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SYNTHESIS OF HETERONUCLEAR CARBONYL COMPLEXES (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgX (X = Cl, Br, I, SCN). CRYSTAL STRUCTURE OF (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgCl

M. CANO *, R. CRIADO, E. GUTIERREZ-PUEBLA, A. MONGE and M.P. PARDO

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid (Spain) and Instituto de Química Inorgánica Elhuyar C.S.I.C., Serrano 113, 28006-Madrid (Spain)

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Summary

Mercury(II) chloride in refluxing methanol or acetone cleaves the molybdenum–tin bond of π-methylcyclopentadienylmolybdenum tricarbonyl triphenylstannyl [(η^5-$C_5H_4CH_3$)$(CO)_3$MoSnPh$_3$] to give (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgCl. The same product was also obtained by reaction of [(η^5-$C_5H_4CH_3$)$(CO)_3$Mo]$_2$Hg with $HgCl_2$ in acetone at room temperature. Similar reactions have given bimetallic complexes of the type (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgX (X = Br, I, SCN). The new complexes are air-stable crystalline solids. The structure of the compound (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgCl has been determined. It crystallizes in space group $P2_1/c$ with $Z = 4$, a 6.613(2), b 13.647(4), c 13.257(4) Å, β 101.85(3)°, D_c 2.81 g/cm^3, $F(000) = 896$, μ(Mo-K_α) 143.56 cm^{-1}. Final $R = 0.055$ for 1696 observed reflexions.

Introduction

The chemistry of organometallic compounds containing with transition-metals bonded to Group IVA elements has received much attention recently. The carbonyl cyclopentadienyl derivatives of Mn, Fe, Mo and W are particularly stable, and so suitable for mechanistic investigations, and kinetic studies have been made on cleavage by iodine of the metal–metal bonds in complexes of the type: [M(Cp)$_n$(CO)$_m$(MR$_3$)], where M′ = transition metal and M = Sn, R = Me, Bu or Ph [1–6]. The process involves electrophilic substitution at the transition metal, and changes in the groups on tin or in the ligand attached to the transition metal affect the reactivity [3].

Iodine cleavages the transition metal–tin bond in the compounds Mo(η^5-C_5H_5)$(CO)_3$SnMe$_3$, Mn$(CO)_5$(SnMe$_3$), Fe(η^5-C_5H_5)$(CO)_2$(SnMe$_3$), and their SnBu$_3$ analogues [3]. In this reaction increase in the electron-donating power of R enhances the reactivity; thus the triphenyltin compounds are less reactive than the trimethyltin compounds.

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The products isolated from the reactions between iodine and $Mn(CO)_5SnPh_3$ [4] or $[(\eta^5\text{-}C_5H_5)(CO)_3MoSnPh_3]$ [3] result from both phenyl–tin and transition metal–tin bond cleavage. For $[(\eta^5\text{-}C_5H_4)(CO)_3MoSnPh_3]$ the effect of the introduction of a methyl group into the cyclopentadienyl ligand has also been examined, and found to lead to double cleavage of molybdenum–tin and phenyl–tin bonds. In addition the compound $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3]$ reacts with iodine 2.6 times more readily than the analogous $\eta^5\text{-}C_5H_5$ derivative, confirming that electron supply enhances the reactivity [3].

Cleavage of tin–transition metal bonds by mercury (II) halides is similar to that by iodine [7]. With the $SnMe_3$ derivatives mercury halides cleave tin–transition metal bonds, whereas with $Mn(CO)_5(SnPh_3)$ or $Fe(\eta^5\text{-}C_5H_5)(CO)_2(SnPh_3)$, mercury(II) bromide cleaves only the phenyl–tin bonds [7,8].

We describe below a study of the reactions of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3]$ with $HgCl_2$ and $HgBr_2$ (reaction 1). Roberts has identified the products of reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoSnMe_3]$ with mercury(II) halides, as $(\eta^5\text{-}C_5H_5)(CO)_3MoHgX$ [9]. We have prepared a number of η^5-methylcyclopentadienylmolybdenum-mercury complexes of the type $(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgX$ (X = Cl, Br, I or SCN) by exchange reactions between $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]_2Hg$ and HgX_2. This method also has previously been used for the analogous cyclopentadienyl derivatives [10].

