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Bis-cyclopentadienyl Molybdenum and Tungsten Compounds with Mercury–Transition Metal–Mercury Bonds.
Part I. Chemical, Spectroscopic and Structural Studies of Halogeno- and Thiolato-derivatives

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Cp_2MH_2 (M = Mo and W) react with HgX_2 (X = Cl, Br, I, SCN, OAc and CN) salts, giving insoluble compounds which have the general formula $Cp_2M(HgX)_2 \cdot xHgX_2$ (I) (x = 0, 1/3, 1/2, 2/3 and 1). These compounds were characterized by using IR and, for some of them, Raman spectroscopy. Frequencies of Hg-X vibrations are discussed in the light of an 'adduct type' structure. Mo–Hg and W–Hg bands are detected in the Raman spectra near 130–140 cm^{-1}. An intermediate polymeric compound $(Cp_2MoHg)_n$ (II) was isolated and characterized by IR spectrum and unit cell parameters.

All compounds (I) and (II) react with thiolates giving non-adduct: i) compounds $Cp_2M(HgSR)_2$ (R = Me, Et, ^iPr and ^nPr) (III) soluble in organic solvents and ii) insoluble compounds $[Cp_2MHg_2(SR)]X$ (X = Cl, Br) (IV). Compounds (IV) with X = Cl also crystallize from solutions of (III) in chloroform. Insoluble $Cp_2M(HgSR)_2$ (R = phenyl or pyrimidine) compounds were obtained by the reaction of (I) with corresponding thiolates. IR spectra of all these derivatives were recorded showing similar features to those of the compounds (I). (^1H), (^{13}C) and (^{199}Hg) NMR spectra of soluble complexes (III) were recorded.

The structure of $[Cp_2MoHg_2(SEt)]Cl$ determined by X-ray analysis is built of infinite chains of Cp_2MoHg_2 moieties and thiolates bridging two mercury atoms from the adjacent Cp_2MoHg_2 units and of essentially ionic chlorides.

Introduction

Much work has been done on the chemistry of organomercurials containing a strong covalent R–Hg bond. The particular danger of one of them ($MeHg^+$), easily formed even in sea water, owing to the methyl transfer from vitamin B_{12} to the 'inorganic' Hg^{2+} has been recognized [1]. The affinity of mercury to form bonds with sulphur atoms is of great importance, especially in the case of methylmercury poisoning of the sulphur containing amino-acids and numerous studies have been undertaken on this subject [2–5]. It was postulated, however, that this affinity could be used to employ a variety of sulphur compounds as an antidote against the mercury action [2, 6–8]. An important structural work has been carried out recently on the X–Hg–SR systems [9–11].

Research on the structure, function and mode of action of molybdenum-containing enzymes has been greatly intensified recently [12] and it has been established that they contain molybdenum–sulphur bonds [12–16]. In spite of the biological importance of both mercury–sulphur and molybdenum–sulphur compounds the chemistry of transition metal–mercury and sulphur-containing systems has been surprisingly little developed. $(C_5H_5)_2N(SCH_2)_2$ (η^5-cyclopentadienyl ligand is hereafter abbreviated as Cp) reacts with $HgCl_2$ to give an insoluble $Cp_2WS(CH_2)_2SHgCl_2$ product with a mercury bound to one sulphur atom [17]. Symmetrical mercurials of Cr, Mo and W have been found to reduce the tetraalkylthiuram disulfides [18] following the equation:

$$[CpM(CO)_3]_2Hg + R_2NC(S)S\text{–}S(S)CNR_2 \rightarrow$$
$$Cp(CO)_3MHgS_2CNR_2 + Cp(CO)_2MS_2CNR_2.$$

Although many carbonyls and monocyclopentadienides in which mercury is bound to a transition metal

TABLE I. Analytical Data (calculated).

Compound	Colour	C	H	S	N	X[a]	M[b]
$(C_5H_5)_2Mo(HgCl)_2$	brown	17.3	1.6			9.8	14.1
(Ia1)		(17.2)	(1.4)			(10.1)	(13.7)
$(C_5H_5)_2Mo(HgCl)_2 \cdot 1HgCl_2$	orange	12.9	1.1			13.4	10.0
(Ia1)		(12.4)	(1.0)			(14.6)	(9.9)
$(C_5H_5)_2Mo(HgCN)_2$	deep-orange	22.0	1.7		3.9		14.1
(Ia6)		(21.2)	(1.5)		(4.1)		(14.1)
$(C_5H_5)_2W(HgI)_2 \cdot 2/3HgI_2$	yellow	8.9	0.9				14.6
(Ib3)		(9.3)	(0.8)				(14.3)
$(C_5H_5)_2W(HgOAc)_2 \cdot 1/3Hg(OAc)_2$	orange-red	19.5	2.2				20.3
(Ib5)		(19.6)	(1.9)				(19.6)
$(C_5H_5)_2Mo(HgSCH_3)_2$	orange	19.8	2.2	8.6			13.3
(IIIa1)		(20.0)	(2.2)	(8.9)			(13.3)
$(C_5H_5)_2Mo(HgSC_2H_5)_2$	orange	21.8	2.6	8.6			12.8
(IIIa2)		(22.4)	(2.7)	(8.6)			(12.8)
$(C_5H_5)_2MoHg_2(SC_2H_5)Cl$	red	19.8	2.1	4.8		5.5	13.7
(IVa2)		(19.9)	(2.1)	(4.4)		(4.9)	(13.2)
$(C_5H_5)_2W(HgS^iC_3H_7)_2$	orange	22.2	2.9	7.4			21.1
(IIIb4)		(22.2)	(2.8)	(7.4)			(21.2)
$(C_5H_5)_2W(HgSC_6H_5)_2$	red	28.3	2.3	7.0			19.8
(III or Vb5)		(28.3)	(2.2)	(6.9)			(19.7)

[a] X = Cl, I. [b] M = Mo, W.

are known, only one dicyclopentadienyl complex of molybdenum containing this bond has been announced by Oliver [19]. By analogy with a zinc derivative studied by X-ray analysis, this author formulated the product of the reaction between Cp_2MoH_2 and $HgCl_2$ in THF as $Cp_2MoH_2 \cdot HgCl_2 \cdot THF$. We do not favour this formulation for two reasons:

1: although Lewis base–acid adducts containing HgX_2 are known [20–23], one of the methods generally adopted to prepare the complexes with metal mercury bonds consists of an 'elimination' reaction between an organotransition metal hydride and a mercuric salt [24], so the hydrogen ligands in Cp_2MoH_2 should be substituted by mercury;

2: the results of the elemental analysis reported by Oliver are not consistent with the calculated values, but rather with the formulation without solvent molecule.

