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Unexpected metal–metal bond formation in the M–Hg–M (M = Cr, Mo, W) structural unit. Synthesis and characterization of $[\eta^5\text{-}RC_5H_4(CO)_3M]_2Hg$ complexes (R = H, M = W; R = CH_3CO, M = Cr, Mo, W)

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Abstract

Trimetallic complexes with the general formula of $[\eta^5\text{-}RC_5H_4(CO)_3M]_2Hg$ (R = H, M = W; R = CH_3CO, M = Cr, Mo, W) were prepared from the reactions of MeHgCl with $Na[\eta^5\text{-}C_5H_5W(CO)_3]$ or with $Na[\eta^5\text{-}CH_3COC_5H_4M(CO)_3]$ (M = Cr, Mo, W) in diglyme. Structures assigned by combustion analysis and spectroscopy were confirmed by X-ray crystal structure determination of one representative complex, $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$. This molecule crystallizes in the monoclinic space group $C2/c$ with $a = 21.119(2)$, $b = 7.067(1)$, $c = 12.033(1)$ Å; $\beta = 91.10(1)°$; $V = 1795.5$ Å^3; $Z = 4$. While the W–Hg–W skeleton possesses a linear configuration, the geometry around each tungsten atom approximates to a square-based pyramid with the cyclopentadienyl ring occupying the apical position.

Introduction

In view of their theoretical significance and potential applications, such as in catalysis, organometallic complexes containing one or more metal–metal bonds have been the subject of a very large number of studies [1]. During the course of our studies involving this kind of complex [2,3], an initial attempt was made to develop a new route for preparing the complex $Cp(CO)_3W\text{–}HgMe$ [4] through the reaction of MeHgCl with sodium cyclopentadienyltricarbonyltungstenate (**2**: M = W, R = H) derived from sodium cyclopentadienide (**1**: R = H) and tungsten hexacarbonyl. Surprisingly, instead of the expected binuclear complex $Cp(CO)_3W\text{–}HgMe$ a trinuclear complex (**3a**) [4–7] containing a W–Hg–W structural unit was isolated in 52% yield. In order to examine the generality of this interesting reaction, we investigated further the reaction of MeHgCl with the sodium salts of acetyl-substituted cyclopentadienyltricarbonyl anions of all the Group VIb metals (**2**). It was revealed that the same type of reaction as that between $Na[Cp(CO)_3W]$ and MeHgCl took place and afforded three corresponding new complexes **3b**–**3d** in 35–54% yields (Scheme 1).

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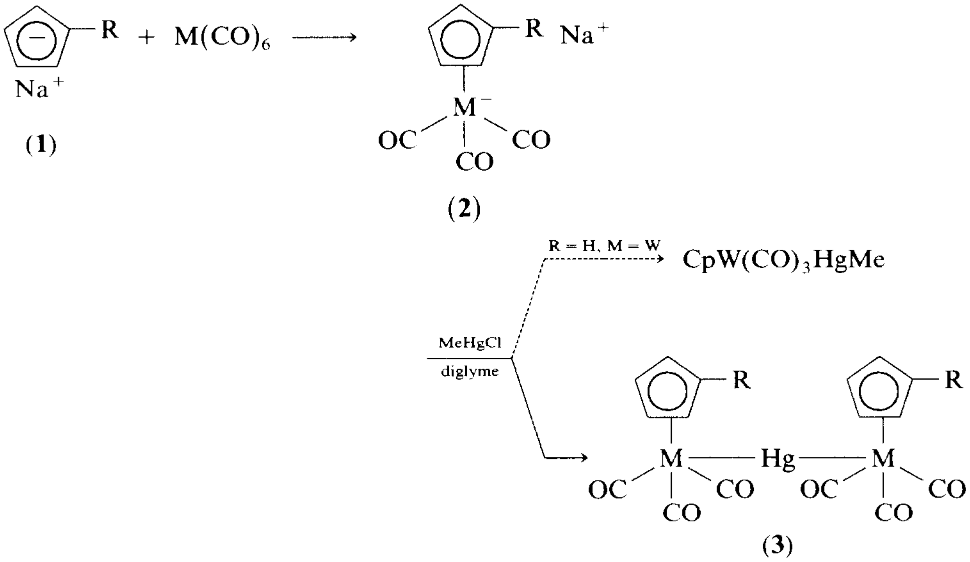

(**3a**: R = H, M = W; **3b**: R = CH_3CO, M = Cr; **3c**: R = CH_3CO, M = Mo; **3d**: R = CH_3CO, M = W)

Scheme 1.