Results and discussion

Compounds of the general formula $(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgX$ were prepared in two ways: (a) By cleavage of molybdenum–tin bonds in the reaction of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3]$ with mercury(II) halides, and (b) by exchange between $[(\eta^5\text{-}C_5H_4CH_3(CO)_3Mo]_2Hg$ and mercury(II) halides.

(a) Reaction of the compound $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3]$ with mercury(II) halides

Refluxing of a solution of $HgCl_2$ and the organometallic compound in methanol gave a product which was shown (IR, melting point) to be the same as that obtained by reaction of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]_2Hg$ and $HgCl_2$ (Table 1 and 2).

TABLE 1

ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES FOR THE NEW COMPOUNDS

Compound	Colour	Yield (%)	Elemental Analyses (Found(calcd.)(%))		M.p. (°C)	Conductivity [a] M (ohm^{-1} cm^2 mol^{-1})
			C	H		
$[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]_2Hg$	yellow-orange	60.2	30.06 (30.08)	1.48 (1.94)	163	1.47
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgCl$	yellow	59.8	21.82 (21.83)	1.24 (1.41)	132-134	0.60
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgBr$	yellow	48.9	19.90 (20.02)	1.12 (1.29)	142	[b]
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgI$	yellow-orange	49.7	18.21 (18.41)	1.05 (1.19)	135	0.24
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgSCN$	yellow	52.3	22.90 (23.19)	1.20 (1.30)	122	0.43

[a] In $C_6H_5NO_2$ at 22°C for concentration ca. 10^{-3} M. [b] Insoluble.

TABLE 2

INFRARED AND NMR SPECTRAL DATA

Compound	ν(CO) (cm^{-1}) ^{a}			ν(Hg–X) ^{b}	NMR ^{c} (ppm)	
					δ(CH$_3$)	δ(C$_5$H$_4$)
$[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]_2Hg$	1870 vs	1886 s	1950 vs		2.05 s	5.45 m
	1870 sh	1896 sh	1965 sh			5.65 m
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgCl$	1916 vs	1930 sh	2000 vs	266 vs	2.05 s	5.65 m
						5.90 m
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgBr$	1890 vs	1922 sh	1996 vs		2.01 s	5.50 m
						5.78 m
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgI$	1884 vs	1816 sh	1992 vs		2.0 s	5.43 m
						5.66 m
$(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgSCN$	1892 vs	1926 sh	2000 vs	240 vs	2.0 s	5.43 m
			2110 ν(SCN)			5.71 m

^{a} Recorded in the 4000–400 cm^{-1} region with KBr discs. ^{b} 400–200 cm^{-1} region with Nujol mulls. ^{c} Relative to Me$_4$Si, measured in DMSO.

The product $(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgCl$, the structure of which is shown in Fig. 1, has a mercury atom coordinated to molybdenum. The IR spectrum of the reaction solution, indicated that this compound was the dominant carbonyl-containing product formed.

Such cleavage of the Mo–Sn bond does not occur for the complexes $[(\eta^5\text{-}C_5H_5)(CO)_2FeSnPh_3]$ and $Mn(CO)_5(SnPh_3)$; for these $HgBr_2$ cleaves the tin–phenyl bonds only.

These reactions can be understood using the concepts of hard and soft acids and bases [8]. Electrophilic attack of mercury(II) halide on either the transition metal or

