPOUNDS. 6. THE STRUCTURE OF η^5-$C_5H_5(CO)_3MoHgCl$

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ABSTRACT

The crystal structure of η^5-$C_5H_5(CO)_3MoHgCl$ has been determined from single crystal X-ray data collected by counter methods. The compound crystallizes in space group $P\bar{4}2_1c$ with 8 molecules per unit cell and lattice constants of a = 12.014(4), c = 15.322(7). Full-matrix least squares refinement gave discrepancy factors R_1 = 0.058 and R_2 = 0.062 for 854 data with $I > 3\sigma(I)$. The critical bond lengths and angles are Mo-Hg = 2.673(3)Å, Hg-Cl = 2.437(8)Å, and Mo-Hg-Cl = 160.0(2)°. Crystals of η^5-$C_5H_5(CO)_3WHgBr$ were shown to be isomorphous with lattice constants of a = 12.068(4)Å and c = 15.643(7)Å.

INTRODUCTION

In a continuation of our studies on compounds containing main group metal-transition-metal bonds we have determined the crystal structure of the compounds $Cp(CO)_3MoHgCl$ (Cp = $\eta^5C_5H_5$) by single crystal X-ray diffraction techniques.[1] The coordination about Hg is of particular importance in view of the variety of species found for the corresponding zinc derivatives in which halide bridged and monomeric derivatives have been observed,[1,2,3] and the wide variation in coordination about mercury.[4]

EXPERIMENTAL

The compounds $[Cp(CO)_3Mo]_2Hg$ and $[Cp(CO)_3W]_2Hg$ were prepared by the procedures outlined by King and Stone.[5] Elemental analysis for the tungsten compounds was 22.17% C; 1.35% H (calculated: 22.07% C; 1.16% H).* A simple exchange process between the transition metal complex and the appropriate mercuric halide produced the title compound.[6] For the preparation of $Cp(CO)_3WHgBr$ 2.7 g (2.5 mmol) of $[Cp(CO)_3W]_2Hg$ (MW = 866.5) and 0.90 g (2.5 mmol) of $HgBr_2$ (MW = 360.4) were mixed in THF (10 ml). The solvent was removed following extended mixing and the yellow residue was recrystallized from ethanol. The melting point of the resulting crystals was 208° (reported 207°)[6]. A similar procedure yielded the molybdenum derivative $Cp(CO)_3MoHgCl$.

X-Ray Data Collection for $Cp(CO)_3MoHgCl$

Crystals of $Cp(CO)_3MoHgCl$ were obtained by slow evaporation of saturated ethanol solutions and mounted on glass fibers with epoxy cement. The dimensions of the crystal of $Cp(CO)_3MoHgCl$ used for the structural determination were 0.027 x 0.017 x 0.028 cm^3. The X-ray data were collected on a Syntex $P2_1$ computer controlled four circle diffractometer. Oscillation and rotation photographs indicated the tetragonal crystal system; this was verified on a precession camera. Lattice constants were obtained by least-squares refinement of 15 reflections obtained with MoK_α radiation (0.71069Å) using a programmed centering routine;[7] they were a = 12.014(4)Å, c = 15.322(7)Å, z = 8, $\mu = 152\ cm^{-1}$.

Intensity data were collected using MoK_α radiation which had been monochromatized with a graphite crystal. The data indicated the space group $P\overline{4}2_1c$ with systematic absences of hhl : l = 2n + 1 and h00 : h = 2n + 1. The θ-2θ scan technique was used with scan rate inversely proportional to peak height and varying between 2 and 24°/min. Background counts of 0.5 times the scan time were taken with a scan range from $2\theta MoK_{\alpha_1} - 1.0°$ to $2\theta MoK_{\alpha_2} + 1.0°$. The intensities of three standard reflections were measured every 50 reflections as a check on crystal and electronic stability. The

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*Midwest Microlab, Ltd., Indianapolis, Indiana standards did not show appreciable variation and no correction for decay was applied.