This paper describes the synthetic procedure and characterization of these trinuclear metal–metal bond complexes as well as the single crystal structure of bis(η^5-cyclopentadienyltungstentricarbonyl)mercury (**3a**).

Results and discussion

Through the unexpected reaction mentioned above, we have synthesized four trinuclear metal complexes **3a–3d**. These complexes containing the M–Hg–M (M = Cr, Mo, W) unit are all air-stable yellow crystalline solids but they are quite air-sensitive when dissolved in organic solvents, particularly the chromium complex (**3b**). The melting points of acetyl complexes **3b–3d** increase gradually from chromium complex (**3b**, m.p. 147–149 °C) to molybdenum complex (**3c**, m.p. 156–158 °C) and to tungsten complex (**3d**, m.p. 169–171 °C). For all the complexes **3a–3d** the combustion analysis, IR and ^1H NMR data are in good agreement with the structures shown as **3a–3d**.

It is worth pointing out that the ^1H NMR spectra for complexes **3b–3d** each have a pair of apparent triplets, in which the downfield triplet has been assigned to the H(2,5) protons of substituted cyclopentadienyl ring while the upfield triplet is assigned to the H(3,4) protons [8]. In addition, the triplet assigned to H(2,5) (or the triplet assigned to H(3,4)) is located in lowest field in the case of the tungsten complex, the intermediate field for the molybdenum complex and in the highest field for the chromium complex and there is a larger difference in chemical shift between the corresponding triplets of the chromium complex and the molybdenum complex than between those of the latter and the tungsten complex. It follows that the ^1H NMR behaviour of the functionally mono-substituted cyclopentadienyl

Table 1

Positional parameters and equivalent isotropic thermal factors for $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$

Atom	x	y	z	B_{eq} (Å^2)
Hg	0.000	0.1195(2)	0.250	2.69(2)
W	0.12086(3)	0.0981(1)	0.33862(5)	2.06(1)
O(11)	0.0320(6)	0.239(3)	0.528(1)	5.8(4)
O(12)	0.2060(5)	0.408(2)	0.447(1)	4.4(3)
O(13)	0.1211(7)	0.400(2)	0.149(1)	4.8(3)
C(11)	0.0620(8)	0.188(3)	0.458(1)	3.6(4)
C(12)	0.1753(7)	0.292(3)	0.406(1)	3.0(3)
C(13)	0.1189(8)	0.288(3)	0.217(1)	3.1(4)
C(21)	0.1184(8)	−0.214(3)	0.400(2)	3.9(4)
C(22)	0.1798(8)	−0.143(3)	0.417(2)	4.2(4)
C(23)	0.2060(8)	−0.099(3)	0.309(2)	4.5(4)
C(24)	0.165(1)	−0.139(3)	0.225(2)	5.0(5)
C(25)	0.111(1)	−0.211(3)	0.270(2)	5.5(5)

protons of **3b**–**3d** parallels that of corresponding mononuclear metal complexes $(\eta^5\text{-}C_5H_4R)M(CO)_3CH_3$ (M = Cr, Mo, W) [8].

In order unambiguously to confirm the structures of the complexes obtained from this type of reaction, we have determined the crystal structure of one representative complex namely **3a**, by X-ray diffraction. Although the crystal structures of some complexes containing a transition metal–mercury bond, such as those of $(BrHg)_2Fe(CO)_4$ [9], $Hg[Co(CO)_4]_2$ [10], and $CpFe(CO)_2HgCo(CO)_4$ [11], have been known for many years, no crystal structure of any organometallic complex containing the W–Hg bond has been reported so far in the literature. This is therefore the first crystal structure for a complex with the W–Hg bond.

The final fractional coordinates with equivalent isotropic thermal parameters are listed in Table 1. Tables 2 and 3 list the bond lengths and bond angles respectively. An ORTEP plot showing the atom labelling scheme is presented in Fig. 1. As seen from Fig. 1, complex **3a** consists of one mercury atom and two identical organometallic moieties $\eta^5\text{-}C_5H_5(CO)_3W$. The bond length of W–Hg equals 2.7513 Å, which is close to the sum of the atomic covalent radii of tungsten and mercury (2.74 Å). The bond angle of W–Hg–W is 173.69°, and thus the mercury atom coordination geometry in complex **3a**, is a diagonal with no significant departure of the W–Hg–W skeleton from linearity. This is as in other transition metal complexes containing mercury [9–11]. The geometry around each tungsten atom approximates to a