One cannot forget however, that the reactivity of Cp_2MoH_2 is connected to the presence of three orbitals on a metal center, two of them being used to form the M–H bonds, and the third one being occupied by the electron pair able to act as a basic site [25–27]. Thus a variety of structures can be adopted by the products, depending on the nature of the reagents, with or without retention of the hydride ligands [19, 28–33]. Another problem concerns the molecular structure of dicyclopentadienyl molybdenum complexes. The Cp_2Mo unit is known to form bonds with main group metals [Li [34], Mg [35] and Al [36]] and the structures of four compounds containing two metal-metal bonds have been solved by X-ray methods. M–Mo–M angles vary widely from 62.7° (Al) to 109° (Mg). The Cp–Mo–Cp angles are in the 143–149° range and are significantly greater than those found in more typical Cp_2MoX_2 complexes (130–133°) [37–39].

In the light of the above discussion it seems to be of importance to carry out chemical and structural studies on the bis-cyclopentadienides of molybdenum by preparing in the first step complexes with molybdenum–mercury bond(s), followed by studies of their behaviour towards sulphur containing compounds.

Experimental

Preparation of Compounds

All reactions were carried out under a nitrogen atmosphere using standard Schlenk tube techniques and freshly distilled, dried and degassed solvents. Dihydrides Cp_2MH_2 (M = Mo, W) [40], $Cp_2Mo(SEt)_2$ [17] and $[Cp(CO)_3Mo]_2Hg$ [41] compounds were prepared as described in the literature. Commercially available mercuric salts and mercaptans were used without purification or distillation.

The $Cp_2M(HgX)_2 \cdot xHgX_2$ (I) compounds ($0 \leqslant x \leqslant 1$; X = Cl, Br, I, SCN, CN, OAc) were prepared by pouring a THF solution of HgX_2 into one of Cp_2MH_2.

Typically, 1.08 g (4 mmol) of $HgCl_2$ dissolved in *ca.* 20 ml of THF was transferred to a 100 ml solution of 0.45 g (2 mmol) of Cp_2MoH_2 in THF. An orange precipitate formed immediately and the suspension was stirred for few minutes, filtered on a glass filter and washed 4 or 5 times with 30–40 ml portions of THF. Either $Cp_2Mo(HgCl)_2$ or $Cp_2Mo(HgCl)_2 \cdot 1HgCl_2$ was obtained even under the same conditions (temperature, concentrations...). Either adduct or non-adduct products were also precipitated if a 3:1 Hg:Mo ratio was used. Depending on the type of product, the yields calculated either for dihydride or for $HgCl_2$ were practically 100%.

When mercuric cyanide or acetate was allowed to react with Cp_2MoH_2 a change of colour from yellow to red was observed as a first step (Hg:Mo ratio $< 1:4$), followed on further addition of HgX_2 by the precipitation of solids (I). If the initial red solution was allowed to stand overnight, red crystals could be isolated. They were stable, even under nitrogen, for only 2–3 days and their decomposition was manifested by metallic mercury deposition. A polymeric structure $[Cp_2MoHg]_n$ (II) is proposed for these crystals (see discussion) but because of the decomposition the analytical data (Table I) do not correspond well to the formula proposed.

The $Cp_2Mo(HgOAc)_2 \cdot x(HgOAc)_2$ compounds were slightly soluble in THF and water, but the solutions decomposed with a deposition of metallic mercury. A change of colour from yellow to red was also observed by the action of $Hg(SCN)_2$ on the solution of Cp_2MoH_2, but no red crystals could be isolated. A brown powder exhibiting (SCN) infrared bands precipitated even if the Hg:Mo ratio was lower than 1:4. Thus the reaction of Cp_2MoH_2 with $Hg(SCN)_2$ proceeded in the same way as with $HgCl_2$, $HgBr_2$ and HgI_2.

Analytical data of some representative $Cp_2Mo(HgX)_2 \cdot xHgX_2$ compounds I are given in Table I.

The $Cp_2M(HgSR)_2$ (III) complexes were prepared by the addition of an excess of HSR/NaOH to suspensions of $Cp_2M(HgX)_2 \cdot xHgX_2$ (I) compounds in THF. Methanol, benzene and chloroform were also used as solvents. In a typical operation 0.98 g (1 mmol) of $Cp_2Mo(HgCl)_2 \cdot HgCl_2$ was suspended in *ca.* 50 ml of THF. About 1.1 ml of HSEt (≅20 mmol or 5 fold excess) followed by 0.4 g (10 mmol) of NaOH dissolved in a minimum amount of water were added to the stirred suspension at room temperature. The organic phase, initially colourless, became red. The solution was then concentrated to about 10–15 ml by evaporation, filtered and allowed to stand overnight. The orange needles formed were washed with a minimum of water and absolute ethanol. Up to 300 mg (≅40% per Mo) of pure $Cp_2Mo(HgSEt)_2$ could be isolated. The compound (IIIa2) (Table I, Fig. 1) thus obtained was the main product of the reaction between all complexes (I) and SEt^-.

In some cases another product crystallizing as red crystals with a very low yield (<1%) formed with (IIIa2). Moreover these crystals (Va2, Fig. 1) often grew with intercalations of the orange (IIIa2) product, so no sample has been submitted for elemental analysis.

When the reaction of (I) with HSEt/NaOH was carried out in methanol or in benzene the same (IIIa2) product was formed, but its solubility in these solvents was lower than in THF.

The soluble compounds (III) were obtained in the same manner (in THF) with R = CH_3, $^nC_3H_7$, and $^iC_3H_7$ (Fig. 1); some representative analytical data are given in Table I. On their dissolution in halogenated hydrocarbons, a change of colour from orange to deep red was observed. The red crystals (IVa2) were isolated from the solution of (IIIa2) in chloroform. The same product with the empirical formula $Cp_2MoHg_2(SEt)Cl$ was obtained by the direct reaction of Cp_2MoH_2 with HSEt/NaOH in chloroform (Table I, Fig. 1). It was soluble neither in THF nor in $CHCl_3$.

The compounds (IV) could also be prepared directly in THF if the SEt/M (compounds I) ratio did not exceed 8:1 (or ≅2 fold excess of SEt^-). $Cp_2WHg_2(SEt)Br$(IVb2, Fig. 1) identified by unit cell determination was isolated as small red crystals with a very low yield from the reaction between 1 mmol of $Cp_2W(HgBr)_2 \cdot 2/3HgBr_2$ and *ca.* 7 mmol of HSEt/NaOH.

The reaction of complexes (I) with HSR/NaOH, where R is aromatic (*e.g.* phenyl, pyrimidine...) in the conditions described for a typical operation gave insoluble red solids formulated as $Cp_2M(HgSR)_2$ (III or V).