The data were reduced to I and $\sigma(I)$ by procedures previously described. Standard deviation on intensities were assigned as:

$$\sigma(I) = [\sigma_{counter}\ (I)^2 + (0.041)^2]^{1/2}$$

where $\sigma_{counter} = (I + k^2B)^{1/2}$, I = net intensity, B = total background counts, and k is the ratio of scan time to background counting time.[7] Absorption corrections were made on the previously mentioned geometry; the range of transmission factors was 0.03 to 0.13. Of the 1940 data examined ($2\theta < 60°$) there were 854 reflections with $I > 3\sigma$ (I). Measured density by flotation was 2.86(3) g-cm^{-3} and the calculated density was 2.894 g-cm^{-3} based on eight molecules per unit cell. Direct methods gave the Hg and Mo positions.[7] Least-squares refinement of the atomic positions resulted in very large thermal parameters and unrealistic distances for the cyclopentadienide ring. The cyclopentadienide ring then was refined as a rigid group with carbon-carbon distances of 1.40Å, carbon-hydrogen distances of 1.00Å, and internal angles of 108°. Final group least-squares refinement of the total of 119 parameters g

$$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.058 \text{ and}$$

$$R_2 = [\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2]^{1/2} = 0.062.$$

The largest shift in the final cycle of group least-squares refinement was 30% of an estimated standard deviation. Isotropic thermal parameters for the hydrogens were set at values 10% larger than those of the attached carbon atoms. Real and imaginary anomalous scattering corrections were included for Hg, Mo, and Cl. The error of fit was 1.77. The highest residual electron density in the final Fourier difference map was 1.66a/Å^3 and occurred in the area between the mercury and the molybdenum atoms. This high electron density may arise from the inadequacy of the absorption correction.

Table I is a listing of atomic coordinates, thermal parameters, and group

TABLE I

A List of Atomic Parameters for $Cp(CO)_3MoHgCl$ [a]

	x	y	z	B(Å)
Hg	0.4048(1)	0.3575(1)	0.1035(1)	
Mo	0.2098(2)	0.2670(2)	0.1481(2)	
Cl	0.6051(7)	0.3873(7)	0.0948(6)	
O(1)	0.1464(26)	0.4764(28)	0.0396(26)	
O(2)	0.0260(25)	0.3671(25)	0.2629(29)	
O(3)	0.3297(23)	0.3089(24)	0.3233(19)	
C(1)	0.1751(29)	0.4114(34)	0.0865(27)	
C(2)	0.0973(32)	0.3339(29)	0.2278(41)	
C(3)	0.2901(26)	0.3008(28)	0.2567(27)	
C(4)	0.0887	0.1248	0.1004	4(1)
C(5)	0.1407	0.1562	0.0254	9(1)
C(6)	0.2559	0.1373	0.0334	8(1)
C(7)	0.2729	0.0927	0.1168	7(1)
C(8)	0.1674	0.0861	0.1564	8(1)

Final Group Least-Squares
Parameters for $Cp(CO)_3MoHgCl$

Basis X = 0.089(2)
Basis Y = 0.125(2)
Basis Z = 0.100(2)
Phi = -2.78(5)
Theta = -1.99(2)
Rho = -2.69(5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.0060(1)	0.0075(1)	0.0045(1)	-0.0020(1)	0.0005(1)	0.0005(1)
Mo	0.0055(2)	0.0052(2)	0.0040(1)	-0.0007(2)	0.0003(2)	0.0004(2)
Cl	0.0057(6)	0.0085(7)	0.0041(4)	-0.0012(5)	-0.0002(5)	0.0009(5)
O(1)	0.0117(30)	0.0162(40)	0.0141(28)	-0.0061(28)	-0.0043(26)	0.0109(31)
O(2)	0.0100(31)	0.0100(30)	0.0154(33)	-0.0019(24)	0.0035(28)	-0.0037(29)
O(3)	0.0126(30)	0.0126(31)	0.0052(15)	-0.0047(26)	0.0019(19)	-0.0013(20)
C(1)	0.0060(27)	0.0094(36)	0.0058(24)	-0.0023(27)	-0.0005(21)	0.0026(26)
C(2)	0.0044(26)	0.0053(29)	0.0157(51)	-0.0000(24)	0.0025(32)	0.0008(30)
C(3)	0.0063(28)	0.0069(29)	0.0048(18)	-0.0015(22)	-0.0001(21)	-0.0017(21)

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[a] The anisotropic thermal parameters were of the form exp $\{-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})\}$.

The estimated standard deviations of the last digit(s) are given in parentheses throughout this paper.

least-squares parameters. A listing of the observed and calculated structure factors is available from the authors on request.