Table 2

Bond lengths (Å) for $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$

Hg–W	2.7513(3)	W–C(25)	2.341(8)
Hg–W	2.7513(3)	O(11)–C(11)	1.117(8)
W–C(11)	2.023(7)	O(12)–C(12)	1.155(8)
W–C(12)	1.951(6)	O(13)–C(13)	1.135(8)
W–C(13)	1.988(6)	C(21)–C(22)	1.400(8)
W–C(21)	2.327(7)	C(21)–C(25)	1.56(2)
W–C(22)	2.301(7)	C(22)–C(23)	1.45(2)
W–C(23)	2.308(7)	C(23)–C(24)	1.35(2)
W–C(24)	2.365(8)	C(24)–C(25)	1.38(1)

Table 3

Bond angles (°) for $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$

W-Hg-W	173.69(2)	C(13)-W-C(24)	93.1(3)
Hg-W-C(11)	71.4(2)	C(13)-W-C(25)	111.6(3)
Hg-W-C(12)	131.0(2)	C(21)-W-C(22)	35.2(3)
Hg-W-C(13)	70.8(2)	C(21)-W-C(23)	59.9(2)
Hg-W-C(21)	98.5(2)	C(21)-W-C(24)	61.4(3)
Hg-W-C(22)	133.6(1)	C(21)-W-C(25)	39.1(2)
Hg-W-C(23)	133.9(2)	C(22)-W-C(23)	36.6(3)
Hg-W-C(24)	100.8(2)	C(22)-W-C(24)	59.6(3)
Hg-W-C(25)	80.7(2)	C(22)-W-C(25)	59.8(2)
C(11)-W-C(12)	81.4(3)	C(23)-W-C(24)	33.5(3)
C(11)-W-C(13)	108.0(3)	C(23)-W-C(25)	56.5(3)
C(11)-W-C(21)	93.2(3)	C(24)-W-C(25)	33.9(3)
C(11)-W-C(22)	106.1(3)	W-C(11)-O(11)	176.6(5)
C(11)-W-C(23)	142.3(3)	W-C(12)-O(12)	177.9(5)
C(11)-W-C(24)	152.6(3)	W-C(13)-O(13)	175.9(6)
C(11)-W-C(25)	119.4(3)	W-C(21)-C(22)	71.4(4)
C(12)-W-C(13)	80.6(3)	W-C(21)-C(25)	70.9(5)
C(12)-W-C(21)	123.4(3)	C(22)-C(21)-C(25)	102.5(6)
C(12)-W-C(22)	92.5(2)	W-C(22)-C(21)	73.5(4)
C(12)-W-C(23)	91.8(2)	W-C(22)-C(23)	71.9(4)
C(12)-W-C(24)	120.1(3)	C(21)-C(22)-C(23)	108.4(6)
C(12)-W-C(25)	147.9(3)	W-C(23)-C(22)	71.4(4)
C(13)-W-C(21)	150.7(3)	W-C(23)-C(24)	75.6(4)
C(13)-W-C(22)	143.6(3)	C(22)-C(23)-C(24)	111.9(5)
C(13)-W-C(23)	107.4(3)	W-C(24)-C(23)	70.9(5)
W-C(24)-C(25)	72.1(5)	W-C(25)-C(24)	74.0(5)
C(23)-C(24)-C(25)	108.0(7)	C(21)-C(25)-C(24)	109.2(6)
W-C(25)-C(21)	69.9(4)		

