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Molecular Structure of Hg-Bridged Tetramethyl[2]ferrocenophane Salt ($[\{C_5H_4(CH_3)_2\}_2Fe–Hg–Fe\{C_5H_4(CH_3)_2\}_2]^{2+}$ $(BF_4^-)_2$) and Related Salts

Masanobu Watanabe,* Akira Nagasawa, Masaru Sato,† Izumi Motoyama,†† and Toshio Takayama††

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338

†Chemical Analysis Center, Saitama University, Urawa, Saitama 338

††Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Yokohama 221

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The crystal form of the salt $[\{C_5H_4(CH_3)_2\}_2Fe–Hg–Fe\{C_5H_4(CH_3)_2\}_2Hg(BF_4)_2$, **1**], prepared by a reaction of tetramethyl[2]ferrocenophane and $Hg(CN)_2$ in ethanol containing HBF_4, is triclinic, space group $P\bar{1}$, a = 9.315(3), b = 12.823(4), c = 14.108(5) Å, α = 106.055(2), β = 100.253(2), γ = 94.460(2)°, Z = 2 and the final R = 0.059 and R_w = 0.072. Two ferrocene moieties are coordinated to the Hg atom from the opposite side, and the previously proposed Fe–Hg–Fe bridged structure has been verified. The structural feature of the cation is found in the conformation of the ferrocene moiety around the Fe–Hg–Fe bond. In order to reduce the steric hindrance between the Hg and ferrocene moieties, each moiety rotates largely with respect to the other (the torsion angle of the Cp_{cnt}–Fe(1)···Fe(2)–Cp_{cnt} is 75(1)° and Cp_{cnt} is defined as the centroid of the Cp-ring). The mean Fe–Hg distance is 2.598(8) Å and the Fe–Hg–Fe bond angle is 176.4(1)°. The two C_5H_4 rings are greatly tilted, the mean tilting angle between them being 33.72°. Analogous Hg(II) salts of ruthenocene (**2**) and osmocene (**3**) were prepared by a similar method. Crystal **2** is monoclinic, space group $P2_1/a$, a = 9.633(1), b = 18.864(3), c = 13.388(1) Å, β = 94.161(9)°, Z = 4 and the final R = 0.058 and R_w = 0.072. The mean Ru–Hg distance is 2.661(2) Å and the Ru–Hg–Ru bond angle is 174.4(1)°; the mean tilting angle between the C_5H_4-planes is 27.39°. The structure of the cation is very similar to that of **1** (the torsion angle of the Cp_{cnt}–Ru(1)···Ru(2)–Cp_{cnt} is 70(1)°).

The crystal form of **3** is triclinic, space group $P\bar{1}$, a = 9.823(1), b = 11.194(1), c = 12.241(1) Å, α = 113.822(8), β = 95.828(8), γ = 90.104(8)°, Z = 2 and the final R = 0.030 and R_w = 0.032. The mean Os–Hg distance is 2.69(2) Å and the Os–Hg–Os angle is 170.1(3)°. The most interesting structural difference of **3** compared with **1**, **2** is found to be the conformation of the osmocene moieties around the Os–Hg–Os bond. The two moieties are coordinated to Hg in parallel, and the torsion angle of Cp_{cnt}–Os(1)···Os(2)–Cp_{cnt} is negligible (2(1)°) so as to reduce the steric hindrance between the cations and the PF_6^- anions.

The present authors have reported that chemistry of tetramethyl[2]ferrocenophane is much closer to those of ruthenocene and osmocene, rather than ferrocene, because it has a "naked" structure of the Fe atom.[1)] For example, [2]ferrocenophane and its analog reacted with I_2 and $SnCl_4$ to give diamagnetic precipitates in which direct Fe–I and Fe–Sn bonds exist, respectively, based on the results of ^{57}Fe- and ^{119}Sn-Mössbauer and X-ray diffraction studies as in the case of ruthenocene and osmocene (the reaction of ferrocene gave only paramagnetic ferrocenium salt).[2—4)] It has also been reported that [2]ferrocenophane and its derivatives and ruthenocene react with $Hg(CN)_2$ in ethanol in the presence of $HClO_4$ or HBF_4 and NH_4PF_6, giving diamagnetic salts with direct metal–metal bonds, M^{II}–Hg^{II}–M^{II}, which has been conformed based on the ^{57}Fe-Mössbauer, ^{13}C-, ^{1}H NMR and ^{13}C CP/MAS NMR, infrared and Raman spectroscopies. For these complexes, although a possible structure, namely $[M^{II}Cp_2–Hg^{II}–M^{II}Cp_2]^{2+}$ $(X^-)_2$ (M = Fe, Ru; X = ClO_4, BF_4, and PF_6), has been proposed,[5—7)] no structural studies of the salts have been reported. In order to answer the question whether or not a direct M^{II}–Hg^{II}–M^{II} bond exits and what form it takes in these complexes, the present study was carried out in order to investigate the structures of **1**—**3** compared with those of the original metallocenes and related compounds.

Experimental

Syntheses. Salt **1** and **2** were prepared by previously reported methods[5,7)] and salt **3** was prepared under the same conditions as those used for **2**. Found: C, 21.32; H, 1.75%. Calcd for $C_{20}H_{20}HgOs_2P_2F_{12}$: C, 21.23; H, 1.78%.

NMR Measurement and X-Ray Structural Analysis. The NMR spectra were recorded at 298 K on a Bruker AM400 spectrometer and referenced to TMS as the external standard. Single crystals suitable for X-ray studies were obtained by the diffusion of diethyl ether vapor into CH_3NO_2 solutions at 270 K. For **1**—**3**, crystals (0.05×0.05×0.2 mm), (0.2×0.1×0.05 mm), and (0.05×0.05×0.1 mm) were selected, respectively. The X-ray intensities were recorded on a MAC Science DIP3000 image processor with graphite-monochromatized Mo $K\alpha$ radiation and a 18-kW rotating-anode generator. For **1**, 6529 reflections were collected using the Weisenberg method in the range $2° < 2\theta < 60°$ ($0 < h < 13$, $-18 < k < 17$, $-18 < l < 18$). Of 5394 unique reflections measured, only 2423 for which $I > 3\sigma$ (I) were used in the structure analysis. The structure was solved by the Dirdif–Patty method in CRYSTAN-GM (software-package for structure determination) and finally refined by the full-matrix least-squares procedure. An anisotropic refinement for non-hydrogen atoms was carried out. All of the hydrogen atoms, partially located from difference Fourier maps, were isotropically refined; $R = 0.059$ and $R_w = 0.072$. For **2**, 6693 reflections were collected using the Weisenberg method over the range $2° < 2\theta < 60°$ $(0 < h < 13,\ 0 < k < 26,\ -17 < l < 16)$. Of 3021 unique reflections measured, only 3021 for which $I > 3\sigma$ (I) were used in the structure analysis. The structure was solved by the same method as that used for **1** and R = 0.058 and R_w = 0.072. For **3**, 2509 reflections were collected using the Weisenberg method over the range $2° < 2\theta < 60°$ $(0 < h < 13,\ -15 < k < 15,\ -17 < l < 17)$. Of 2509 unique reflections measured, 2509 for which $I > 3\sigma$ (I) were used in the structure analysis. The structure was solved by the same method as that used for **1**; $R = 0.030$ and $R_w = 0.032$. The Crystallographic data for **1**, **2**, and **3** and some of the experimental conditions for the X-ray structure analysis are listed in Table 1. The complete $F_o - F_c$ data are deposited as Document No. 71029 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The Structure of Salt 1. Salt **1** crystallized in the triclinic space group $P\bar{1}$. The final atomic coordinate, equivalent isotropic temperature factors of non-hydrogen atoms and selected interatomic distance for **1** are given in Tables 2 and 3, and ORTEP drawing of the cation are illustrated in Fig. 1, along with the atom-num-