A single crystal structure determination of $Cp(CO)_3WHgBr$ was also carried out. The lattice constants were a = 12.068(7)Å and c = 15.643(7)Å. The compound was found to be isomorphous with the $Cp(CO)_3MoHgCl$. The presence of tungsten, mercury, and bromine atoms in this compound resulted in such a lack of precision that no chemically interesting conclusions beyond the isostructuralism can be drawn, so this structure is not reported. Details of this structure are available in the Ph.D. dissertation of Michael J. Albright.[8]

Crystal Structure of $Cp(CO)_3MoHgCl$

The crystal structure of $Cp(CO)_3MoHgCl$ consists of discrete molecular units which are stacked along the screw axis so that each mercury has two

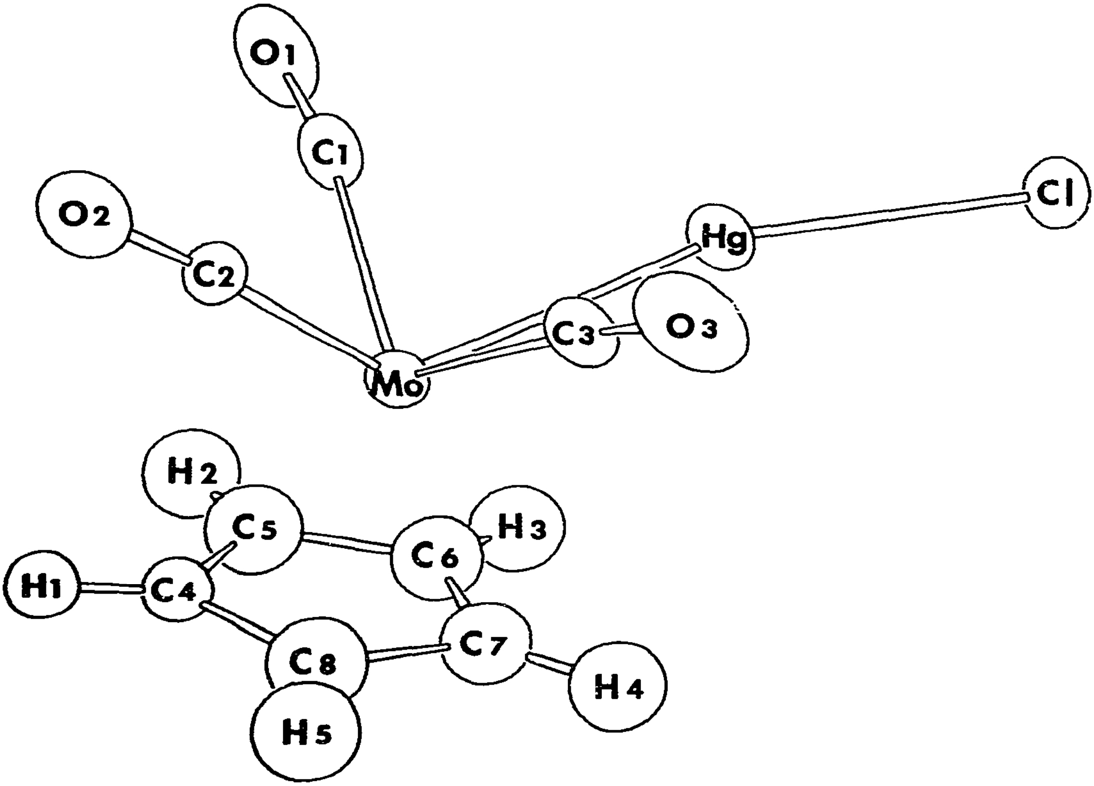

Figure 1 A perspective view of the $Cp(CO)_3MoHgCl$ molecule with the labeling scheme.

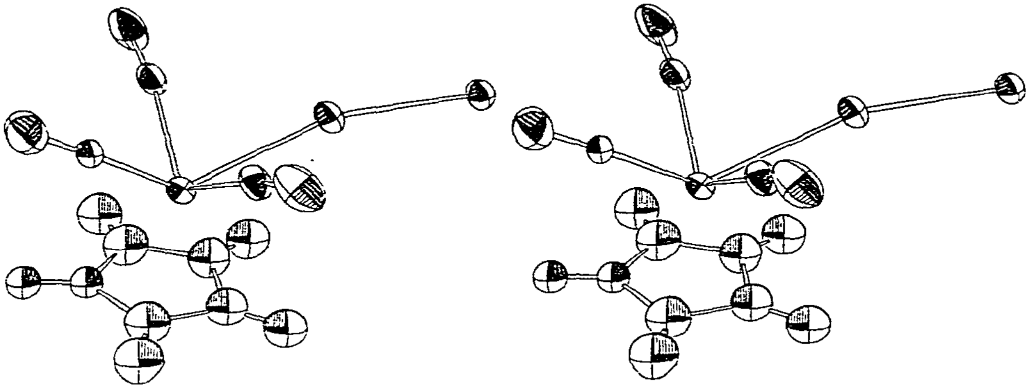

Figure 2 A stereoscopic view of the $Cp(CO)_3MoHgCl$ molecule. The atoms are represented by 50% probability thermal ellipsoids

additional chloride atoms at long, but interacting distances. A perspective view of a single molecule, including the atom labeling scheme, is shown in Figure 1. A stereoscopic view of a molecule of $Cp(CO)_3MoHgCl$ is shown in Figure 2. Intramolecular bond distances and bond angles are given in Table II.

