Synthesis and Characterization of Novel M−Hg−M (M = Cr, Mo, W) Heterotrimetallic Complexes Bridged by a Functionally Substituted Bis(cyclopentadienyl) Ligand. Crystal and Molecular Structure of [Mo(CO)$_3$(η^5-C$_5$H$_4$CH$_2$CH$_2$OCH$_2$CH$_2$C$_5$H$_4$-η^5)(CO)$_3$-Mo]Hg

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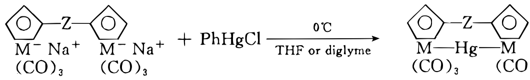
Summary: The bridged heterotrimetallic complexes with a general formula of [M(CO)$_3$(η^5-C$_5$H$_4$ZC$_5$H$_4$-η^5)(CO)$_3$-M]Hg (M = Cr, Mo, W, Z = C(O)CH$_2$CH$_2$C(O); M = Mo, Z = CH$_2$CH$_2$OCH$_2$CH$_2$) can be readily prepared through reaction of PhHgCl with appropriate dianions $^-$M(CO)$_3$-(η^5-C$_5$H$_4$ZC$_5$H$_4$-η^5)(CO)$_3$M$^-$ in THF or diglyme. Their structures assigned by combustion analysis and spectroscopy are further confirmed by X-ray crystallography for one representative complex [Mo(CO)$_3$(η^5-C$_5$H$_4$CH$_2$-CH$_2$OCH$_2$CH$_2$C$_5$H$_4$-η^5(CO)$_3$Mo]Hg.

Introduction

Nonbridged M−Hg−M (M = Cr, Mo, W) trimetallic complexes containing cyclopentadienyl[1−8] or substituted cyclopentadienyl[9−12] ligands are well documented in the literature. There is, however, no corresponding bridged M−Hg−M trimetallic complex reported yet in the literature, up to now. In view of our interest in both the novel formation method for M−Hg−M linkage and the use of functionally substituted bis(cyclopentadienyl) ligands in the synthesis of heteromultinuclear complexes,[13] we initiated this study. In this paper we report the synthetic results of a series of M−Hg−M trimetallic compounds bridged with functionally substituted bis(cyclopentadienyl) ligands, 1,4-bis(cyclopentadienyl)-1,4-butadione and 1,5-bis(cyclopentadienyl)-3-oxapentane. Structural characterization of the products and an X-ray diffraction analysis for one representative compound are also described.

Results and Discussion

The functionally substituted bis(cyclopentadienyl)-bridged group 6 metal dianion salts **1**, derived from M(CO)$_6$ (M = Cr, Mo, W) and [1,1′-(1,4-dioxabutane-1,4-diyl)dicyclopentadienyl]disodium,[14] or from Mo(CO)$_6$ and [1,1′-(3-oxapentamethylene)dicyclopentadienyl]disodium,[15] have been shown to react in THF or diglyme with PhHgCl to give four novel products **2a−d** (eq 1) as slightly air-sensative yellow solids in 35−65% yields.



(1)

1 **2**

Complexes	**2a**	**2b**	**2c**	**2d**
M	Cr	Mo	W	Mo
Z	[C(O)CH$_2$]$_2$	[C(O)CH$_2$]$_2$	[C(O)CH$_2$]$_2$	(CH$_2$CH$_2$)$_2$O

The bridged products **2a−d** are much less soluble in organic solvents than corresponding nonbridged M−Hg−M compounds.[1−12] For example, they all do not dissolve in petroleum ether. While **2d** is soluble in CHCl$_3$, CH$_2$Cl$_2$, and ether, **2a−c** are not, but they are soluble in more polar organic solvents such as THF and DMSO. For **2a−c**, the solubility decreases in the order of **2b** > **2c** > **2a**. The characterizing data for **2a−d** are in good agreement with the structures shown in eq 1. For example, the IR spectra of **2a−c** showed three bands for terminal carbonyls in the range 1876−2033 cm^{-1} and one band at about 1670 cm^{-1} for the ketone carbonyls, while the IR spectrum of **2d** exhibited three bands for terminal carbonyls at 1950−1861 cm^{-1} and one C−O stretching band at about 1134 cm^{-1}. The ^{1}H NMR spectra of **2a−d** all showed the presence of their corresponding functionally substituted cyclopentadienyl ligands; the EI mass spectrum of **2d** showed its molecular ion peak at m/z 766, while those of **2a−c** exhibited only their respective fragment ion peaks.