Table 1. Crystal and Intensity Collection Data

	1	**2**	**3**
Formula	$C_{32}H_{40}Fe_2HgF_8B_2$	$C_{20}H_{20}Ru_2HgF_{12}P_2$	$C_{20}H_{20}Os_2HgF_{12}P_2$
Formula weight	910.56	953.04	1131.36
Space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
a/Å	9.315(3)	9.633(1)	9.823(1)
b/Å	12.823(4)	18.864(3)	11.194(1)
c/Å	14.108(5)	13.388(1)	12.241(1)
α/°	106.055(2)	—	113.822(8)
β/°	100.253(2)	94.161(9)	95.828(8)
γ/°	94.460(2)	—	90.104(8)
V/Å	1579.1(9)	2426.4(5)	1331.3(2)
Z	2	4	2
D_X/g cm^{-3}	1.914	2.608	3.051
μ/cm^{-1}	58.122	77.49	168.6
No. of ref.	6529	6693	2509
No. of obsd	2423 $(I > 3.0(I))$	3021 $(I > 3.0(I))$	2509 $(I > 3.0(I))$
R	0.059	0.058	0.030
R_w	0.072	0.072	0.032

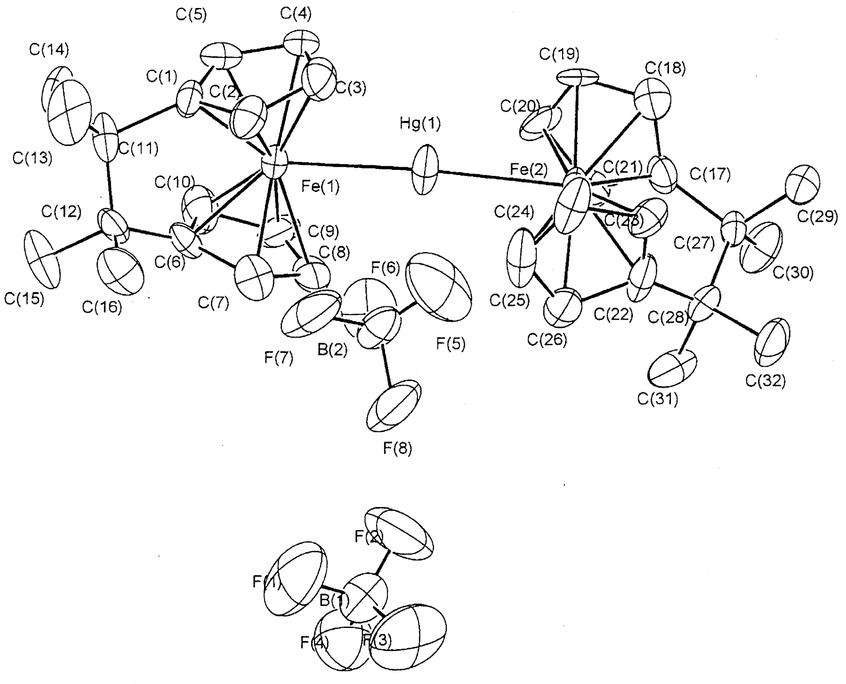

Fig. 1. ORTEP drawing of **1** with the numbering scheme of the atoms.

Table 2. Atomic Coordinate and U_{iso} for Salt **1**

Atom	x/a	y/b	z/c	U(iso)
Hg(1)	0.05110(12)	0.02980(8)	−0.26180(9)	0.0709(6)
Fe(2)	0.2229(3)	−0.1212(2)	−0.2771(2)	0.039(2)
Fe(1)	−0.1301(3)	0.1742(2)	−0.2407(2)	0.037(2)
F(1)	0.178(3)	0.283(2)	1.117(2)	0.16(2)
F(2)	0.320(2)	0.203(2)	1.021(2)	0.20(2)
F(3)	0.265(3)	0.135(2)	1.135(2)	0.16(2)
F(4)	0.096(2)	0.132(2)	1.006(2)	0.12(1)
F(5)	0.3978(19)	0.2244(21)	0.5313(16)	0.15(2)
F(6)	0.2014(19)	0.2093(14)	0.4135(12)	0.10(1)
F(7)	0 210(2)	0.317(1)	0.563(1)	0.11(1)
F(8)	0.186(2)	0.140(1)	0.539(1)	0.12(1)
C(1)	−0.1229(19)	0.3389(13)	−0.1768(15)	0.04(1)
C(2)	−0.028(2)	0.296(2)	−0.112(2)	0.05(1)
C(3)	0.085(2)	0.254(2)	−0.166(2)	0.06(1)
C(4)	0.049(2)	0.267(2)	−0.264(2)	0.07(1)
C(5)	−0.080(2)	0.319(2)	−0.269(2)	0.06(1)
C(6)	−0.338(2)	0.177(2)	−0.215(1)	0.04(1)
C(7)	−0.274(2)	0.095(2)	−0.181(1)	0.05(1)
C(8)	−0.245(2)	0.013(1)	−0.269(2)	0.05(1)
C(9)	−0.286(2)	0.050(1)	−0.356(2)	0.05(1)
C(10)	−0.344(2)	0.152(2)	−0.323(2)	0.06(1)
C(11)	−0.275(2)	0.379(2)	−0.155(2)	0.05(1)
C(12)	−0.375(2)	0.282(2)	−0.147(2)	0.05(1)
C(13)	−0.231(3)	0.477(2)	−0.056(2)	0.08(2)
C(14)	−0.331(3)	0.433(2)	−0.240(2)	0.07(2)
C(15)	−0.542(2)	0.291(2)	−0.188(2)	0.08(2)
C(16)	−0.360(3)	0.273(2)	0.039(2)	0.07(1)
C(17)	0.291(2)	−0.230(2)	−0.389(2)	0.05(1)
C(18)	0.398(2)	−0.127(2)	−0.352(2)	0.05(1)
C(19)	0.316(2)	−0.046(2)	−0.365(2)	0.06(1)
C(20)	0.174(3)	−0.083(2)	−0.418(2)	0.07(1)
C(21)	0.151(2)	−0.201(2)	−0.429(2)	0.06(1)
C(22)	0.228(3)	−0.253(2)	−0.223(2)	0.06(1)
C(23)	0.349(2)	−0.172(1)	−0.167(2)	0.05(1)
C(24)	0.291(3)	−0.073(2)	−0.118(2)	0.07(1)
C(25)	0.139(3)	0.095(2)	−0.142(2)	0.08(2)
C(26)	0.087(3)	−0.211(2)	−0.210(2)	00.6(1)
C(27)	0.319(2)	−0.344(1)	−0.382(2)	0.04(1)
C(28)	0.233(2)	−0.363(1)	−0.297(1)	0.04(1)
C(29)	0.491(2)	−0.341(2)	−0.346(2)	0.06(1)
C(30)	0.270(3)	−0.429(2)	−0.482(2)	0.06(1)
C(31)	0.074(3)	−0.425(2)	−0.347(2)	0.07(1)
C(32)	0.310(3)	−0.436(2)	−0.237(2)	0.07(1)
B(1)	0.219(3)	0.187(2)	1.072(2)	0.06(2)
B(2)	0.253(4)	0.224(2)	0.514(2)	0.06(2)