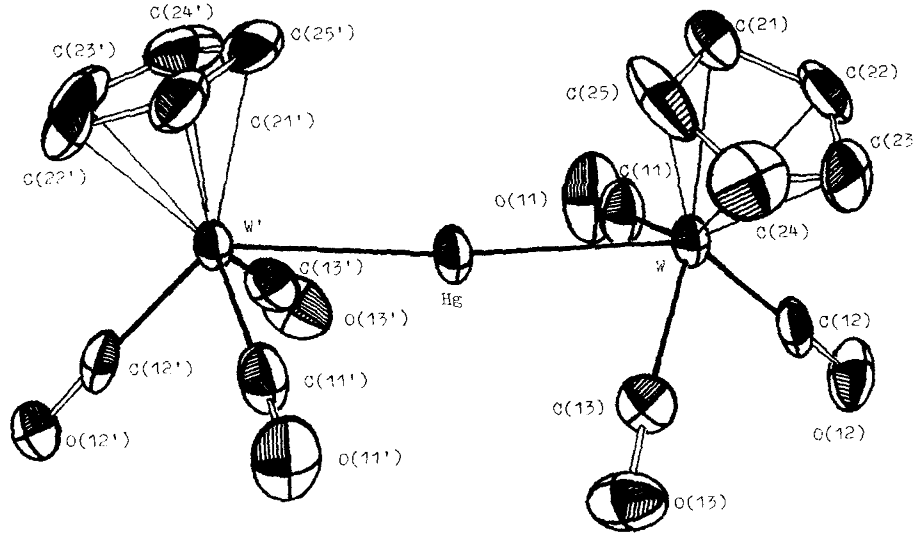

Fig. 1. ORTEP plot of $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$.

square-based pyramid with the cyclopentadienyl group occupying the apical position and is very similar to that around the molybdenum atom in the complex $(C_2\text{-}^tBu)Ru_3(CO)_9HgMo(\eta^5\text{-}C_5H_5)(CO)_3$ [12].

Experimental

The reaction was carried out under an atmosphere of prepurified tank nitrogen. Diglyme was distilled under nitrogen from sodium benzophenone ketyl and purged with nitrogen before use. Chromium, molybdenum and tungsten hexacarbonyls were purchased from Strem Chemicals and methylmercuric chloride from Alfa Ventron. Sodium acetylcyclopentadienide [13,14] was prepared according to standard procedures. Chromatographic silica gel was of about 300 mesh. IR spectra were recorded on a Model SP3-300 infrared spectrophotometer. ^1H NMR spectra were recorded on a JEOL JNMPMX 60 Si NMR spectrometer. C, H analyses were performed by a 204C analyzer. Melting points were determined on a PHMK-3003 apparatus.

Synthesis of $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$ *(3a)*

In a 100-ml three-necked flask fitted with a magnetic stir-bar, a rubber septum and reflux condenser topped with a nitrogen inlet tube, sodium cyclopentadienide was prepared from 0.046 g (2.0 mmol) of sodium sand, 0.20 ml (2.40 mmol) of cyclopentadiene and 20 ml of diglyme [15]. To this pink solution was added 0.70 g (2.0 mmol) of tungsten hexacarbonyl and the mixture was refluxed for 2–3 h. After the resulting mixture had been cooled to about 80 ° C, 0.50 g (2.0 mmol) of methylmercuric chloride was added and the mixture was stirred for 13–14 h. Solvent was removed from the orange reaction mixture *in vacuo*. The residue was extracted with acetone and the extracts were subjected to column chromatography. Acetone eluted a yellow band which was collected under nitrogen. Removal of the solvent *in vacuo* and recrystallization from acetone gave 0.454 g (52%) of $[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg$ (**3a**) as a yellow solid, m.p. 210–212 ° C (dec.). Anal. Found: C, 22.37; H, 1.17. $C_{16}H_{10}HgO_6W_2$ calcd.: C, 22.18; H, 1.16%. IR (KBr disc): terminal C≡O, 1990s, 1945s, 1850vs cm^{-1}, ^1H NMR ($CDCl_3$): δ 5.49 (s, 10H, $2C_5H_5$) ppm.

Synthesis of $[\eta^5\text{-}CH_3COC_5H_4(CO)_3Cr]_2Hg$ *(3b)*

A 100-ml three-necked flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube, was charged with 1 g (4.54 mmol) of chromium hexacarbonyl, 0.95 g (4.70 mmol) of sodium acetylcyclopentadienide and 20 ml of diglyme. The mixture was refluxed for 4–5 h and cooled to about 80 ° C. Then 1.02 g (4.05 mmol) of methylmercuric chloride was added and the mixture was stirred for about 14 h. Solvent was removed *in vacuo* from the yellow reaction mixture. The residue was extracted with 50% (v/v) CH_2Cl_2/petroleum ether and the extracts were subjected to column chromatography. A yellow band was eluted out with 50% CH_2Cl_2/petroleum and collected under nitrogen. Solvent was removed in vacuo and the yellow solid was recrystallized from 50% CH_2Cl_2/petroleum to give 0.538 g (35%) of $[\eta^5\text{-}CH_3COC_5H_4(CO)_3Cr]_2Hg$ (**3b**) as a yellow solid, m.p. 147–149 ° C. Anal. Found: C, 35.16; H, 2.11. $C_{20}H_{14}Cr_2HgO_8$ calcd.: C, 34.97; H, 2.05%. IR (KBr disc): terminal C≡O, 2000s, 1967vs, 1918s, 1860vs, 1836s cm^{-1}; CH_3CO, 1679s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.33 (s, 3H, CH_3); 5.14 (t, 2H, H(3,4)); 5.54 (t, 2H, H(2,5)) ppm.