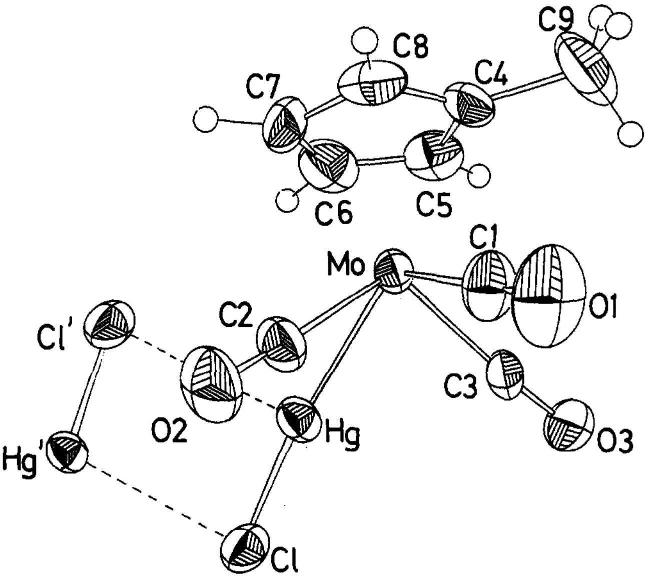

Fig. 1. Structure of $(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoHgCl$, with atom numbering scheme.

TABLE 3

BOND LENGTHS (Å) AND PRINCIPAL BOND ANGLES (°) IN (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgCl (e.s.d. in parentheses)

Mo–Hg	2.680(2)	Hg–Mo–C(1)	128.0(5)
Mo–C(1)	2.00(2)	Hg–Mo–C(2)	72.5(4)
Mo–C(2)	2.01(1)	Hg–Mo–C(3)	72.33(5)
Mo–C(3)	1.98(2)	C(1)–Mo–C(2)	79.1(7)
Mo–C(4)	2.32(2)	C(1)–Mo–C(3)	79.1(7)
Mo–C(5)	2.35(2)	C(2)–Mo–C(3)	111.2(6)
Mo–C(6)	2.35(2)	Mo–Hg–Cl	172.0(1)
Mo–C(7)	2.34(2)	Cl–Hg...Cl [a]	82.2(2)
Mo–C(8)	2.31(2)	Mo–C(1)–O(1)	171.0(2)
		Mo–C(2)–O(2)	176.0(1)
C(1)–O(1)	1.13(2)	Mo–C(3)–O(3)	176.0(1)
C(2)–O(2)	1.14(2)		
C(3)–O(3)	1.16(2)		
C(4)–C(5)	1.41(2)		
C(4)–C(8)	1.42(3)		
C(4)–C(9)	1.51(3)		
C(5)–C(6)	1.38(3)		
C(6)–C(7)	1.35(3)		
C(7)–C(8)	1.42(3)		
Hg–Cl	2.398(5)		
Hg...C(1) [a]	3.053(4)		
Hg...C(2)	2.82(2)		
Hg...C(3)	2.81(2)		

[a] $1-x, -y, -z$.

aromatic carbon can in principle result in Sn–Ph or transition metal–Sn bond cleavage, and so there is competition between the molybdenum and the aromatic carbon which depends on the softness of the two centres present. The cyclopentadienyl is a weaker donor ligand than CO, and attaching a methyl group to this ligand should increase the softness of the molybdenum centre, and so fission of the Mo–Sn bond might be favoured.

The analogous reaction with $HgBr_2$ gives (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgBr through cleavage of the Mo–Sn bond.

Figure 1 shows the geometry of the organometallic (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgCl and the atom numbering [11]. Table 3 gives the bond lengths and angles. The molecular structure is quite similar to that (η^5-C_5H_5)$(CO)_3$MoHgCl [12]. The Mo atom is seven-coordinate, with the aromatic ring occupying three coordination positions and the mercury atom the seventh position.

The three C atoms of the carbonyl groups and the Hg atom are displaced by ±0.05 Å from their best least-squares plane. This plane is virtually parallel to the plane of the ring. The dihedral angle between the planes is 2°. The coordination polyhedron can be considered as a pseudo-square pyramid with the centre of the ring in the apical position. The plane of the three carbonyl groups carbon atoms forms a dihedral angle of 6.3° [12], with the plane of the $C_5H_4CH_3$ ligand.