Table 3. Selected Bond Distance and Angles for **1**

Atom Atom 2	Dist/Å	Atom 1 Atom 2	Dist/Å
Hg(1)–Fe(1)	2.609(4)	Hg(1)–Fe(2)	2.586(4)
Fe(1)–C(1)	2.05(2)	Fe(2)–C(17)	2.02(3)
Fe(1)–C(2)	2.06(3)	Fe(2)–C(18)	2.10(3)
Fe(1)–C(3)	2.12(3)	Fe(2)–C(19)	2.04(3)
Fe(1)–C(4)	2.10(3)	Fe(2)–C(20)	2.15(3)
Fe(1)–C(5)	2.04(3)	Fe(2)–C(21)	2.06(3)
Fe(1)–C(6)	2.03(2)	Fe(2)–C(22)	2.04(3)
Fe(1)–C(7)	2.06(3)	Fe(2)–C(23)	2.06(3)
Fe(1)–C(8)	2.16(2)	Fe(2)–C(24)	2.12(3)
Fe(1)–C(9)	2.15(3)	Fe(2)–C(25)	2.14(3)
Fe(1)–C(10)	2.08(3)	Fe(2)–C(26)	2.15(3)
C(1)–C(2)	1.41(3)	C(1)–C(5)	1.39(3)
C(2)–C(3)	1.46(4)	C(3)–C(4)	1.41(4)
C(4)–C(5)	1.42(4)	C(6)–C(7)	1.41(3)
C(6)–C(10)	1.46(4)	C(7)–C(8)	1.48(4)
C(8)–C(9)	1.43(4)	C(9)–C(10)	1.45(3)
C(11)–C(12)	1.53(3)	C(11)–C(13)	1.56(4)
C(11)–C(14)	1.58(4)	C(12)–C(15)	1.58(3)
C(12)–C(16)	1.54(4)	C(17)–C(18)	1.50(3)
C(17)–C(21)	1.44(3)	C(17)–(27)	1.54(3)
C(18)–C(19)	1.38(4)	C(19)–C(20)	1.38(4)
C(20)–C(21)	1.47(3)	C(22)–C(23)	1.42(3)
C(22)–C(26)	1.47(4)	C(22)–C(28)	1.52(3)
C(23)–C(24)	1.45(4)	C(24)–C(25)	1.38(4)
C(25)–C(26)	1.53(4)	C(27)–C(28)	1.62(3)
C(27)–C(29)	1.59(3)	C(27)–C(30)	1.50(3)
C(28)–C(31)	1.56(3)	C(28)–C(32)	1.56(3)
B(1)–F(1)	1.34(4)	B(1)–F(2)	1.35(4)
B(1)–F(3)	1.28(4)	B(1)–F(4)	1.36(4)
B(2)–F(5)	1.33(4)	B(2)–F(6)	1.36(4)
B(2)–F(7)	1.34(4)	B(2)–F(8)	1.37(4)

bering system. The results of an X-ray diffraction study which revealed coordination of the Fe atom in tetramethyl [2]ferrocenophane to the Hg atom, and the cationic and dimeric Hg-bridged structure being the metal–metal (Fe–Hg–Fe), namely $[\{C_5H_4C(CH_3)_2\}_2Fe–Hg–Fe\{C_5H_4C(CH_3)_2\}_2]^{2+}$, have been verified. The Fe(1)–Hg and Fe(2)–Hg distances are 2.609(4) and 2.586(4) Å, respectively. Both bond lengths are much smaller than the sum (2.74 Å) of the atomic radius of the Hg (1.48 Å) and Fe (1.26 Å) atoms, and are closer to the reported Fe–Hg values of $[Fe_4(CO)_{13}HgMo(CO)_3Cp]^-$ (2.664(1) and 2.686(1) Å)[8] and $[Fe(CO)_3(Si(OMe_3)(dppm)]_2Hg$ (2.574(1), 2.576(1) Å),[9] $[NEt_4]_2[\{(CO)_4FeSnCl_2Fe(CO)_4\}_2Hg]$ (2.571(1) Å);[10] thus, Fe–Hg–Fe bond formation is beyond question. The Fe(1)–Hg(1)–Fe(2) bond is pseudo linear (Fe(1)–Hg–Fe(2) angle, 176.4(1)°), as in the case reported for some linear Fe–Hg–Fe complexes, $[Fe(CO)_3\{Si(OMe)_3\}(dppm)]_2Hg$ (178.0(1)°)[9] and $[NEt_4]_2[\{(CO)_4FeSnCl_2Fe(CO)_4\}_2Hg]$ (180.0°).[10] The Hg···C(3), Hg···C(8), Hg···C(20), and Hg···C(25) distances were found to be 2.79(3), 2.73(3), 2.76(3), and 2.70(2) Å, respectively; these values are much less than the sum of the van der Waals radii of C (1.70 Å) and Hg (1.55 Å).[14] Thus, the C_5H_4 plane in complex **1** is highly slanted so as to reduce the steric repulsion between them, the tilting angle of planes C(1—5) and C(6—10) is 33.54° and that of the planes C(11—15) and C(16—20) is 33.90°. Both values are larger by ca. 10° than the value in the neutral [2]ferrocenophane (23°)[1] and smaller by ca. 9° than the value of iodotetramethyl[2]ferrocenophanium cation (42°),[3] due to the much smaller van der Waals radii of the Hg atom compared with that of the I atom (2.15 Å). The Fe(1)···C(11), Fe(1)···C(12), Fe(2)···C(27), and Fe(2)···C(28) distances are 3.09(3), 3.07(2), 3.11(1), and 3.05(2) Å; these values are larger than the corresponding values of the neutral [2]ferrocenophane (2.97 and 2.96 Å)[1] because the Fe atoms are squeezed out of the center of the C_5H_4 rings in terms of the formation of the Fe–Hg bond. The mean Fe(1)–C_{ring} (C_{ring} is defined as the C atom of the Cp-ring),