Synthesis of [η^5-$CH_3COC_5H_4(CO)_3Mo]_2Hg$ (3c)

To the flask described in the preparation of **3b** was added 1 g (3.8 mmol) of molybdenum hexacarbonyl, 0.8 g (4.0 mmol) of sodium acetylcyclopentadienide and 20 ml of diglyme. The mixture was refluxed for 4–5 h and then cooled to about 80 °C. Methylmercuric chloride (0.9 g, 3.82 mmol) was added and the mixture stirred for about 14 h. The same workup as in preparation of **3b** gave 0.56 g (38%) of [η^5-$CH_3COC_5H_4(CO)_3Mo]_2Hg$ (**3c**) as a yellow solid, m.p. 156–158 °C. Anal. Found: C, 30.95; H, 1.81. $C_{20}H_{14}HgMo_2O_8$ calcd.: C, 31.00; H, 1.82%. IR (KBr disc): terminal C≡O, 2007s, 1983vs, 1918s, 1868vs, 1844s cm^{-1}; CH_3CO, 1680s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3); 5.56 (t, 3H, H(3,4)); 6.00 (t, 2H, H(2,5)) ppm.

Synthesis of [η^5-$CH_3COC_5H_4(CO)_3W]_2Hg$ (3d)

To the same flask described in the preparation of **3b** was added 1.0 g (2.8 mmol) of tungsten hexacarbonyl, 0.56 g (2.8 mmol) of sodium acetylcyclopentadienide and 20 ml of diglyme. The mixture was refluxed for 3–4 h and then 0.70 g (2.80 mmol) of methylmercuric chloride was added at about 80 °C. The mixture was stirred for about 13 h at 80 °C. After the same workup as in preparation of **3b**, 0.717 g (54%) of [η^5-$CH_3COC_5H_4(CO)_3W]_2Hg$ (**3d**) was isolated as a yellow solid, m.p. 169–171 °C. Anal. Found: C, 25.49; H, 1.47. $C_{20}H_{14}HgO_8W_2$ calcd.: C, 25.27; H, 1.48%. IR (KBr disc): terminal C≡O, 2008vs, 1975vs, 1901vs, 1860vs cm^{-1}; CH_3CO, 1680s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.33 (s, 3H, CH_3); 5.66 (t, 2H, H(3,4)); 6.05 (t, 2H, H(2,5)) ppm.

X-Ray crystallography

A solution of **3a** dissolved in 50% (v/v) CH_2Cl_2/petroleum ether was slowly evaporated at room temperature to give a yellow crystal suitable for X-ray work. The crystal (approximate dimensions 0.1 × 0.2 × 0.3 mm) was mounted on a glass fibre in an arbitrary orientation. Preliminary examination and data collection were performed with Mo-K_α radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 1665 independent reflections was collected in the range of $2 \leqslant \theta \leqslant 25°$ by ω–2θ scan technique at room temperature, of which 1291 reflections with $I > 3\sigma(I)$ were considered to be observed and used for the subsequent refinement. The corrections for Lp factors and absorption were applied.

The crystal is monoclinic space group $C2/c$ with $a = 21.119(2)$, $b = 7.067(1)$, $c = 12.033(1)$ Å, $\beta = 91.10(1)°$, $V = 1795.5$ Å^3, $M_r = 866.54$, $Z = 4$, $D_x = 3.20$ g/cm^3, $\mu = 216.2$ cm^{-1}, $F(000) = 1628$.

The structure was solved by a direct method (RANTAN). The Hg and two W atoms were located from an E-map. The coordinates of the remaining non-hydrogen atoms were found by successive difference Fourier syntheses. The hydrogen atoms were not included in the refinements. The final refinement by full-matrix least-squares method with anisotropic thermal parameter for non-hydrogen atoms converged with unweighted and weighted R factors of 0.032 (R) and 0.041 (R_w). The highest peak on the final difference Fourier map had a height of 0.99 e/Å^3.

All calculations were performed on a PDP11 44 computer using SDP-PLUS program system.

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