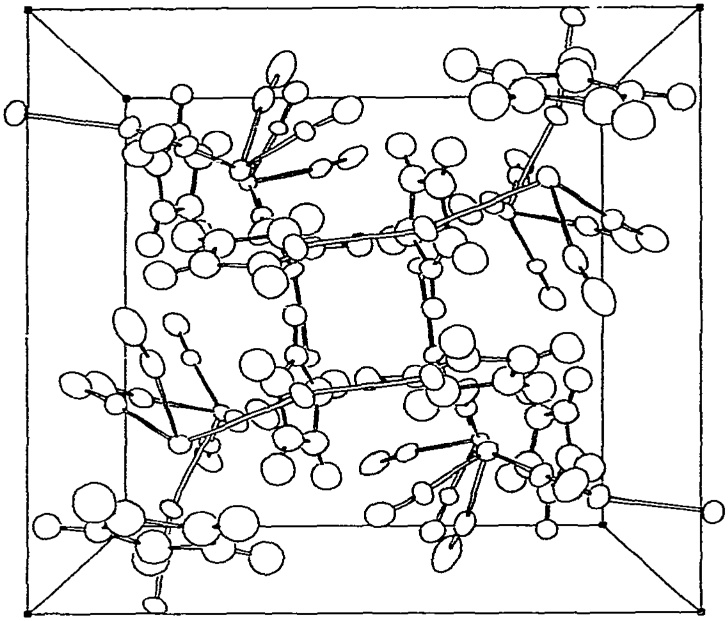

Figure 3 Packing of the $Cp(CO)_3MoHgCl$ unit cell looking down the screw axis.

TABLE II

Interatomic Distances (Å) and Angles (degrees) for $Cp(CO)_3MoHgCl$ [a]

Atoms	Distance	Atoms	Angle
Hg-Mo	2.673(3)	Mo-Hg-Cl	160.0(2)
Hg-Cl	2.437(8)		
		Hg-Mo-C(1)	73.(1)
Mo-C(1)	2.02(4)	Hg-Mo-C(2)	126.(1)
Mo-C(2)	1.99(5)	Hg-Mo-C(3)	73.(1)
Mo-C(3)	1.97(4)		
		Mo-C(1)-O(1)	165.(4)
C(1)-O(1)	1.12(4)	Mo-C(2)-O(2)	171.(5)
C(2)-O(2)	1.09(4)	Mo-C(3)-O(3)	171.(3)
C(3)-O(3)	1.13(4)		
		C(1)-Mo-C(2)	79.
Mo-C(4)	2.36	C(2)-Mo-C(3)	74.
Mo-C(5)	2.47	C(3)-Mo_C(1)	110.
Mo-C(6)	2.44		
Mo-C(7)	2.29	Cl-Hg-Cl'	83.6(3)
Mo-C(8)	2.24	Cl-Hg-Cl''	89.5(3)
		Cl-Hg-C(3)	124.5(7)
Hg Cl'	3.072(9)	O(3)-C(3)-Hg	122.(3)
Hg Cl''	3.078(9)		
Hg C(1)	2.85(4)		
Hg C(3)	2.81(4)		
Hg Hg'	4.118(2)		
Hg Hg''	4.303(5)		
Cl Cl'	3.70(2)		
Cl Cl''	3.91(2)		
Cl Cl'''	3.91(2)		

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[a] The symmetry operators used in this table are: single prime('): 1-x, 1-y, z
double prime(''): y, 1-x, -z
triple prime('''): 1-y, x, -z

The coordination around the transition metal is consistent with earlier reports of the $Cp(CO)_3Mo$ and $Cp(CO)_3W$ moieties.[9] The transition metal may be regarded formally as seven coordinate with the cyclopentadienyl ring occupying three coordination positions, the carbonyl groups three positions and the mercury atom the final position. The latter four ligands are displaced ±0.06Å from their mean plane, such that these ligands and the center of the ring form a pseudo-square pyramid structure. The plane of the ring and the mean plane containing the four donor atoms of the other ligands are parallel. The dihedral angle between these planes is 1.8°. Alternatively, one may