The distances Hg–Mo 2.680(2), Hg–Cl 2.398(5) and Hg–Cl 3.053(4) Å are similar in (η^5-C_5H_5)$(CO)_3$MoHgCl [12]. In that compound, in addition to the Hg–Cl bond there is an interaction between the Hg atom and two chlorine atoms of neighbouring molecules. A similar interaction is observed in our compound, (η^5-$C_5H_4CH_3$)-$(CO)_3$MoHgCl, but in this case only between the Hg and one chlorine atom of a neighbouring molecule. The difference is attributable to the difference in the crystal packing probably because of the presence of the methyl group in our compound.

The distances C(9)–C(1) 3.42(3), C(9)–C(2) 3.92(3), C(9)–C(3) 3.72(4) and C(9)–Hg are > 5 Å, and the torsion angles C(1)–Mo–C(4)–C(9) 31° (2), C(2)–Mo–C(4)–C(9) −48° (2), C(3)–Mo–C(4)–C(9) 106° (2) and Hg–Mo–C(4)–C(9) −127° (1) show that the methyl group is situated as far as possible from the Hg–Cl ligand.

(b) Reactions of the compound [(η^5-$C_5H_4CH_3$)$(CO)_3$Mo]$_2$Hg with mercury(II) halides

Some η^5-methylcyclopentadienylmolybdenum-mercury complexes of the type (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgX (X = Cl, Br, I, SCN) were obtained by exchange between [(η^5-$C_5H_4CH_3$)$(CO)_3$Mo]$_2$Hg and HgX_2 in acetone. The reaction takes place immediately at room temperature.

The new complexes and some of their physical properties are listed in Table 1. They are air-stable crystalline compounds, moderately soluble in polar organic solvents, in which decomposition with formation of metallic Hg occurs. The products were characterized by elemental analysis and IR and ^{1}H NMR spectroscopy. They are non conductors in nitrobenzene solution (Tables 1 and 2).

IR spectra

The IR spectra (Table 2), in the carbonyl stretching region strongly resemble those for (η^5-C_5H_5)$(CO)_3$MoHgX complexes, although the bands are generally at frequencies 20–40 cm^{-1}lower than those for the latter. In all cases three bands are observed, and these are shifted towards the lower frequencies by change of X in the order X = Cl < SCN < Br < I. These shifts are consistent with a variation in the acceptor character of HgX_2 group [13] and with the electronegativity of X [14].

In addition, the thiocyanate complex shows in this region a ν(CN) band at ca. 2110 cm^{-1}, this is somewhat shifted with respect to that of $Hg(SCN)_2$ [15].

In the lower frequency region 300–200 cm^{-1}, the HgCl derivatives give a band at ca. 266 cm^{-1}corresponding to HgCl stretching vibrations. In the mercury thiocyanate derivative there is a band at ca. 240 cm^{-1} assignable to the Hg–SCN stretching vibration; this band appears at 258 cm^{-1} in complexes containing Mo–HgSCN bonds [16].

^{1}H NMR spectra

The ^{1}H NMR spectra of all the compounds (Tab. 2) showed two peaks from C_5H_4 rings in the range δ = 5.4–5.9 ppm and one peak, at ca. 2.00 ppm, from the CH_3 group of the $C_5H_4CH_3$ ligand. The separation of the two signals from the C_5H_4 ring is decreased in the following order: Cl < SCN ≃ Br < I. The minimum separation is obtained for [(η^5-$C_5H_4CH_3$)$(CO)_3$Mo]$_2$Hg, which is consistent with the covalent character of the Mo–Hg bond.

Electronic spectra

The electronic spectra of the tricarbonyl derivatives (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgX were recorded in CCl_4 solution at 265–500 nm. The absorption maxima (λ_{max}) and their intensities (log ε) are listed in Table 4.