Physical Measurements

Infrared spectra of samples prepared as Nujol mulls on CsI plates were recorded in the 4000–200 cm^{-1} region on Pye Unicam SP 2000 and Perkin Elmer 225 spectrophotometers.

Raman spectra were observed by using a JEOL JRS-S1 spectrometer with argon ion Laser 52G coherent radiation (488 nm at about 150 mW) and a rotation cell technique at the Technical University of Wrocław, Poland.

Mass spectra were recorded on a Varian Mat 311 Spectrometer of the "Groupement Régional des Mesures Physiques de l'Ouest" operating at source pressures of 8×10^{-7} mmHg, 70 eV ionising energy, 32 nA ionising current, resolution of 1500 and 2.97 kV accelerating voltage.

Proton, carbon and mercury n.m.r. spectra were recorded on a JEOL FX 100 spectrometer operating at 99.60 MHz for (^1H), 25 MHz for (^{13}C) and 17.78 MHz for (^{199}Hg) using freshly prepared solutions in $CDCl_3$. For proton and carbon, chemical shifts were measured relative to an internal reference of tetramethylsilane and for mercury relative to an external reference of $HgMe_2$.

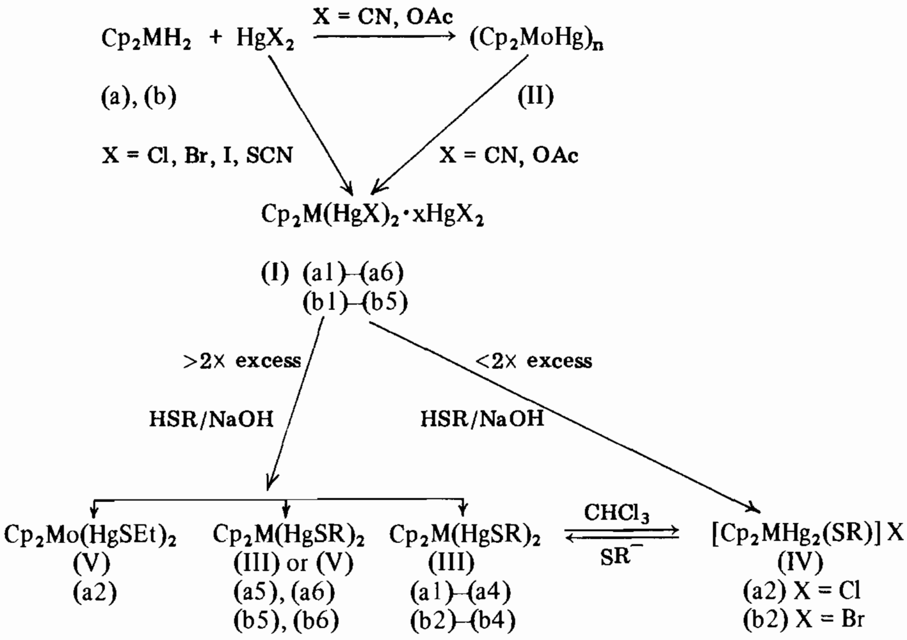


Fig. 1. Reactions of metal–mercury compounds.
a = Mo, b = W in compounds (I)–(V); 1 = Cl, 2 = Br, 3 = I, 4 = SCN, 5 = OAc and 6 = CN in compounds (I); 1 = Me, 2 = Et, 3 = ^{n}Pr, 4 = ^{i}Pr, 5 = Ph and 6 = pyrimidine in compounds (III)–(V).

Elemental analyses were performed in the Centre de Microanalyses du C.N.R.S. of Lyons.

X-ray Measurements and Structure Determination

Preliminary Weissenberg photographs of the mixed complex $Cp_2MoHg_2(SEt)Cl$ (IVa2) indicated orthorhombic $P2_12_12_1$ space group. Unit cell and intensity measurements were carried out on an Enraf Nonius CAD3 diffractometer at room temperature (λMoK_α = 0.71069 Å, graphite monochromator). A dark red crystal with dimensions of 0.40 × 0.14 × 0.12 mm along the [100], [011] and [0$\bar{1}$1] directions, respectively, was used. Intensities of 1716 reflections were collected, 1567 with $I > 2\sigma$ (I) were regarded as observed. Routine corrections for Lorentz and polarization factor as well as for absorption were introduced.

An application of MULTAN program permitted location of the mercury and molybdenum atoms (discrepancy was of 0.15). All remaining nonhydrogen atoms were revealed from two subsequent Fourier difference series. Scattering factors of Hg and Mo atoms were corrected for anomalous dispersion $\Delta f'$ and $\Delta f''$, thus permitting choice of enantiomer.

Refinement of positional parameters with anisotropic temperature factors for all atoms gave the final R values of 0.040 (R_1) and 0.044 [R_w, $w = 1/\sigma^2(F)$].

Because of the low precision in the positions of carbon atoms we did not try to locate the hydrogens.

The positional and thermal parameters are given in Table IV and the interatomic distances and angles in Table V. The equations of planes of cyclopentadienyl rings and $MoHg_2$ unit in the system of crystallographic axes are presented in Table VI.

Results and Discussion

Biscyclopentadienyl compounds of molybdenum and tungsten studied here are the first ones containing two mercury atoms bound to one Mo or W. These compounds represent the first examples of transition metal derivatives with metal–mercury bonds in a pseudotetrahedral configuration. The products (I) (Fig. 1) have a lattice adduct type structure $Cp_2M(HgX)_2 \cdot xHgX_2$ with x = 0, 1/3, 1/2, 2/3 or 1, varying even with the same X or M. Formation of adducts with HgX_2 is known for some organotransition metal and organic compounds [20–23, 42–45] but they possess generally an entire number of HgX_2 molecules. The presence of lattice HgX_2 may be responsible for the stability of the compound (I), owing to a developed system of Hg–X···Hg interactions.

Infrared spectra of all compounds (I) exhibit the bands which are typical of π-bonded bent cyclopentadienides. However the ring bending vibrations are sometimes split and shifted [*e.g.* 885s, 865s, 845m, 835m, 784vs, 758m and 682 m cm^{-1} in Cp_2-

TABLE II. Mercury–X Vibrations (cm^{-1}); Infrared and Raman Spectra of Solid Samples (if no reference is given spectra were recorded by us).