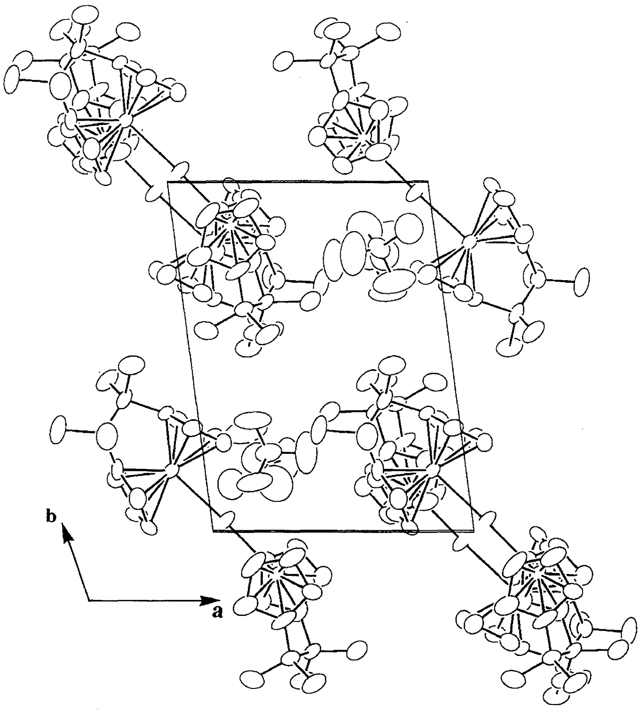

Fig. 2. Projection of the unit cell of **1** along *c* axis.

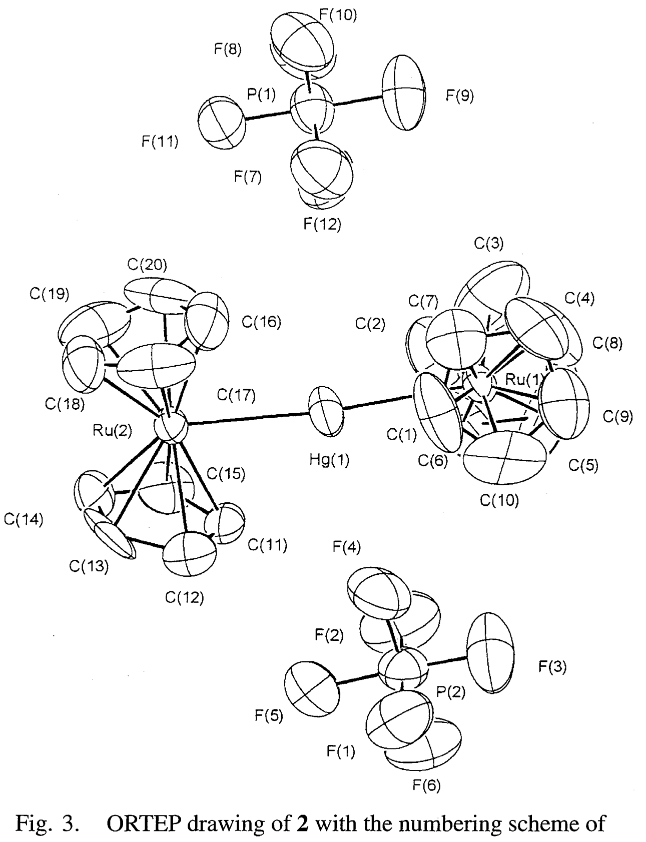

Fig. 3. ORTEP drawing of **2** with the numbering scheme of the atoms.

Table 4. Atomic Coordinate and U_{iso} for Salt **2**

Atom	x/a	y/b	z/c	U(iso)
Hg(1)	0.48350(6)	−0.00420(3)	0.24630(5)	0.0630(3)
Ru(1)	0.67610(9)	0.09700(5)	0.25480(8)	0.0442(4)
Ru(2)	0.31060(10)	−0.11440(5)	0.24310(8)	0.0415(4)
P(1)	0.8326(16)	−0.1242(7)	0.5061(15)	0.066(7)
P(2)	0.2379(18)	0.1523(13)	0.0382(15)	0.07(1)
F(1)	0.228(3)	0.142(2)	−0.079(2)	0.12(2)
F(2)	0.237(4)	0.159(2)	0.150(1)	0.14(2)
F(3)	0.355(3)	0.207(1)	0.034(2)	0.14(2)
F(4)	0.3431(18)	0.0887(17)	0.0540(23)	0.12(1)
F(5)	0.117(3)	0.095(2)	0.033(2)	0.12(2)
F(6)	0.1272(15)	0.2128(9)	0.0226(15)	0.130(8)
F(7)	0.819(2)	−0.119(1)	0.388(3)	0.11(1)
F(8)	0.847(3)	−0.130(2)	0.623(2)	0.12(2)
F(9)	0.945(3)	−0.064(1)	0.512(1)	0.12(2)
F(10)	0.9530(14)	−0.1796(11)	0.4973(21)	0.11(1)
F(11)	0.723(2)	0.185(2)	0.501(3)	0.09(2)
F(12)	0.714(2)	−0.065(1)	0.512(2)	0.11(1)
C(1)	0.5131(12)	0.1431(7)	0.3427(10)	0.138(6)
C(2)	0.5832(15)	0.0933(8)	0.3990(12)	0.115(8)
C(3)	0.7196(16)	0.1090(10)	0.4217(11)	0.164(9)
C(4)	0.7440(17)	0.1582(9)	0.3759(13)	0 126(9)
C(5)	0.6298(15)	0.1952(8)	0.3228(14)	0.179(9)
C(6)	0.6886(19)	0.0343(9)	0.1152(17)	0.11(1)
C(7)	0.796(2)	0.020(1)	0.174(1)	0.10(1)
C(8)	0.8784(19)	0.0823(10)	0.1952(13)	0.11(1)
C(9)	0.8058(16)	0.1343(7)	0.1415(13)	0.105(8)
C(10)	0.6896(15)	0.1060(9)	0.0875(14)	0.12(1)
C(11)	0.191(3)	−0.012(1)	0.230(1)	0.06(1)
C(12)	0.1701(18)	−0.0514(10)	0.1387(10)	0.08(1)
C(13)	0.1088(4)	−0.1150(2)	0.1668(4)	0.096(2)
C(14)	0.0900(5)	−0.1169(3)	0.2675(4)	0.069(2)
C(15)	0.141(2)	−0.054(1)	0.307(3)	0.08(1)
C(16)	0.528(2)	−0.152(1)	0.257(1)	0.11(1)
C(17)	0.455(6)	−0.189(1)	0 180(2)	0.10(2)
C(18)	0.350(3)	−0.227(2)	0.230(2)	0.10(2)
C(19)	0.358(3)	−0.210(2)	0.326(1)	0.11(2)
C(20)	0.465(3)	−0.171(2)	0.346(2)	0.11(2)