TABLE III

Selected Metal-Metal or Metal-Atom Distances in Compounds Containing the $Cp(CO)_3Mo$ and $Cp(CO)_3W$ Moieties

Compound	M-M' Distance (Å)	Bond Shortening (Å) Relative to Sums of Metal Radii
$[Cp(CO)_3Mo]_2Zn$	2.538(1)[a]	0.26 - 0.36
$[Cp(CO)_3MoZn.Cl.Et_2O]_2$	2.632(1)[a]	0.17 - 0.27
$[Cp(CO)_3Mo]ZnBr.2THF$	2.711(1)[b]	0.09 - 0.19
$Cp_2MoH_2.ZnBr_2.DMF$	2.793(3)[c]	0.01 - 0.11
$[Cp(CO)_3Mo]_2$	3.235[d] 3.222[e]	----
$Cp(CO)_3MoEt$	2.38 (Mo-C)[f]	----
$Cp(CO)_3MoHgCl$	2.673(3)	0.13 - 0.23
$Cp(CO)_3WGaMe_2$	2.708(3)[g]	0.05 - 0.15
$[Cp(CO)_3W]_3Ga$	2.739[h]	0.02 - 0.12
$[Cp(CO)_3W]_2$	3.222[i]	----
$Cp(CO)_3WHgBr$	2.698(4)[j]	0.1 - 0.2

[a] Reference 2
[b] Reference 3
[c] Reference 1
[d] Reference 9a
[e] Reference 9b
[f] Reference 9c
[g] Reference 9d
[h] Reference 9e
[i] Reference 9a
[j] Reference 8

consider the plane of the three carbonyl carbon atoms, which forms a dihedral angle of 4.1° with the plane of the Cp group and from which the Hg atom is displaced 0.27Å toward the Cp ring.

In $Cp(CO)_3MoHgCl$ the Hg-Mo distance is 2.673(3)Å and the Hg-Cl distances are 2.437(8)Å, 3.072(9)Å and 3.078(9)Å with the latter two distances to chlorine atoms in adjacent molecules. The Mo-Hg-Cl angle to the bound chlorine atom is 160.0(2)°. In $Cp(CO)_3WHgBr$[8] the W-Hg distance is 2.698(4)Å and the Hg-Br distances are 2.565(8)Å, 3.132(8)Å and 3.174(9)Å. The non linearity of the M-Hg-X bond is most likely the result of the secondary halogen interactions, as indicated in the packing diagram. The mercury-halogen distances are comparable to those observed in HgCl ,[10,11] and the methylmercuric halides.[12,13,14]

The metal-metal distances determined in this work and from a number of papers are summarized in Table III. Examination of these data shows that the observed transition metal to mercury or zinc distances are substantially shorter than predicted by the addition of the metal radii determined from metal-carbon or from the single homoatomic metal-metal bond distances. Further if one examines the data presented in the Table for the zinc derivatives it shows that there is a significant increase in proceeding from the linear bis molybdenum derivative to the tetrahedral bridged species and finally to the monomeric derivative with the strongly coordinating THF molecules. Examination of the Hg-Mo bonded species again shows "bond shortening" of 0.13 - 0.23Å depending on the choices made for the radii of mercury and molybdenum atoms.

Similar results, although based on fewer data, are observed for the tungsten-metal bonds with the Hg-W bond distance 0.1 - 0.2Å shorter than the predicted value. In the derivatives containing Ga-W bonds the bond shortening appears to be smaller as one might expect for these tricoordinate systems.

It has been suggested by several authors[15] that this bond shortening is a result of dπ → pπ back bonding from the filled transition metal d orbitals to the vacant p orbitals on the main group. This explanation is in qualitative accord with observations made in this work. The greatest bond shortening occurs in the linear derivatives of zinc in which the p orbitals may overlap the d orbitals of the transition metal more effectively. Alternative explanations involving bond shortening due to charge separation might also be invoked. In any event the bond shortening appears to be a general effect observed between main group-transition metal bonded compounds and is predicted to occur in the cadmium derivatives as well as on the basis of these observations.

A more detailed explanation must await additional experimental results in which a series of similar derivatives are compared as a function of the main group metal (for examples a series Zn, Cd, Hg) with all other factors remaining fixed and in a series in which the main group element is constant with variations of the transition metal and of the substituents on it.

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