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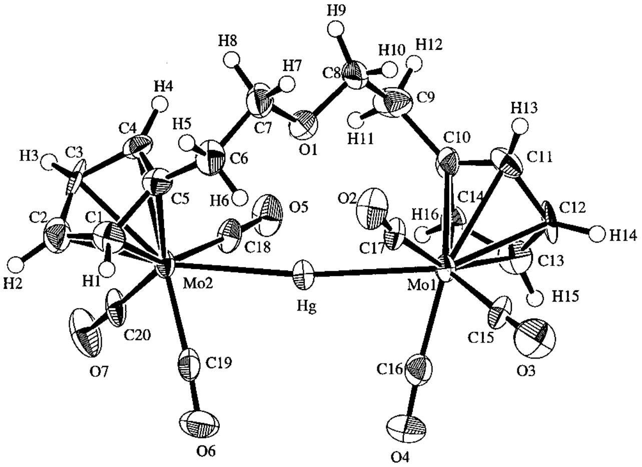


Figure 1. ORTEP drawing of **2d** with the atom-numbering scheme.

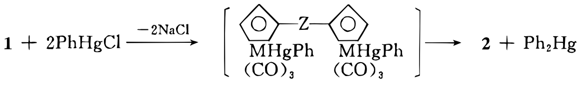
Table 1. Selected Bond Lengths and Angles of 2d

	Lengths (Å)		
Hg−Mo(1)	2.754(2)	Hg−Mo(2)	2.772(1)
Mo(1)−C(10)	2.39(1)	Mo(1)−C(11)	2.34(1)
Mo(1)−C(15)	1.94(1)	Mo(2)−C(1)	2.35(1)
Mo(2)−C(2)	2.34(2)	Mo(2)−C(18)	1.93(2)
O(1)−C(7)	1.42(2)	O(3)−C(15)	1.16(2)
O(5)−C(18)	1.20(2)	C(1)−C(2)	1.43(2)
C(5)−C(6)	1.51(2)	C(6)−C(7)	1.50(2)
	Angles (deg)		
Mo(1)−Hg−Mo(2)	171.43(4)	Hg−Mo(1)−C(10)	86.6(4)
Hg−Mo(1)−C(11)	118.4(5)	Hg−Mo(1)−C(15)	130.0(5)
Hg−Mo(1)−C(16)	71.7(5)	Hg−Mo(1)−C(17)	72.4(4)
Hg−Mo(2)−C(18)	67.7(4)	Hg−Mo(2)−C(19)	70.0(5)
Hg−Mo(2)−C(20)	129.9(5)	C(7)−O(1)−C(8)	112(1)
Mo(1)−C(15)−O(3)	177(1)	Mo(1)−C(16)−O(4)	176(1)
Mo(1)−C(17)−O(2)	171(1)	Mo(2)−C(18)−O(5)	176(1)
Mo(2)−C(19)−O(6)	176(1)	Mo(2)−C(20)−O(7)	178(1)

To confirm the structures of such bridged complexes and to explore the possible Lewis acid−base interactions between mercury and oxygen atoms, an X-ray diffraction analysis for **2d** was undertaken. The molecular structure of **2d** is depicted in Figure 1. Selected bond lengths and angles are summarized in Table 1.