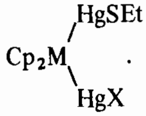
X	Cl		Br		SCN	CN		SMe
Compound	IR	R	IR	R	IR	IR	ν(C≡N)	IR
HgX_2	375^a	313^a	251^a	187^a	313	442^b	2194^b	338^c
MeHgX	315^d	289^d	214^d	228^d	283^e	376^f	2180^e	329^c
Mo^g–HgX	287 271	280	204	170	258	284^i or 328	2070	297
W^h–HgX	285	282		177	260	–		–

[a] Ref. 46. p. 71. [b] Ref. 46 p. 165. [c] Ref. 4. [d] J. H. S. Green, *Spectrochim. Acta, 24A,* 863 (1968). [e] N. Iwasaki, *Bull. Chem. Soc. Japan, 49,* 2735 (1976). [f] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc., 62,* 1423 (1966). [g] (Ia) and (IIIa1) compounds. [h] (Ib) compounds. [i] ν(Hg–C) was observed in infrared spectrum at 330 cm^{-1} but ν(CN) at 2146 cm^{-1} in solid $K_2[Hg(CN)_4]$, ref. 46, p. 168.

$Mo(HgBr)_2 \cdot 2/3\ HgBr_2$ and 890m, 862w, 847w, 825s and 776w cm^{-1} in $Cp_2W(HgCl)_2]$. The positions of the antisymmetric metal–ring vibrations observed as strong doublets near 422–395 cm^{-1} (compounds Ia) and 404–380 cm^{-1} (Ib) and the very weak symmetric stretches at 330 ± 5 cm^{-1} (Ia) and 335 ± 5 cm^{-1} (Ib) are quite similar in all compounds (I). No metal–hydrogen vibration was detected suggesting that our compounds are not the same as the one obtained by Oliver by pouring THF on an equimolar solid mixture of Cp_2MoH_2 and $HgCl_2$ [19].

It appears that an increase of up to four in the coordination number is not easily attainable by mercury, strongly bound to molybdenum or tungsten (*vide infra*), although this occurs with zinc as proved by X-ray structure analysis [19]. Rather weak Hg–X bonds, *trans* to M–Hg are expected on the basis of vibrational spectroscopy as well as of the X-ray structure of the (IVa2) compound discussed below. The compounds (I) when x = 0 (non adduct structures) are less stable, as manifested by their decomposition in air as well as in the laser beam of Raman spectrometer. Their stability depends also on the nature of X; iodides, bromides and acetates are the most stable whereas the cyanide derivative (Ia6) is the least stable. When X = Cl, compound (Ia1) with x = 1, slowly changes colour from orange to brown when exposed for some hours to air. The Raman spectra of a few adducts could be recorded and rather low positions of Hg–X (X = Cl, Br and I) bands were observed (~280, ~174 and ~140 cm^{-1}, respectively) in (Ia) and (Ib) complexes. These positions are not significantly different from those found in HgX_3^- anions [46], suggesting either an increase in the coordination number of probably 'adduct' mercury, or/and weak Hg–X bonds involving a mercury atom bound to a transition metal. The ν(Hg–X) vibrations occur at lower frequencies than in linear HgX_2 molecules, or even in MeHgX where a strong covalent Hg–CH_3 bond exists (Table II). Weak bonds between the Cp_2MoHg_2 moiety and X's are also suggested by the i.r. spectrum of $Cp_2Mo(HgCN)_2$ with a non-adduct type structure. The low position (2070 cm^{-1}) of ν(CN) band indicates an increase in the ionic nature of interactions (2080 cm^{-1} in KCN [47]) and in the negative charge on the nitrogen atom. Consequently, significant interactions between mercury and CN$^-$ via nitrogen can exist in the compound (Ia6) showing a 'pseudo-bridged' behaviour of CN$^-$ ligands, each of them interacting with at least two mercury atoms.

All insoluble compounds (I) react with an excess of NaOH/HSR giving as main products the complexes (III) soluble in common organic solvents. Their infrared spectra are comparable with those of the compounds (I) except for the splittings and shifts of ring bending vibrations. The ν(Hg–S) vibrations are observed as weak to medium bands in the 297–270 cm^{-1} region, lower than in corresponding $Hg(SR)_2$ and MeHgSR linear molecules, thus indicating weak Hg-S bonds with increased ionic character.

However, the different nature of the mercury–sulphur bonds (more covalent than mercury–halogen bonds) is manifested by the fact that no adduct type structure was attained by the complexes (III). Moreover, as will be shown below, this difference plays a determining role in the building of the structure of 'mixed' compounds (IV), which in reality have an ionic formulation $[Cp_2MHg_2SEt]^+X^-$ and not a molecular one 

$Cp_2M\genfrac{}{}{0pt}{}{\diagup HgSEt}{\diagdown HgX}$.

The (^1H) chemical shifts of some compounds (III) are listed in Table III. For comparison the thiolatocomplex $Cp_2Mo(SC_2H_5)_2$ [17] without

TABLE III. N.M.R. Spectra. ^1H Chemical shifts in ppm (δ).

Complexes	(C_5H_5)	(SR)	
$(C_5H_5)_2Mo(HgSCH_3)_2$	4.82	$s(SCH_3)$	2.68
$(C_5H_5)_2Mo(HgSC_2H_5)_2$	4.80	$t(CH_3)$	1.33–1.46–1.60
		$q(SCH_2)$	3.12–3.25–3.38–3.50
$(C_5H_5)_2Mo(HgS^iC_3H_7)_2$	4.74	$d(CH_3)$	1.42–1.49
		h(SCH)	centered at 4.03
$(C_5H_5)_2Mo(HgS^nC_3H_7)_2$	4.79	$t(CH_3)$	0.95–1.07–1.18
		$b(CH_2)$	centered at 1.68
		$t(SCH_2)$	3.11–3.23–3.35
$(C_5H_5)_2W(HgSC_2H_5)_2$	4.72	$t(CH_3)$	1.34–1.41–1.48
		$q(SCH_2)$	3.14–3.22–3.29–3.37
$(C_5H_5)_2W(HgS^iC_3H_7)_2$	4.70	$d(CH_3)$	1.41–1.47
		h(SCH)	centered at 4.02
$[(C_5H_5)_2MoHg]_n + 2nNaSC_2H_5$	5.17[a]	[a] $t(CH_3)$	1.10–1.22–1.34
		$q(SCH_2)$	2.06–2.19–2.31–2.43
	4.75[b]	[b] $t(CH_3)$	1.30–1.43–1.55
		$q(SCH_2)$	3.07–3.19–3.31–3.42
$(C_5H_5)_2Mo(SC_2H_5)_2$	5.22	$t(CH_3)$	1.14–1.27–1.39
		$q(SCH_2)$	2.11–2.24–2.37–2.50

s: singlet, d: doublet, t: triplet, q: quartet, h: heptet, b: broad.
[a] Relative to $(C_5H_5)_2Mo(SC_2H_5)_2$. [b] Relative to $(C_5H_5)_2Mo(HgSC_2H_5)_2$. Solutions in $CDCl_3$, internal reference: tetramethylsilane.

mercury is reported. The positions of the peaks in $Cp_2Mo(HgSC_2H_5)_2$ differ by 0.4 ppm towards higher fields for the Cp rings and by 1 ppm towards lower fields for the SCH_2 groups from those observed for $Cp_2Mo(SEt)_2$. For the (^{13}C) resonance recorded with total decoupling three peaks are detected with $Cp_2Mo(SEt)_2$ [95.4 ppm (C_5H_5); 31.2 ppm (SCH_2); 19.3 ppm (CH_3) relative to TMS] whereas only two appear with the mercuric compound [72.5 ppm (C_5H_5); 23.1 ppm (SCH_2 + CH_3)]. In the absence of decoupling, the 23.1 ppm peak consists of a quartet of triplets and a triplet of quartets centered with a very small difference of 0.12 ppm.