Fe(2)–$\mathrm{C_{ring}}$, Fe(1)–Cp, and Fe(2)–Cp distances were found to be 2.09(4), 2.09(4), 1.689(4), and 1.688(9) Å, respectively. These values are somewhat longer to those of typical ferrocene (2.045, 1.65 Å[11]) and tetramethyl[2]ferrocenophane (2.045, 1.64(1) Å),[1] and are closer to the value of the ferrocenium cation (2.075, 1.68 Å),[12] although the formal oxidation state of the Fe atom is not $\mathrm{Fe^{III}}$, but $\mathrm{Fe^{II}}$. The longer Fe–Cp distance found in **1** was caused by the ligation of e_{2g} electrons of the Fe atom to the Hg atom based on the results of ^{57}Fe-Mössbauer studies,[4] because anomalously large quadrupole splitting values (3.08 $\mathrm{mm\,s^{-1}}$ at 300 K, and 3.12 $\mathrm{mm\,s^{-1}}$ at 78 K) compared with that of the neutral [2]ferrocenophane (2.36 $\mathrm{mm\,s^{-1}}$ at 78 K) were found for **1**. The fact that similar larger quadrupole splitting values (3.40 and 3.53 $\mathrm{mm\,s^{-1}}$ at 4.2 and 300 K, respectively)[13] were found for some analogous Sn complexes prepared from [2]ferocenophane and $\mathrm{SnCl_4}$ may support the presence of the Fe–Sn–Fe bridged dimeric structure, $[\{\mathrm{C_5H_4C(CH_3)_2}\}_2\mathrm{Fe^{II}}\text{–}\mathrm{Sn^{IV}Cl_2}\text{–}\mathrm{Fe^{II}}\{\mathrm{C_5H_4C(CH_3)_2}\}_2]^{2+}$, similar to the structure found in the Hg complex **1** for the latter Sn complexes. Unfortunately, many attempts to grow stable single crystals of the Sn-complexes have been failed because they are very hygroscopic and unstable in all polar organic

Table 5. Selected Bond Distance and Angles for **2**

Atom 1 Atom 2	Dist/Å	Atom 1 Atom 2	Dist/Å
Hg(1)–Ru(1)	2.659(2)	Hg(1)–Ru(2)	2.662(2)
Ru(1)–C(1)	2.21(1)	Ru(2)–C(11)	2.25(3)
Ru(1)–C(2)	2.19(2)	Ru(2)–C(12)	2.22(2)
Ru(1)–C(3)	2.26(2)	Ru(2)–C(13)	2.13(5)
Ru(1)–C(4)	2.06(2)	Ru(2)–C(14)	2.17(5)
Ru(1)–C(5)	2.13(2)	Ru(2)–C(15)	2.21(3)
Ru(1)–C(6)	2.22(3)	Ru(2)–C(16)	2.21(3)
Ru(1)–C(7)	2.18(2)	Ru(2)–C(17)	2.18(5)
Ru(1)–C(8)	2.18(2)	Ru(2)–C(18)	2.16(3)
Ru(1)–C(9)	2.15(2)	Ru(2)–C(19)	2.14(4)
Ru(1)–C(10)	2.26(2)	Ru(2)–C(20)	2.22(4)
C(1)–C(2)	1.35(3)	C(1)–C(5)	1.53(2)
C(2)–C(3)	1.36(3)	C(3)–C(4)	1.15(3)
C(4)–C(5)	1.45(3)	C(6)–C(7)	1.29(3)
C(6)–C(10)	1.40(3)	C(7)–C(8)	1.43(3)
C(8)–C(9)	1.38(3)	C(9)–C(10)	1.39(3)
C(11)–C(12)	1.43(3)	C(11)–C(15)	1.41(4)
C(12)–C(13)	1.40(2)	C(13)–C(14)	1.37(1)
C(14)–C(15)	1.38(3)	C(16)–C(17)	1.39(5)
C(16)–C(20)	1.42(4)	C(17)–C(18)	1.44(6)
C(18)–C(19)	1.31(3)	C(19)–C(20)	1.28(5)
P(1)–F(1)	1.58(5)	P(1)–F(2)	1.56(4)
P(1)–F(3)	1.58(4)	P(1)–F(4)	1.57(3)
P(1)–F(5)	1.56(4)	P(1)–F(6)	1.60(3)
P(2)–F(7)	1.58(4)	P(2)–F(8)	1.50(3)
P(2)–F(9)	1.53(4)	P(2)–F(10)	1.57(4)
P(1)–F(11)	1.59(4)	P(1)–F(12)	1.57(3)

solutions.

The most interesting feature of cation **1** is found in the conformation of ferrocene moieties around the Fe–Hg–Fe bond. The two moieties, coordinated to the Hg atoms, are greatly rotated about each other (the torsion angle of the Cp_{cnt}–Fe(1)···Fe(2)–Cp_{cnt} is 75(1)°) to allow the two Fe atoms in metallocene and the Hg atoms to approach each other, as in the case of [1.1]ruthenocenophanium(2+) (ca. 75°)[15] and

Table 6. Atomic Coordinate and U_{iso} for Salt **3**

Atom	x/a	y/b	z/c	U(iso)
Hg(1)	0.9919(5)	0.7591(5)	0.2584(5)	0.0470(9)
Os(1)	0.8022(5)	0.8473(5)	0.1412(4)	0.0372(7)
Os(2)	1.2001(5)	0.6483(5)	0.3400(4)	0.0380(7)
P(1)	0.2888(12)	0.1469(11)	0.3523(11)	0.038(4)
P(2)	0.6993(17)	0.3445(20)	0.1355(18)	0.082(7)
F(1)	0.401(3)	0.243(4)	0.337(4)	0.14(2)
F(2)	0.175(3)	0.053(4)	0.360(2)	0.09(1)
F(3)	0.399(3)	0.093(2)	0.427(2)	0.07(1)
F(4)	0.275(2)	0.252(2)	0.482(2)	0.05(1)
F(5)	0.168(2)	0.196(2)	0.289(2)	0.06(1)
F(6)	0.296(4)	0.037(3)	0.222(3)	0.08(1)
F(7)	0.815(4)	0.429(3)	0.102(2)	0.09(2)
F(8)	0.598(5)	0 263(4)	0.159(4)	0.16(3)
F(9)	0.814(4)	0.277(4)	0.187(3)	0.14(2)
F(10)	0.682(4)	0.460(4)	0.265(3)	0.09(1)
F(11)	0.581(3)	0.410(4)	0.099(3)	0.14(2)
F(12)	0.721(3)	0.218(2)	0.004(2)	0.10(1)
C(1)	0.993(3)	0.851(4)	0.064(3)	0.05(2)
C(2)	0.940(4)	0.985(4)	0.124(4)	0.08(2)
C(3)	0.801(4)	0.977(3)	0.053(4)	0.05(2)
C(4)	0.789(5)	0.843(4)	−0.033(5)	0.06(2)
C(5)	0.901(5)	0.771(5)	−0.016(5)	0.12(3)
C(6)	0.704(3)	0.799(4)	0.293(3)	0.10(2)
C(7)	0.709(3)	0.919(5)	0.320(3)	0.09(2)
C(8)	0.632(4)	0.942(4)	0.234(3)	0.05(2)
C(9)	0.585(3)	0.825(4)	0.158(3)	0.07(2)
C(10)	0.623(6)	0.730(6)	0.173(5)	0.08(2)
C(11)	1.2951(19)	0.7575(22)	0.2552(22)	0.04(1)
C(12)	1.375(5)	0.766(5)	0.354(4)	0.06(2)
C(13)	1.416(2)	0.641(3)	0.354(3)	0.06(1)
C(14)	1.351(4)	0.537(4)	0.221(3)	0.07(2)
C(15)	1.268(3)	0.613(3)	0.171(3)	0.07(1)
C(16)	1.052(4)	0.724(4)	0.499(4)	0.06(2)
C(17)	1.188(4)	0.696(4)	0.539(4)	0.06(2)
C(18)	1.194(4)	0.571(3)	0.479(3)	0.06(2)
C(19)	1.094(3)	0.502(4)	0.391(3)	0.05(1)
C(20)	1.003(3)	0.591(3)	0.390(3)	0.04(1)