From Figure 1 it can be seen that the structure of **2d** consists of a metal−metal skeleton Mo−Hg−Mo, a 1,1′-(3-oxapentamethylene)dicyclopentadienyl ligand and six carbonyls. Among six carbonyls the C(15)O(3) and C(20)O(7) are away from the Mo−Hg−Mo skeleton, while C(16)O(4), C(17)O(2), C(18)O(5), and C(19)O(6) are close to the skeleton. For the former two carbonyls the Mo−C−O bond angles are 177(1) and 178(1)°, while those for the latter four are 171(1) and 176(1)°, respectively. The Hg−Mo−C(O) bond angles for the former two are 130.0(5) and 129.9(5)°, while those for the latter four are in the range 67−73°. The two bond lengths of Mo−Hg equal 2.754(2) and 2.772(1) Å, which are close to the sum of the atomic covalent radii of molybdenum and mercury (about 2.73 Å). The bond angle of Mo(1)−Hg−Mo(2) is 171.43(4)°, and thus the mercury atom coordination geometry is diagonal with no significant departure from linearity. The geometry around each Mo atom approximates to a square-based pyramid with the substituted cyclopentadienyl group occupying the apical position and is very similar to that around the chromium, molybdenum, and tungsten atoms in complexes [η^5-EtC$_5$H$_4$(CO)$_3$Cr]$_2$Hg,[11] [η^5-C$_5$H$_5$(CO)$_3$Mo]$_2$Hg,[7] [η^5-EtO$_2$CC$_5$H$_4$(CO)$_3$Mo]$_2$Hg,[10] and [η^5-C$_5$H$_5$(CO)$_3$W]$_2$Hg.[9] Two differences between **2d** and its nonbridged analogue [η^5-EtO$_2$CC$_5$H$_4$(CO)$_3$Mo]$_2$Hg[10] should be indicated. First, the bond angle of Mo−Hg−Mo in **2d** is 171.43(4)° as mentioned above, while that of the analogue is exactly the linear value of 180.03°; second, with respect to the Mo−Hg−Mo structural unit the two cyclopentadienyl rings (or six carbonyls) in **2d** are cis to each other, while those in the analogue are trans (namely the analogue is centrosymmetric). Obviously, these are due to the presence of the bridge (CH$_2$)$_2$O(CH$_2$)$_2$ linked to two cyclopentadienyl rings in **2d**. It is worth pointing out that the distance between O(1) and Hg is only 2.87 Å, which is less than sum of their van der Waals radii of 2.9−3.13 Å. This implies that an intramolecular interaction between oxygen and mercury atoms is present. Such kinds of weak interactions between Hg and heteroatoms were already described in the literature.[16,17] These could be construed as arising from the acceptor nature of the mercury center and the donor nature of the oxygen atom.

It is interesting to note that the bridged trimetallic complexes **2** could be regarded as macrocyclic ring compounds involved with σ- and η^5-π-types of bonds. At present, it is not clear about the mechanism for this ring-closure reaction by the action of PhHgCl on dianion salts **1**. According to a related mechanistic study,[10] however, the ring-closure reaction, namely the formation of a M−Hg−M linkage would be probably accomplished by a symmetrization process of the active tetrametallic intermediates **m** formed from a condensation reaction of **1** with PhHgCl (eq 2).



m

(2)

Experimental Section

All reactions and manipulations were carried out under highly purified tank nitrogen using standard Schlenk or vacuum line techniques. Tetrahedrofuran (THF), diethyl ether, and diglyme were distilled from sodium benzophenone ketyl under nitrogen. Dimethyl sulfoxide (DMSO) and petroleum ether were dried over anhydrous CaCl$_2$; methylene dichloride was distilled from P$_2$O$_5$. All solvents were degassed by bubbling nitrogen for about 15 min prior to use. Column chromatography and TLC were carried out by using silica gel of 300−400 mesh and silica gel G (10−40 μm), respectively. M(CO)$_6$ (M = Cr, Mo, W) were purchased from Strem Chemicals Inc., and PhHgCl was prepared according to the literature.[18] IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL FX 90Q NMR spectrometer. Elemental analysis and MS determinations were performed by a 240C analyzer and HP 5988A spectrometer, respectively. Melting points were determined on a MP-500 Yanaco micromelting point apparatus.