The two Cp rings give rise to one signal in the (^1H) NMR spectrum. In the same manner only one set of peaks was detected for the two SR ligands, suggesting at least a C_2 symmetry of the molecules in solution.

The (^{199}Hg) chemical shifts for the two compounds investigated are +70 ppm [$Cp_2W(HgS^iPr)_2$] and +202 ppm [$Cp_2Mo(HgSEt)_2$] relative to $HgMe_2$ in $CDCl_3$ solutions (positive δ values indicate downfield shift). These positions close to that of $HgMe_2$ suggest covalently bound systems.

The crystallization of the main product (III) from the reaction between (I) and NaSEt was sometimes accompanied by the formation of red insoluble crystals (see experimental). No by-product was obtained with NaSMe or NaSPr. These crystals (Va2) (Fig. 1) are monoclinic. Space group is $P2_1/c$ and a = 10.05, b = 17.75, c = 10.20 Å and β = 114°. The density measured in a tetrabromoethane–ethylene bromide mixture is ~2.91 g cm^{-3} and corresponds to four $Cp_2Mo(HgSEt)_2$ molecules in the unit cell. For comparison, the unit cell of the orange needles (IIIa2) was determined: C2/c or Cc, a = 31.19, b = 8.00, c = 20.91 Å, β = 97°, d_{meas} = 2.89 g cm^{-3}, Z = 12. Thus the $Cp_2Mo(HgSEt)_2$ forms two monoclinic modifications.

Correct analytical data were obtained for the $Cp_2M(HgSR)_2$ complexes prepared in the reactions of (I) with phenyl and pyrimidine mercaptans. Unfortunately, these products are not soluble, so no n.m.r. study was possible. To solve the problem of the choice of structural modification (III or V) we are looking for crystals of (IIIa2) and (Va2) and at least one with R = phenyl or pyrimidine suitable for X-ray structure analysis.

Some small red crystals were also obtained as by-product in the reaction between (Ib2) and a moderate excess of NaSEt. Structural parameters [$P2_12_12_1$, a = 8.12, b = 10.81 and c = 17.62 Å] suggest that it is isostructural with a mixed compound (IVa2) and thus should be formulated as [$Cp_2WHg_2(\mu$-SEt)]Br.

Crystallographic parameters of (IVa2) are: $P2_12_12_1$, a = 7.741(5), b = 10.562(2), c =

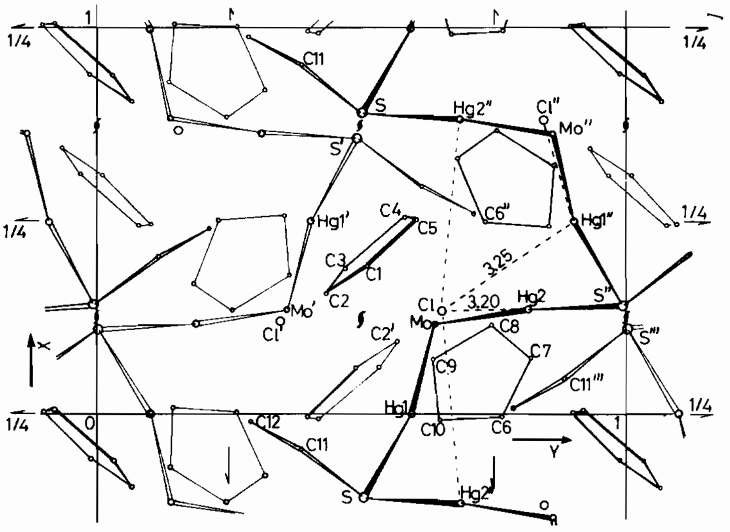


Fig. 2. A projection of the unit cell of $[Cp_2MoHg_2(\mu\text{-SEt})]Cl$ down the *z* axis. Ionic Hg•••Cl interactions are indicated by dashed lines. Symmetry code: (') ½ – x, $\bar{y}$, ½ + z; ('') ½ + x, ½ – y, $\bar{z}$; (''') $\bar{x}$, ½ + y, ½ – z; unprimed atoms have the coordinates x, y, z.

TABLE IV. Positional and Thermal Parameters β_{ij} ($\times 10^{-4}$) and Their Estimated Standard Deviations. The temperature factor is given by $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg1	0.00035(15)	0.5954(1)	0.91116(5)	114(2)	75(1)	19.1(2)	4(2)	10(1)	6(1)
Hg2	0.26818(15)	0.8128(1)	0.90957(6)	163(2)	56(1)	24.1(3)	–4(2)	–10(1)	–11(1)
Mo	0.2316(2)	0.6383(3)	0.7996(1)	72(4)	44(2)	13.3(5)	3(3)	–2(1)	–1(1)
S	–0.2170(9)	0.5041(7)	1.0016(3)	86(11)	50(6)	20(2)	2(9)	2(4)	–1(3)
Cl	0.263(1)	0.6533(7)	1.0657(3)	184(16)	80(8)	18(2)	13(11)	2(5)	1(3)
C1	0.382(4)	0.511(3)	0.884(1)	80(48)	125(42)	29(10)	19(41)	–29(17)	–14(17)
C2	0.312(4)	0.433(3)	0.826(1)	122(55)	95(38)	26(9)	5(40)	–22(18)	–6(15)
C3	0.379(4)	0.468(3)	0.756(1)	66(51)	167(49)	35(11)	86(44)	0(18)	13(19)
C4	0.512(5)	0.581(3)	0.769(2)	148(58)	191(54)	37(11)	161(59)	12(25)	4(21)
C5	0.507(5)	0.602(3)	0.848(1)	171(56)	99(36)	31(9)	39(53)	–52(23)	–21(17)
C6	–0.004(5)	0.766(3)	0.761(2)	248(73)	156(47)	26(9)	153(63)	16(27)	32(18)
C7	0.162(4)	0.818(3)	0.731(2)	417(106)	26(24)	53(14)	20(48)	–100(33)	6(16)
C8	0.232(5)	0.745(3)	0.682(2)	249(83)	188(57)	23(10)	71(72)	2(30)	23(19)
C9	0.142(4)	0.636(3)	0.676(2)	390(102)	68(34)	22(9)	121(55)	–57(25)	–12(15)
C10	–0.013(5)	0.646(3)	0.725(1)	219(72)	125(43)	55(14)	–128(57)	–93(29)	54(21)
C11	–0.092(3)	0.384(3)	1.056(1)	199(64)	44(29)	21(8)	4(38)	–23(18)	4(13)
C12	–0.019(5)	0.287(3)	1.000(2)	183(65)	39(27)	61(13)	58(45)	2(28)	–9(17)

17.464(5) Å, $Z = 4$, $d_{calc} = 3.37$ g cm^{-3} and $\mu = 230$ cm^{-1}.