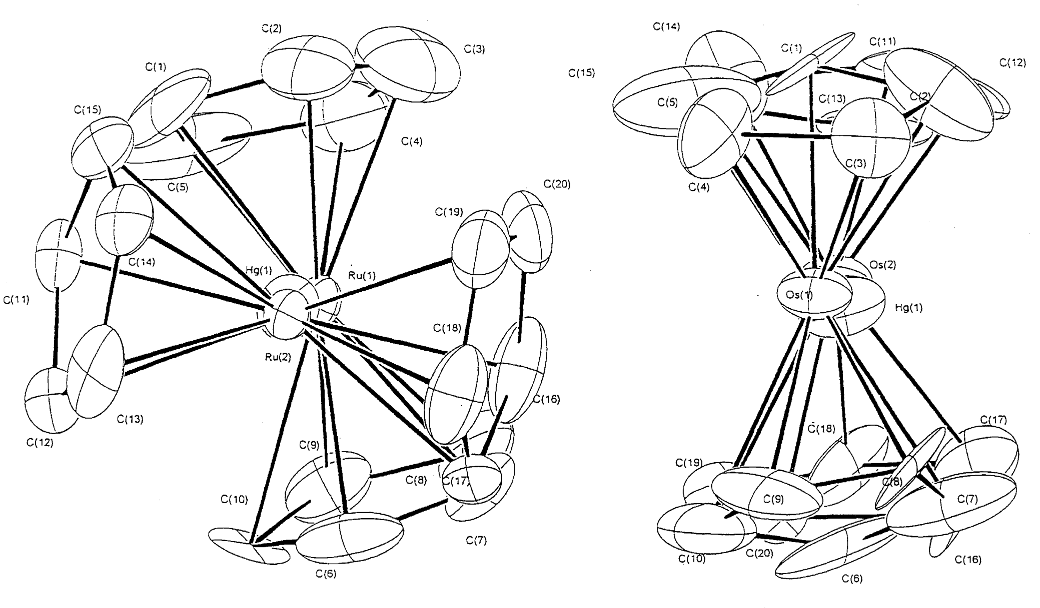

Fig. 4. Side views of cations **2** and **3** showing different conformation.

Table 7. Selected Bond Distance and Angles for **3**

Atom 1 Atom 2	Dist/Å	Atom 1 Atom 2	Dist/Å
Hg(1)–Os(1)	2.667(8)	Hg(1)–Os(2)	2.704(8)
Os(1)–C(1)	2.19(4)	Os(2)–C(11)	2.25(3)
Os(1)–C(2)	2.13(5)	Os(2)–C(12)	2.22(2)
Os(1)–C(3)	2.13(4)	Os(2)–C(11)	2.25(3)
Os(1)–C(4)	2.11(6)	Os(2)–C(12)	2.22(2)
Os(1)–C(5)	2.10(6)	Os(2)–C(11)	2.25(3)
Os(1)–C(6)	2.42(4)	Os(2)–C(12)	2.22(2)
Os(1)–C(7)	2.29(4)	Os(2)–C(11)	2.25(3)
Os(1)–C(8)	2.15(5)	Os(2)–C(12)	2.22(2)
Os(1)–C(9)	2.19(4)	Os(2)–C(11)	2.25(3)
Os(1)–C(10)	2.35(6)	Os(2)–C(12)	2.22(2)
C(1)–C(2)	1.50(7)	C(1)–C(5)	1.30(6)
C(2)–C(3)	1.52(6)	C(3)–C(4)	1.44(6)
C(4)–C(5)	1.41(8)	C(6)–C(7)	1.25(7)
C(6)–C(10)	1.50(7)	C(7)–C(8)	1.34(6)
C(8)–C(9)	1.31(6)	C(9)–C(10)	1.20(8)
C(11)–C(12)	1.35(5)	C(11)–C(15)	1.54(4)
C(12)–C(13)	1.46(7)	C(13)–C(14)	1.63(6)
C(14)–C(15)	1.44(6)	C(16)–C(17)	1.46(5)
C(16)–C(20)	1.58(5)	C(17)–C(18)	1.29(6)
C(18)–C(19)	1.35(5)	C(19)–C(20)	1.34(5)
P(1)–F(1)	1.61(4)	P(1)–F(2)	1.56(4)
P(1)–F(3)	1.62(3)	P(1)–F(4)	1.57(3)
P(1)–F(5)	1.57(3)	P(1)–F(6)	1.58(4)
P(2)–F(7)	1.66(4)	P(2)–F(8)	1.48(5)
P(2)–F(9)	1.58(5)	P(2)–F(10)	1.62(4)
P(1)–F(11)	1.50(5)	P(1)–F(12)	1.69(3)

the dimeric osmocenium cation (90°).[16] The projection of the unit cell along the *c*-axis is shown in Fig. 2. The crystal structure is constituted by respective columns of cations and BF$_4^-$ anions parallel to the *c*-axis, which develops in the *c*-axis directions. The two small BF$_4^-$ anions are located in a gap between the cations. The average B–F distance and average F–B–F angles are 1.32(3) and 109(3)°, respectively, for B(1)F$_4^-$ and 1.36(1), 109(2)° for B(2)F$_4^-$, respectively; the values are within the range of the normal BF$_4^-$ anion. The shortest intramolecular distance between the F atom in BF$_4^-$ and the C atom in the cation is 3.09 Å (F(8)···(20)), which is slightly larger than the sum of the van der Waals radii of C (1.70 Å) and F (1.35 Å), implying no van der Waals contact between them, which is in sharp contrasts to the case of **3** described latter.

Salts 2 and 3. Although the single crystals of BF$_4^-$ salts of ruthenocene and osmocene were obtained by recrystallization from a solution of CH$_3$CN or CH$_3$NO$_2$, both crystals are quite unstable upon standing at room temperature. Thus, their structure-diffraction studies were carried out using their PF$_6^-$ salts (ruthenocene (**2**) and osmocene (**3**)). Crystals of **2** and **3** recrystallized from the CH$_3$NO$_2$ solution are monoclinic $P2_1/a$, and triclinic $P\bar{1}$, respectively. The final atomic-coordinate, equivalent isotropic temperature factors of non-hydrogen atoms and select interatomic distance for **2** and **3** are summarized in Tables 4, 5, 6, 7, and 8. An ORTEP drawing of **2** is illustrated in Fig. 3, along with the atom-numbering system. As can be seen from the drawing, the structure of the cation has great similarity with those of **1**, and the possible structure $[(C_5H_5)_2Ru^{II}–Hg^{II}–Ru^{II}(C_5H_5)_2]^{2+}$ proposed by Hendrickson[7] has been verified. The Ru(1)–Hg and Ru(2)–Hg distances are 2.659(2) and 2.662(2) Å, respectively. These are ca. 0.05—0.06 Å larger than the corresponding values of **1**, due to the larger atomic radius of the Ru atom