Preparation of 2a. a 100 mL three-necked flask equipped with a stir bar, a N$_2$ inlet tube, and serum caps was charged with 0.86 g (3.90 mmol) of Cr(CO)$_6$, 0.516 g (2.00 mmol) of [NaC$_5$H$_4$C(O)CH$_2$], and 25 mL of diglyme. The mixture was refluxed for 6 h. Upon cooling of the sample to 0 °C, to the mixture was added 1.00 g (3.20 mmol) of PhHgCl, and the new mixture was stirred for additional 1 h. After evaporation of

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Table 2. Crystal Data and Details of the Structure Refinement for 2d

empirical formula	$C_{20}H_{16}O_7HgMo_2$
fw	760.81
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a/Å	15.932(3)
b/Å	19.322(4)
c/Å	13.774(3)
V/Å^3	4240(1)
Z	8
D_c/g cm^{-3}	2.383
F(000)	2848.00
μ(Mo Kα)/cm^{-1}	84.44
radiation	Mo Kα (λ = 0.710 69 Å)
temp/K	293
scan type	$\omega-2\theta$
2θ/deg (max)	50.0
no. of reflcns measd	4070 (total)
no. of observns ($I > 3.00\sigma(I)$)	2665
no. of variables	272
R; R_w	0.056; 0.054
goodness of fit indicator	3.14

the solvent at reduced pressure the residue was subjected to column chromatography on silica gel with THF as eluent to give crude product **2a**. Further purification of **2a** by recrystallization from DMSO/Et_2O/CH_2Cl_2, followed by wash with acetone and diethyl ether, gave 0.48 g (35%) of pure **2a** as a slightly air-sensitive yellow solid, mp 165 °C (dec). ^{1}H NMR (DMSO-d_6, TMS): δ 2.88−3.08 (m, 4H, CH_2CH_2), 5.28−5.40 (m, 4H, β-H of Cp ring), 5.78−588 (m, 4H, α-H of Cp ring) ppm. IR (KBr, disk): 2032.4 (w), 1966.8 (s), 1884.8 (vs, $\nu_{C\equiv O}$), 1671.5 (m, $\nu_{C=O}$) cm^{-1}. MS (EI, Cr^{52}, Hg^{202}) [*m*/*z* (relative intensity)]: 202 (Hg$^+$, 67.9), 200 [$C_5H_4Cr(CO)_3^+$, 53.7], 64 ($C_5H_4^+$, 7.6), 52 (Cr$^+$, 16.9). Anal. Calcd for $C_{20}H_{12}Cr_2HgO_8$: C, 35.07; H, 1.77. Found: C, 34.82; H, 2.05.

Preparation of 2b. A flask described as above was charged with 1.01 g (4.00 mmol) of $Mo(CO)_6$, 0.516 g (2.00 mmol) of $[NaC_5H_4C(O)CH_2]_2$, and 25 mL of THF. The mixture was refluxed for 15 h. Upon cooling of the sample to 0 °C, to the mixture was added 1.00 g (3.20 mmol) of PhHgCl, and the new mixture was stirred for additional 1 h. After evaporation of the solvent at reduced pressure the residue was subjected to column chromatography on silica gel with THF as eluent to give crude product **2b**. Further purification of crude **2b** by TLC with 1:1 petroleum ether/THF as a developer, followed by wash with diethyl ether, gave 0.86 g (56%) of pure **2b** as a slightly air-sensitive yellow solid, mp 127−129 °C. ^{1}H NMR (DMSO-d_6, TMS): δ 2.90−3.20 (m, 4H, CH_2CH_2), 5.72−5.98 (4H, β-H of Cp ring), 6.12−6.46 (m, 4H, α-H of Cp ring) ppm. IR (KBr, disk): 2007.8 (s), 1975.0 (vs), 1884.8 (vs, $\nu_{C\equiv O}$), 1671.5 (m, $\nu_{C=O}$) cm^{-1}. MS (EI, Mo^{98}, Hg^{202}) [*m*/*z* (relative intensity)]: 364 ($C_5H_4MoHg^+$, 13.0), 274 [$OCC_5H_4Mo(CO)_2^+$, 10.2], 218 [$C_5H_4Mo(CO)_2^+$, 7.9], 202 (Hg$^+$, 100), 190 ($C_5H_4Mo(CO)^+$, 21.3), 162 ($C_5H_4Mo^+$, 15.3), 98 (Mo$^+$, 19.4). Anal. Calcd for $C_{20}H_{12}HgMo_2O_8$: C, 31.09; H, 1.57. Found: C, 31.09; H, 1.64.