TABLE 4

ELECTRONIC SPECTRAL DATA

Compound	Conc.(mol l^{-1})	λ(nm) [a]	log ε	Assignment
$[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{Mo}]_2\text{Hg}$	4.00×10^{-5}	370	3.03 [b]	d-d + CT M → π^*(CO)
		290 sh	3.04	CT M → π^*(CO)
		275	3.16	CT M → π^*(CO)
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{MoHgCl}$	1.00×10^{-4}	365	3.83 [b]	d-d + CT M → π^*(CO)
		280	4.13	CT M → π^*(CO)
		255 sh	4.24	CT M → π^*(CO)
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{MoHgBr}$	2.36×10^{-5}	365	3.40 [b]	d-d + CT M → π^*(CO)
		280 sh	4.12	CT M → π^*(CO)
		265	4.16	CT M → π^*(CO)
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{MoHgI}$	1.40×10^{-4}	380	2.93 [b]	d-d + CT M → π^*(CO)
		305	4.23	CT M → π^*(CO)
		265	4.17	CT M → π^*(CO)
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{MoHgSCN}$	9.00×10^{-5}	365	4.38 [b]	d-d + CT M → π^*(CO)
		275	4.05	CT M → π^*(CO)
		290	4.01	CT M → π^*(CO)

[a] Measured in CCl_4. [b] See text.

The spectra of our compounds are similar to those for other tricarbonyl complexes $[\text{Mo(arene)(CO)}_3]$ [17–21], $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{X})]$ [22–24], $[\text{Mo}_2(\eta^5\text{-C}_5(\text{CH}_3)_5)_2(\text{CO})_6]$ [25], and heteronuclear M–M′ bond species $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_3\text{M}']$ ($\text{M}' = \text{Co(CO)}_4$, Mn(CO)_5, Re(CO)_5) [26–28], and analogous environments around the transition metal are suggested.

The position and intensity of the absorbtion at ca. 365 nm, suggest that it arises from a $\sigma_b \rightarrow \sigma^*$ transition, characteristic of metal–metal bonds in the tricarbonyl complexes. However contribution of $d \rightarrow d$ and CT M → π^*(CO) transitions to these bands is also possible [13], [29–32].

Experimental

All reactions were carried out under nitrogen using Schlenk tube techniques and freshly distilled, dried, and degassed solvents.

Reagents

The complexes $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{MoSnPh}_3]$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_3\text{MoHgCl}$ were prepared by methods similar to those described previously for similar cyclopentadienyl derivatives [33,10]. Commercially available mercuric salts were used without purification.

Analyses

The C, H and N analyses were carried out by the Elemental Micro-Analyses Ltd. Laboratories, Amberley, Beaworthy (Devon) England.

Physical measurements

Infrared spectra in the 4000–200 cm^{-1} region were recorded on a Perkin–Elmer 325 spectrophotometer with KBr disks or Nujol mulls. Electronic spectra in the

500–265 nm region were recorded with CCl_4 solution on an Kontron Uvikon 820 spectrophotometer.

Preparation of $(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3$

The compound $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3]$ was prepared from the reaction of $Na^+[Mo(\eta^5\text{-}C_5H_4CH_3)(CO)_3]^-$ [34] and Ph_3SnCl at room temperature, under N_2 in dry THF. The reaction was stirred for several hours. The solvent was removed and the residue extracted with pentane. The combined extracts were concentrated to give an oil, which was treated with cold MeOH to give a yellow solid (yield 35%). (The procedure is similar to that used to prepare the related compound with C_5H_5 as ligand [33].

Synthesis of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]_2Hg$

A solution of $Hg(CN)_2$ (20 g, 0.08 mol) in water was added with stirring to a THF solution (50 ml) of $Na^+[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]^-$ [34], and a yellow precipitate separated. Stirring was continued for 30 min., then the solid was filtered off, washed with water (6 portions of 100 ml), and recrystallized from acetone (yield 60.2%).

Cleavage of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3MoSnPh_3]$ *by mercury halides* HgX_2 $(X = Cl, Br)$

A solution of $HgCl_2$ (0.07 g; 0.2 mmol) in dry MeOH (5 ml) was added to a solution of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo\text{-}SnPh_3]$ (0.08 g; 0.1 mmol) in dry MeOH (5 ml) under N_2. The mixture was refluxed for 5 min and then kept at 0°C overnight. The yellow crystals were filtered off and sucked dry.