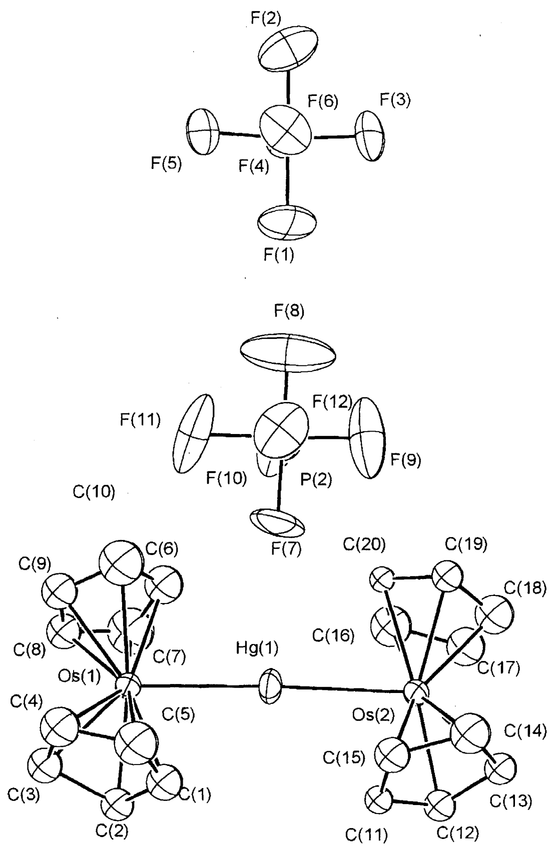

Fig. 5. ORTEP drawing of **3** with the numbering scheme of the atoms.

Table 8. Selected Bond Lengths (Å) and Angle (deg)

	1	2	3
M–Hg/Å	2.609(4), 2.586(4)	2.659(2), 2.662(2)	2.667(8), 2.704(8)
M–C$_{ring}$/Å	2.09(4), 2.09(4)	2.18(6), 2.19(4)	2.21(9), 2.21(9)
M–Cp/Å	1.689(4), 1.688(9)	1.841(9), 1.845(3)	1.863(11), 1.841(9)
M–Hg–M	176.4(1)	174.4(1)	170.1(3)
Cp–M–Cp[a)]	33.54, 33.90	27.16, 27.62	34.46, 27.32
Cp$_{cnt}$–M(1)···M(2)–Cp$_{cnt}$[b)]	75(1)	70(1)	2(1)

a) Tilting angle between planes. b) Torsion angle, Cp$_{cnt}$ is defined as the centroid Cp-plane.

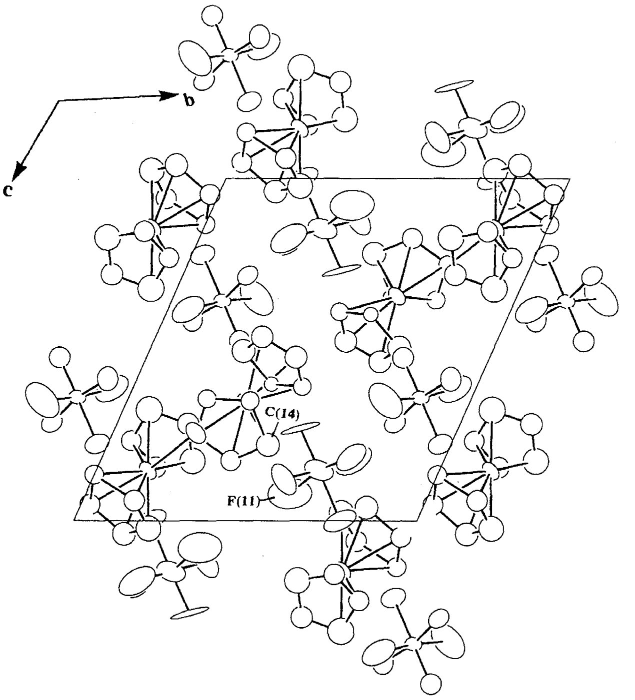

Fig. 6. Projection of the unit cell of **3** along *a* axis.

(1.33 Å) compared with the Fe atom (1.24 Å), and are close to the reported values of the HgX_2 adducts of ruthenocene (2.65 and 2.60 Å for $[Ru(C_5H_5)_2]\cdot3HgCl_2$ and 2.74 Å for $Ru(C_5H_5)_2\cdot HgBr_2$) and the other Ru–Hg complex $[HgRu(CO)_4]_4$ (2.68(1) Å).[17,18] The Ru(1)–Hg–Ru(2) bond is also pseudo-linear (the bond angle; 174.4(1)°). As in the case of **1**, the two ruthenocene moieties coordinated to the Hg atom are greatly rotated about each other, as shown in Fig. 4. The torsion angle, Cp_{cnt}–Ru(1)···Ru(2)–Cp_{cnt} is 70(1)°, is smaller by ca. 5° than that of **1**, because of the significantly longer Ru–Hg distance compared with that of the Fe–Hg. The mean Ru(1)–C_{ring}, Ru(2)–C_{ring}, Ru(1)–Cp and Ru(2)–Cp distances were found to be 2.18(6), 2.19(4), 1.841(9), and 1.845(3) Å, respectively (see Table 8). These values are similar to those of iodoruthenocenium (2.197 and 1.84 Å)[19] and chlororuthenocenium cations (2.218, 1.864 Å).[20] The Hg···C(1), Hg···C(6), Hg···C(22), and Hg···(17) distances were found to be 2.85(4), 2.87(4), 2.80(2), and 2.82(3) Å, respectively. Although these values are longer than the corresponding values in **1** (2.70—2.79 Å), they are much shorter than the sum (3.25 Å) of the van der Waals radii of C and Hg. The tilting angle of planes C(1—5) and C(6—10) is 27.16°, and that of planes C(11—15) and C(16—20) is 27.62°; which are smaller by ca. 6.3 ° and 5° than the corresponding values of **1** and iodoruthenocenium (32.2°), respectively, and similar to the value of [1.1]ruthenocenophanium^{2+} cation (28°), in which a Ru^{III}–Ru^{III} bond of 2.951(1) Å is found.[15] The PF_6^- anions and cations are constituted by respective columns in the direction along the *a*- and *b*-axes. The PF_6^- anions are sandwiches between the cations. The shortest intermolecular distance between the F atom in PF_6^- anions and the C atom in the cation is 3.16 Å (F(7)···C(14)), which is larger than the sum (3.05 Å) of the van der Waals radii of C and F, implying the absence of a van der Waals contact between them, which is in sharp contrast with the case of **3**. The average P–F distance was found to be 1.59(2) Å for $P(1)F_6^-$ and 1.59(7) Å for $P(2)F_6^-$; both values are within the range of normal PF_6^-.