Preparation of 2c. The same procedure as that of **2a** was followed, but 1.38 g (4.00 mmol) of $W(CO)_6$ was used instead of $Cr(CO)_6$. Further purification of crude product **2c** by recrystallization from DMSO at −20 °C gave 0.72 g (38%) of pure **2c** as a slightly air-sensitive yellow solid, mp 180 °C (dec). ^{1}H NMR (DMSO-d_6, TMS): δ 2.88−3.12 (m, 4H, CH_2CH_2), 5.74−5.94 (m, 4H, β-H of Cp ring), 6.12−6.42 (m, 4H, α-H of Cp ring) ppm. IR (KBr, disk): 1999.6 (s), 1958.6 (vs), 1876.6 (vs, $\nu_{C\equiv O}$), 1679.7 (m, $\nu_{C=O}$) cm^{-1}. MS (EI, W^{184}, Hg^{202}) [*m*/*z* (relative intensity)]: 576 [$CH_2C(O)C_5H_4WHg(CO)_3^+$, 12.9], 332 [$C_5H_4W(CO)_3^+$, 1.0], 276 [$C_5H_4W(CO)^+$, 12.4], 202 (Hg$^+$, 73.2), 64 ($C_5H_4^+$, 0.8). Anal. Calcd for $C_{20}H_{12}HgO_8W_2$: C, 25.32; H, 1.28. Found: C, 25.06; H, 1.64.

Preparation of 2d. The same procedure as that of **2b** was followed, but 0.492 g (2.00 mmol) of $(NaC_5H_4CH_2CH_2)_2O$ was used instead of $[NaC_5H_4C(O)CH_2]_2$. Further purification of crude product **2d** by TLC with 1:1 petroleum ether/CH_2Cl_2 as a developer, followed by recrystallization from 1:1 petroleum ether/CH_2Cl_2, gave 0.80 g (53%) of pure **2d** as a slightly air-sensitive yellow solid, mp 81−83 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 2.40−2.90 (m, 4H, $CH_2CH_2OCH_2CH_2$), 3.36−3.92 (m, 4H, CH_2OCH_2), 5.00−5.64 (m, 8H, two C_5H_4) ppm. IR (KBr, disk): 1950.4 (vs), 1895.0 (vs), 1860.1 (vs, $\nu_{C\equiv O}$), 1113.7 (w, ν_{C-O}) cm^{-1}. MS (EI, Mo^{98}, Hg^{202}) [*m*/*z* (relative intensity)]: 766 (M$^+$, 0.2), 476 [$CH_2CH_2C_5H_4Mo(CO)_3Hg^+$, 1.8], 448 [$CH_2CH_2C_5H_4Mo(CO)_2Hg^+$, 3.3], 420 [$CH_2CH_2C_5H_4Mo(CO)Hg^+$, 0.4], 392 ($CH_2CH_2C_5H_4MoHg^+$, 7.5), 364 ($C_5H_4MoHg^+$, 2.9), 202 (Hg$^+$, 66.1), 162 ($C_5H_4Mo^+$, 1.5). Anal. Calcd for $C_{20}H_{16}HgMo_2O_7$: C, 31.57; H, 2.12. Found: C, 31.73; H, 2.14.

X-ray Structure Analysis of 2d. Crystals of **2d** suitable for crystallography were obtained by recrystallization from petroleum ether/CH_2Cl_2 (1:1) in a refrigerator. Crystal data and results of structural refinement were summarized in Table 2. A yellow prismatic crystal having approximate dimensions 0.2 × 0.2 × 0.3 mm was used for unit cell measurements and intensity collection on a Rigaku AFC 7R diffractometer. The structure was solved by direct methods (SHELXS 86)[19] and expanded using Fourier techniques. The final refinement was accomplished by the full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically. Data were corrected for *Lp* and absorption factors. All calculations were performed on a Micro-Vax II computer using the TEXSAN program package.[20]

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Supporting Information Available: Full tables of characterization data for the new compounds, text describing X-ray procedures, and tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **2d** (11 pages). Ordering information is given on any current masthead page.

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