The structure of this compound is based on an infinite wrinkled chain of Cp_2MoHg_2 and thiolate groups running parallel to the *a* axis and on the chloride ions. The sulphur atom bridges symmetrically two mercury atoms from adjacent Cp_2MoHg_2 units (Fig. 2).

Polymeric chain structures consisting of a set of mercury–thiolate backbones were found in a number of RSHgX (X = OAc, Cl, Br; R = Me, Et, Pr, Bu) compounds, where the chains are crosslinked by ionic interactions between X and mercury atoms from different chains [9–11]. Formal analogy between (IVa2) and RSHgX compounds follows from treatment of the Cp_2MoHg_2 moiety in (IVa2) as Hg in RSHgX, so the unexpected chain structure of the former is not surprising. However, the mode of ionic interactions involving the X atom in these two structures is different. Mercury–chlorine distances in (IVa2) are 3.20 (Hg2), 3.25 (Hg1''), 3.43 (Hg1) and 3.95 and 3.87 Å (Hg2''), all these mercury

TABLE V. Interatomic Distances (A) and Bond Angles (Degrees). Symmetry operations are as on Figure 2.[a]

Mo–Hg1	2.684(3)	Hg1–Mo–Hg2	70.5(1)
Mo–Hg2	2.676(3)	Mo–Hg1–S	166.4(7)
Hg1–S	2.50(1)	Mo–Hg1–Cl	98.3(4)
Hg2–S″	2.48(1)	Mo″–Hg1″–Cl	109.2(3)
Hg1″···Cl	3.25(1)	S″–Hg1″–Cl″	88.3(3)
Hg2···Cl	3.20(1)	S–Hg1–Cl″	81.7(3)
Hg1···Cl	3.43(1)	Cl–Hg1″–Cl″	95.3(3)
Hg1···Hg2	3.093(2)	Mo–Hg2–S″	171.8(7)
Hg2···Hg1″	3.737(2)	Mo–Hg2–Cl	104.3(4)
S···C11	1.86(4)	Cl–Hg2–S″	83.0(3)
C11···C12	1.51(6)	Hg2–S″–Hg1″	97.2(4)
		Hg1–Cl–Hg1″	125.3(3)
Mo–C1	2.31(5)	Hg2–Cl–Hg1″	70.7(3)
Mo–C2	2.30(4)	Hg1–Cl–Hg2	55.4(3)
Mo–C3	2.26(5)	Hg1–S–C11	103.4(1.5)
Mo–C4	2.32(5)	S–C11–C12	109(6)
Mo–C5	2.32(5)	Hg2″–S–C11	103.9(1.5)
Mo–C6	2.36(6)		
Mo–C7	2.30(6)	C1–C2–C3	110(8)
Mo–C8	2.34(6)	C2–C3–C4	108(8)
Mo–C9	2.28(5)	C3–C4–C5	104(8)
Mo–C10	2.30(6)	C4–C5–C1	109(7)
		C5–C1–C2	109(7)
C1–C2	1.41(6)	C6–C7–C8	112(10)
C2–C3	1.39(7)	C7–C8–C9	110(10)
C3–C4	1.59(7)	C8–C9–C10	108(9)
C4–C5	1.39(7)	C9–C10–C6	106(9)
C5–C1	1.50(6)	C10–C6–C7	102(9)
C6–C7	1.49(8)		
C7–C8	1.28(8)	Hg1–Mo–G1	106.1(1.5)
C8–C9	1.35(8)	Hg1–Mo–G2	106.4(1.8)
C9–C10	1.48(8)	Hg2–Mo–G1	104.9(1.5)
C10–C6	1.42(8)	Hg2–Mo–G2	106.2(1.8)
		G1–Mo–G2	141(4)
Mo–G1	1.94(5)		
Mo–G2	1.98(6)		

[a] G1 and G2 are the centers of C1–C5 and C6–C10 cyclopentadienyl rings, respectively.

atoms belonging to the same chain. The shortest distance between a chloride and a mercury atom of the second chain crossing the unit cell is 6.83 Å (Hg1′). Thus a chloride assures an additional cohesion over a chain via ionic interactions with the mercury atoms of adjacent Cp_2MoHg_2 moieties bridged by thiolates. The two shortest Hg–Cl distances are comparable with a value of 3.232(5) Å found in $Hg[SCH_2CH(NH_3)COO][SCH_2(NH_3)COOH]Cl\cdot0.5H_2O$ [50]. Inside the same chain, very weak interactions are possible between the Hg2″ and Cl atoms, in spite of the long distances separating them. This suggestion may be supported by the fact that the temperature parameters β_{11} of Cl and Hg2 atoms are much greater than β_{22} and β_{33}. This indicates roughly the elongation of the corresponding ellipsoids in the x direction, which is the direction of the chain. The ionic interactions are limited over one chain, so only Van der Waals forces act between the chains.

A comparison of interatomic distances involving mercury and halogens in polymeric MeSHgBr(A), tetrameric $(BuS)_4Cl_4Hg_4(C_6H_7N)_2$ (B) and (IVa2) shows that the coordination number around mercury may be considered as high as five in (A) (Hg–Br = 2.814, 2.998 and 3.210 Å), four in (B) (Hg_a–Cl = 2.479, Hg_a–N = 2.39 and Hg_b–Cl = 2.748 and 2.749 Å) but only two in (IVa2). Because the radii of atoms depend strongly (particularly in the case of mercury) on the coordination number adopted, one should expect a decrease of Hg–S bond lengths in the order (A) > (B) > (IVa2). The corresponding mean lengths of two Hg–S bonds are equal to 2.44 in (A) 2.39 for Hg_b and 2.50 Å for Hg_a in (B). Only the last value is close to that predicted on the basis of tetrahedral covalent radii of mercury (1.48 Å) and sulphur (1.04 Å) [48]. The lengths of 2.49(1) Å found in (IVa2) are significantly greater than those expected for two-coordinated mercury and observed in the 2.31–2.38 Å range in some Hg(II) complexes [5, 49–51]. In other polymeric RSHgX compounds, where mercury has a pseudotetrahedral configuration, mean Hg–S bond lengths are in the range 2.40–2.47 Å, thus in all cases shorter than in (IVa2). It seems reasonable to conclude that the nature of the bonds in the organometallic Cp_2MoHg_2 moiety, but not the bridging nature of thiolate, is responsible for the elongation of the Hg–S bonds. A Hg–Cl distance of 2.437(8) Å has been found in $Cp(CO)_3MoHgCl$ [52]. If one takes into account the difference (0.05 Å [48]) in covalent radii of Cl and S atoms a value of 2.49 Å for the Hg–S bond length is expected. Thus the nature of a metal-mercury bond must play an important role in the determination of the structural parameters in organotransition metal–main group metal compounds.