Although the structure of **2** is quite similar to that of **1**, the structure of **3** is greatly different from those of **2** and **1**. As can be seen from the drawing in Fig. 5, the coordination of the Os atom to the Hg atom has been verified. The Os(1)–Hg and Os(2)–Hg distances were found to be 2.667(8) and 2.704(8) Å, respectively, which are somewhat longer than the values for **1** and **2** and shorter than that for the Hg–Os clusters: $[Os_{20}HgC_2(CO)_{48}]^{2-}$ (2.866(2), 2.902(2) Å), $[Os_{18}Hg_2C_2(CO)_{42}]^{4-}$ (2.813(2), 2.898(2) 2.747(2) Å), $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ (2.678(6), 2.696(5), 2.761(5) Å),[21,22] and $[Os_3(CO)_9HgCl(C_2Ph_2)]$ (2.830(1), 2.712(2) Å).[23] Complex **3** is the first non-cluster complex containing the Os–Hg bond, to our knowledge. The Os(1)–Hg–Os(2) bond angle is 170.1(3)°, which is ca. 5° smaller than those of **1** and **2**. The mean Os–C_{ring} distances found for Os(1)-Cp_2 and Os(2)Cp_2 have the same value (2.21(9) Å), which is similar to the value in osmocene (2.22 Å).[24] The tilting angle of planes C(1—5) and C(6—10) is 34.46° and that of planes C(11—15) and C(16—20) is 27.32°, the former being ca. 7° larger than that of the latter. The mean tilting angle (30.9°) is by ca. 3° larger than that in **2** due to the somewhat larger Os atomic size than that of the Ru atom and by ca. 5° smaller than the value in $[Cp_2Os^{III}–Os^{III}Cp_2]^{2+}$ cation (35.5°).[16] The Os–Cp distances in complex **3** were found to be 1.863(11) Å for the Os(1) site and 1.841(9) Å for the Os(2) site (the former is significantly longer than the latter probable because of the less extend of wedge-shape of the Os(1)Cp_2 moiety than the Os(2)Cp_2 moiety). The mean value (1.852 Å) of the Os–Cp distance is larger than those in **1** and **2**, probably because of the larger atomic radius of the Os atom (1.34 Å) compared with those of the Ru and Fe atoms, and is close to the value of osmocene, itself (1.855 Å).[24]

The most interesting difference is found in the conformation of two osmocene moieties around Os–Hg–Os. The two osmocene moieties are coordinated parallel to each other, as shown in Fig. 4 (the torsion angle, Cp_{cnt}–Os(1)···Os(2)Cp_{cnt}, 2(1)°). A projection of the unit cell along with the *a*-axis is shown in Fig. 6. The structure is constituted by separate columns of the cations and PF_6^- ions along the bisector of the *b*- and *c*-axes, where both ions are stacked side-to-side in the columns that develop in the direction of the *a*-axis. The shortest intramolecular distance between the F and C is 2.90(5) Å (F(11)···C(14)), which is much smaller than the sum of the van der Waals radii of C and F atoms, implying the presence of a steric repulsion between them, which is in contract with the cases of salts **1** and **2**. This strong van der Waals contact and the above-mentioned packing fashion determine the conformation of **3**. Because of the demand for closed packing between the cations and anions, two osmocene moieties are coordinated to the Hg atom in parallel fashion when salt **3** is crystallized from solution. The van der

Waals contact between F(11)···C(14) also gave a less extent of the wedge-shape structure of the Os(2)Cp_2 moiety than that of the Os(1)Cp_2 moiety.

NMR Studies and Conclusion. All of the Hg salts (**1**—**3**) could be well dissolved in some polar solvent, which is in sharp contrast with $HgCl_2$ adducts of metallocene, which are less soluble in polar solvents. As previously reported the dimer structures of salts **2** and **3** in a solid remains intact in solution, because the stability of the Hg–Os and Hg–Ru bonds prevents the decomposition of the dimer structures in solutions.$^{25)}$ On the other hand, dimer slat **1** with a Fe–Hg–Fe bridge is not very stable in acetonitrile and other polar solvents, compared to slats **2** and **3**, reported previously.$^{5)}$ However, since salt **1** is relatively stable in a mixed solvent of $CD_3NO_2/CDCl_3$ (1/1), ^{1}H NMR studies were carried out using a mixed solvent. A sharp single signal for the Cp-ring proton was found at $\delta = 5.48$ for **2** and at $\delta = 5.60$ for **3**; both signals shifted to a lower field compared with the corresponding neutral metallocenes. The value of the shift ($\Delta\delta$) caused by the formation of the M–Hg–M dimer is 1.01 ppm for **2** ($\delta = 4.47$ for ruthenocene) and 0.89 ppm for **3** ($\delta = 4.71$ for osmocene), which are much smaller than the values in iodoruthenocenium ($\Delta\delta = 1.87$ ppm) and chlororuthenocenium ($\Delta\delta = 1.74$ ppm),$^{26)}$ probably arising from the higher oxidation state (M^{IV}) of the central metal atoms for the latter salts. For **1**, three sharp signals were found ($\delta = 5.37$ for the α-protons, $\delta = 5.22$ for the β-protons, and $\delta = 1.53$ for the methylene protons), which are shifted to lower field compared with those of the neutral [2]ferrocenophane in the same solvent ($\delta = 4.70$, 3.93, and 1.31, respectively). The mean $\Delta\delta$ of the ring protons is 0.98 ppm, which is similar to those in **2** and **3**, whose dimeric structure is relatively stable in a less-polar solvent. Since salt **1** is not very stable in acetonitrile and acetone, the color of the solution changes to green, which is typical for ferrocenium salt, from orange-yellow upon standing at room temperature for ca. 24 h. The ^{1}H NMR signals of **1** in CD_3CN showed a sharp signal at $\delta = 1.48$, assigned as methyl, and two broad signals at $\delta = 5.34$ and 5.09 for the α- and β-position of C_5H_4-ring, respectively. The broad ring peaks became broader due to slow oxidation with an accompanying rupture of the Fe–Hg bond. As previously reported, the reaction of ferrocene and $Hg(CN)_2$ in the presence of HBF_4 under similar conditions to those in the preparation of salts **2** and **3** gave the ferrocenium salt alone, and no dimeric salt with the Fe–Hg–Fe bridge was prepared.$^{5)}$ Because the softness of the metal atom increases in the order Fe < Ru < Os, the hardness of the Fe atom and shorter Cp–Fe distance in ferrocene may prevent a stable Hg-dimeric salt. Only [2]ferrocenophane derivatives gave stable dimeric salts with the Hg-bridge in a solid, because they have much softer and less steric hindrance in donating e_{2g}-electrons compared with those of ferrocene derivatives; however, the Fe–Hg–Fe bond in **1** is not very stable in some polar solvents.

All of the results obtained in the present studies suggest that the reaction products of tetramethyl [2]-ferrocenophane, ruthenocene and osmocene with $Hg(CN)_2$ have dimeric structures with the Hg-bridge, namely $[Cp_2M^{II}–Hg–M^{II}Cp_2]^{2+}$. All of the M–Hg–M bonds are pseudo linear and the metallocene moieties greatly rotates (ca. 70—75°) with respect to each other for salts **1** and **2**, so as to reduce the steric repulsion between the Hg atom and the metallocenes. On the other hand, the two osmocene moieties are coordinated to the Hg atom in parallel in order to satisfy the closed packing of the cations and PF_6^- anions when the salt **3** is crystallized.

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