The reaction with $HgBr_2$ was carried out in the same way.

Reaction of $[(\eta^5\text{-}C_5H_4CH_3)(CO)_3Mo]_2Hg$ *with mercuric salts* HgX_2 $(X = Cl, Br, SCN)$

A solution of bis(tricarbonyl-η^5-methylcyclopentadienylmolybdenum)mercury in acetone (5 ml) was mixed with a solution of mercuric salt in acetone (5 ml) (1/1). The solvent was removed and the products recrystallized from methanol.

X-Ray study of $(\eta^5\text{-}C_5H_4CH_3)MoHgCl$

A prismatic crystal was mounted on a Nonius CAD-4 diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflexions. Intensities of 2047 unique reflexions with $1° < \theta < 25°$, *hkl* 0, 0, -15 to 7, 16, 15 were measured at 295 K with monochromatic Mo-K_α radiation (λ 71069 Å) and a $\omega/2\theta$ scan technique; three reflexions monitored periodically during data collection revealed no crystal decomposition; the intensities were corrected for Lorentz and polarization effects, and 1696 of these with $I < 3\sigma(I)$, were considered as observed.

Scattering factors for neutral atoms and anomalous dispersion corrections for Hg, Mo and Cl were taken from International Tables for X-Ray Crystallography, 1974 [35].

The heavy atoms were located from the three dimensional Patterson map. The remaining non-hydrogen atoms were located in a Fourier synthesis.

An empirical absorption correction [36] was applied at the end of the isotropic refinement using unit weights when the conventional R was 0.058. The H atoms were fixed at the calculated positions. In order to prevent bias in ΔF vs. F_0 or

TABLE 5

ATOMIC COORDINATES FOR (η^5-$C_5H_4CH_3$)$(CO)_3$MoHgCl, WITH THERMAL PARAMETERS AS $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star a_i a_j$

Atom	x/a	y/b	z/c	U_{eq}
Hg	0.58372(8)	0.08445(4)	0.13072(4)	376(2)
Mo	0.4617(2)	0.12454(8)	0.30686(9)	286(4)
Cl	0.7207(7)	0.0692(3)	−0.0226(3)	524(14)
O(1)	0.7393(24)	0.3349(12)	0.0236(11)	817(58)
O(2)	0.7126(18)	0.3077(8)	0.2570(10)	560(44)
O(3)	0.7253(23)	−0.0681(9)	0.3478(12)	677(53)
C(1)	0.6382(26)	0.1510(12)	0.4455(12)	492(54)
C(2)	0.6285(21)	0.2390(10)	0.2750(11)	343(42)
C(3)	0.6307(24)	0.0035(11)	0.3289(12)	427(48)
C(4)	0.1750(21)	0.1955(13)	0.3527(13)	463(54)
C(5)	0.1452(22)	0.2043(14)	0.2444(13)	493(56)
C(6)	0.1285(27)	0.1106(16)	0.2042(15)	593(66)
C(7)	0.1443(24)	0.0428(13)	0.2793(16)	579(63)
C(8)	0.1724(27)	0.0940(14)	0.3743(16)	550(65)
C(9)	0.1888(33)	0.2794(22)	0.4284(22)	1067(114)

sin θ/λ, the last steps of the refinement were carried out with weights $\omega = \omega_1 \cdot \omega_2$ where $\omega_1 = 1/(a + b|F_0|)^2$ and $\omega_2 = 1/(c - d \sin\theta/\lambda)$ with coefficients calculated by the program PESOS [37], $a = 5.45$, $b = -0.13$ for : $|F_0| \leqslant 27.5$ and $a = 0.45$, $b = 0.04$ for other data. Final $R = 0.055$ and $R_\omega = (\Sigma_\omega \Delta^2/\Sigma\omega|F_0|^2)^{1/2} = 0.068$. Table 5, shows the final atomic parameters.

Most of the calculations were carried out with the X-RAY 80 program [38] but the LS planes and torsion angles were computed with the PARST 5 program [39].

Lists of thermal parameters and observed and calculated structure factors are available from the authors.

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