The Hg2–S–Hg1 angle (97.2°) lies in the lower range of angles found in polymeric RSHgX compounds (96.8–108.6°) [9–11]. The deviation of the Mo–Hg–S bond from linearity is most likely due to the interactions of mercury atoms which chlorides.

Molybdenum–mercury distances of 2.684(3) and 2.676(3) Å are very close to the value of 2.673(3) Å found in $Cp(CO)_3MoHgCl$ [52] indicating the same nature of metal–metal bonds in both structures. It is only slightly smaller than in $[(bipy)Mo(CO)_3(HgCl)Cl]$ –2.700(7) Å where Mo(II) is seven-coordinate [53]. The average distance of 2.68 Å is shorter than that predicted from the sum of covalent radii of Mo (usually put at 1.62 Å as derived by halving the length of the Mo–Mo bond in $[Cp(CO)_3Mo]_2$ [54]) and of Hg (proposed as 1.16 Å on the basis of data found in symmetric mercury–bis (transition metal carbonyls) [55]). As has been suggested by several authors, this significant bond shortening

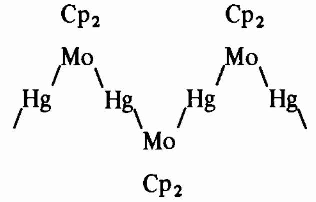
TABLE VI. Equations of the Least-squares Planes of the Form $Ax + By + Cz + D = 0$ (x, y, z in Å refer to the crystallographic axes) and the Distances from the Planes of the Atoms Defining Them.

Plane I	$-0.743x + 0.657y - 0.126z - 0.415 = 0$				
distances	C1	C2	C3	C4	C5
	0.008	−0.010	0.009	−0.004	−0.002
Plane II	$-0.511x + 0.419y - 0.750z - 6.049 = 0$				
distances	C6	C7	C8	C9	C10
	0.016	−0.023	0.022	−0.009	−0.004
Plane III (Mo, Hg1 and Hg2)	$x - 0.8943y + 0.7108z - 5.6895 = 0$				

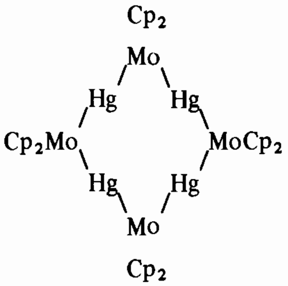
[0.09 Å in (IVa2)] can be a result of $d\pi$–$p\pi$ back bonding from the filled transition metal *d* orbitals to the vacant *p* orbitals on the main group atom. The Hg–Mo–Hg angle of 70.5° is the smallest one observed to date (80.9° in $[Fe(CO)_4(HgCl)_2]$ [56], 80.3° in $[Fe(CO)_4(HgCl)(HgCl_2)]^-$ [57] and 77° in $[Fe(CO)_4[HgCl(py)]_2]$ [58]. Consequently there is also a short Hg1···Hg2 contact [3.093(2) Å]. The short Mo–Hg bonds, the small Hg–Mo–Hg angle and the short Hg···Hg distance can indicate that the bonding electrons are delocalized over a metallic $MoHg_2$ unit.

Within standard errors the cyclopentadienyl rings are planar (Table VI). The angle between the rings is 41.4°. The angle between the centers of the rings and molybdenum [141(4)°] is greater than in Cp_2MoX_2 (X-nonmetallic ligands) complexes [37–39] but smaller than in main group metal-containing derivatives of the Cp_2Mo unit [148° Li [34], 149° Mg [35] and 144° and 151° Al [36]]. The angles between the $MoHg_2$ plane (Table VI) and the ring planes are 20.7° (G1), and 20.8° (G2), indicating no significant influence of Hg···Cl interactions on the geometry of the Cp_2MoHg_2 unit.

An examination of Fig. 1 suggests that the preparation of the compounds (I) from Cp_2MH_2 proceeds by the intermediate formation of (II) which can be isolated if final reaction (see below) is slow enough to permit its crystallization. Once isolated, this compound (IIa) is not soluble in THF. The bands generated only by ring vibrations were observed in its infrared spectrum suggesting a polymeric structure $(Cp_2MoHg)_n$. This compound crystallizes in tetragonal $P\bar{4}2_1c$ space group with a = 17.72 and c = 8.27 Å and probably with 16 Cp_2MoHg units in the unit cell, or two Cp_2MoHg units in its independent part (no systematic extinction suggests the occupation of special positions). This shows that there is no crystallographic evidence for distinguishing between a polymeric chain structure:

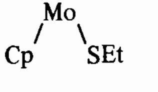


and a tetrameric one, established by X-ray analysis



in $[CdFe(CO)_4]_4 \cdot 2C_3H_6O$ [59] and in $[Cp_2M(H)Li]_4$ (M = Mo and W) [34].

The bonding of molybdenum to two mercury atoms in the compound under consideration is also suggested by its reaction with NaOH/HSEt in THF. Concentration of the resulting red solution leaves deep orange and red crystals. Their (^1H) n.m.r. spectrum exhibits two peaks of C_5H_5 rings and two sets of peaks due to two different SC_2H_5 groups. The positions of the peaks correspond well to that of $Cp_2Mo(HgSC_2H_5)_2$ and $Cp_2Mo(SC_2H_5)_2$ (Table III) suggesting that a mixture of these two compounds is formed. This idea is supported by the measured integrated intensities of the peaks: each Cp ring has its corresponding SC_2H_5 group, but the relative intensities between two C_5H_5-SEt; C_5H_5'-SEt′ sets vary. There are more hydrogens present with a compound containing mercury than with $Cp_2Mo(SEt)_2$. This agrees with the higher solubility of the latter as compared with that of $Cp_2Mo(HgSEt)_2$ – more mercury compound is contained in the solid taken for the n.m.r. measurements. The formation of an asymmetric complex



in which the proton chemical shifts should be comparable with those in $Cp_2Mo(SEt)_2$ and (IIIa2) can be definitely ruled out on the basis of unit cell determinations carried out on the crystalline products. The deep orange crystals have the same space group and unit cell parameters as compounds (IIIa2). Two different red crystals were separated from the product, one of them being the same as (Va2), and the second one having the following cell: $a = 6.92$, $b = 13.28$, $c = 15.53$ Å and $\beta \cong 90°$. The oscillation and Weissenberg photographs of the $\mathrm{Cp_2Mo(SEt)_2}$ crystal were recorded for the purpose of comparing the diffraction patterns of the two compounds. The distribution and the intensities of reflections on both sets of photographs are the same.

The formation of symmetrical compounds $\mathrm{Cp_2Mo(HgSEt)_2}$ and $\mathrm{Cp_2Mo(SEt)_2}$ in the reaction between a polymeric compound (II) and NaOH/HSEt is a good proof of the tendency of the $\mathrm{Cp_2M}$ unit to form two bonds with mercury atoms.

Raman spectroscopy is a sensitive probe for the detection of metal–metal interactions. We tried to record the spectra of all compounds but most of them decompose even on adjusting the apparatus. Another inconvenience is due to the colour of the compounds. The spectra which could be recorded up to about 400 cm^{-1} exhibit very strong bands at 132 cm^{-1} [(Ia2), 2/3$\mathrm{HgBr_2}$], 130 cm^{-1} [(Ia3), 1$\mathrm{HgI_2}$], 140 cm^{-1} [(Ib1), 1$\mathrm{HgCl_2}$], 129 cm^{-1} [(Ib2), 2/3-$\mathrm{HgBr_2}$], 129 cm^{-1} [(Ib3), 2/3$\mathrm{HgI_2}$], 133 cm^{-1} (IVa2), 130 cm^{-1} (IIIa4) and 134 cm^{-1} (III or Va5), and medium ones near 225 cm^{-1} (Mo) and 210 cm^{-1} (W). We attribute the strong bands to the metal–mercury symmetric stretches for the following reasons: (i) antisymmetric Co–Hg stretches were observed in IR at 197 cm^{-1} in $\mathrm{Hg[Co(CO)_4]_2}$ and Mo–Hg at 176 cm^{-1} in $\mathrm{Hg[Mo(CO)_3Cp]_2}$ [60]; a strong Raman band at 161 cm^{-1} in the former was assigned to a ν_s(Co–Hg) mode [61]; ν_s(Mo–Hg) in the latter was observed by us at 153 cm^{-1}, (ii) ν_{as}-(Mn–Hg) band was observed at 186 cm^{-1} in the symmetrically bridged $\mathrm{Hg[Mn(CO)_5]_2}$ and shifts to lower frequencies on the substitution of $\mathrm{Mn(CO)_5^-}$ moiety by $\mathrm{X^-}$ (X = Cl, I) in $\mathrm{XHgMn(CO)_5}$ [60]. Thus one expects that ν_s(Mo–Hg) vibrations in the compounds studied here should be observed at frequencies lower than 153 cm^{-1}. Moreover, their shifts can be considerable because of the presence of two metal–mercury bonds in the molecule. In the case of iodides, ν(M–Hg) stretches are possibly mixed with ν(Hg–I) observed as the shoulders at 138 cm^{-1} (Ia3) and 140 cm^{-1} (Ib3). There is no significant difference in the frequencies of Mo–Hg and W–Hg vibrations, but the same was observed for *e.g.* $\mathrm{(OC)_5MMn(CO)_5^-}$ compounds (M = Mo – 150 cm^{-1}, M = W – 149 cm^{-1}) [62].

Because of the possible mercury–mercury interactions, no stable $\mathrm{MHg^+}$ ion was detected in the mass spectra of some compounds (I) and (III). The $\mathrm{Cp_2MX_2^+}$, $\mathrm{Cp_2MX^+}$, $\mathrm{CpMX^+}$, $\mathrm{CpMX_2^+}$, $\mathrm{Cp_2M^+}$, $\mathrm{HgX_2^+}$, $\mathrm{Hg^+}$ and their doubly-charged counterparts were identified as stable species. Thus, although chemically strong, the metal–mercury bond does not seem to be thermally stable. The mercury deposition is immediate on heating.

In the light of the above discussion the following sequence of equations is proposed for the formation and interconversion reactions of the compounds studied:

$$\mathrm{Cp_2MH_2 + HgX_2 \rightarrow 1/n}\underset{\text{(II)}}{\mathrm{(Cp_2MHg)_n}}\mathrm{ + 2HX} \tag{1}$$

$$\mathrm{(II) + HgX_2 \rightarrow} \underset{\text{(I)}}{\mathrm{Cp_2M(HgX)_2}} \tag{2}$$

$$\underset{\text{(I)}}{\mathrm{Cp_2M(HgX)_2}}\mathrm{ + xHgX_2} \rightleftarrows \underset{\text{(I)}}{\mathrm{Cp_2M(HgX)_2 \cdot xHgX_2}} \tag{3}$$

$$\mathrm{(I)} \underset{\mathrm{X^-}}{\overset{\mathrm{SR^-}}{\rightleftarrows}} \underset{\text{(IV)}}{\mathrm{[Cp_2MHg_2(\mu\text{-}SR)]X}} + \mathrm{xHg(SR)_2 + (1 + 2x)X^-} \tag{4}$$

$$\mathrm{(IV) + SR^-} \rightleftarrows \underset{\text{(III)}}{\mathrm{Cp_2M(HgSR)_2}}\mathrm{ + X^-} \tag{5}$$

It was observed that both orange powder (Ia1) and red crystals (IVa2) were formed when the solution of $\mathrm{Cp_2Mo(HgSEt)_2}$ (IIIa2) in $\mathrm{CHCl_3}$ was allowed to stand for some days under nitrogen.

Attempts to prepare the compounds containing the Mo–Hg–$\mathrm{CH_3}$ bond were unsuccessful. No reaction between $\mathrm{Cp_2MoH_2}$ and $\mathrm{HgMe_2}$ was observed at room temperature and at 50 °C over 3 days. The infrared spectrum of the product obtained by reaction of $\mathrm{Cp_2Mo(HgCl)_2}$ with $\mathrm{CH_3I}$ is identical with that of $\mathrm{Cp_2MoCl_2}$. This compound and $\mathrm{Cp_2Mo(HgCl)_2}$ were identified by infrared spectroscopy as the products of the reaction between $\mathrm{Cp_2MoH_2}$ and MeHgCl. The difficulties in preparing the organomercury–organotransition metal derivatives in the biscyclopentadienyl family of compounds is not surprising because few organomercury–transition metal carbonyls have been prepared and generally they are unstable [63, 64].

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