

# Systematic syntheses of $[\text{Hg}\{\text{M}(\text{CO})_4\}_2]^{2-}$ , $[\text{Hg}\{\text{M}(\text{CO})_4\}]_x$ (M = Fe, Ru, Os), and structures of $[\text{Hg}\{\text{M}(\text{CO})_4\}_2]^{2-}$ (M = Ru, Os)

Sung-Ho Chun, Edward A. Meyers, Fu-Chen Liu, Soyoung Lim, Sheldon G. Shore \*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA

Received 4 September 1997; received in revised form 11 February 1998

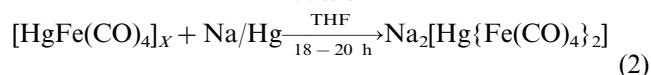
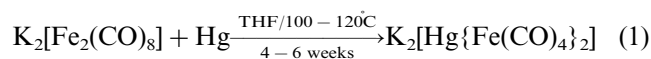
## Abstract

The  $[\text{Hg}\{\text{M}(\text{CO})_4\}_2]^{2-}$  (M = Fe, Ru, Os) anions were prepared by the reaction of  $\text{K}_2\text{M}(\text{CO})_4$  (M = Fe, Ru, Os) with  $\text{HgCl}_2$  in a 2:1 molar ratio in THF in high yields. The complexes,  $\text{K}_2[\text{Hg}\{\text{M}(\text{CO})_4\}_2]$  (M = Ru, Os) are thermally stable.  $\text{K}_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  decomposes at ca. 170°C, while  $\text{K}_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  decomposes at ca. 220°C. The structures of  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  and  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  were determined from single crystal X-ray diffraction analyses. The anions  $[\text{Hg}\{\text{M}(\text{CO})_4\}_2]^{2-}$  (M = Ru, Os), are isostructural with  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_2]^{2-}$ . These consist of two  $\text{M}(\text{CO})_4$  units, trigonal-bipyramidal fragments, joined at apical sites by a mercury atom in a linear M–Hg–M array with a staggered arrangement of the three equatorial CO's of the  $\text{M}(\text{CO})_4$  units. Crystal data for  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2] \cdot 2\text{CH}_3\text{CN}$ : space group  $P\bar{1}$ ,  $a = 12.615(2)$ ,  $b = 13.374(2)$ ,  $c = 13.822(2)$  Å,  $\alpha = 104.97(1)$ ,  $\beta = 106.18(1)$ ,  $\gamma = 108.92(1)^\circ$ ,  $V = 1956.4(6)$  Å<sup>3</sup>,  $Z = 1$ , mol. wt. = 1786.15,  $\rho = 1.481$  g cm<sup>-3</sup>,  $\mu = 24.6$  cm<sup>-1</sup> for Mo–K $\alpha$  radiation.  $R_f = 0.022$ ,  $R_{w_f} = 0.028$  for 5261 independent reflections with  $I \geq 3\sigma(I)$ . Crystal data for  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$ : space group  $P\bar{1}$ ,  $a = 11.437(2)$ ,  $b = 13.532(2)$ ,  $c = 14.698(2)$  Å,  $\alpha = 83.98(2)$ ,  $\beta = 83.88(2)$ ,  $\gamma = 78.41(2)^\circ$ ,  $V = 2207.5(6)$  Å<sup>3</sup>,  $Z = 2$ , mol. wt. = 1359.68,  $\rho = 2.046$  g cm<sup>-3</sup>,  $\mu = 93.35$  cm<sup>-1</sup> for Mo–K $\alpha$  radiation.  $R_f = 0.0327$ ,  $R_{w_f} = 0.0832$  for 5375 independent reflections with  $I \geq 3\sigma(I)$ . When a 1:1 molar ratio of  $\text{Na}_2[\text{M}(\text{CO})_4]$  (M = Fe, Ru, Os) and  $\text{HgCl}_2$  was employed the polymeric complexes  $[\text{Hg}\{\text{M}(\text{CO})_4\}]_x$  were obtained. The polymers are stable in air, but they are not soluble in common organic solvents and in water. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:**  $[\text{Hg}\{\text{M}(\text{CO})_4\}]_x$ ;  $[\text{Hg}\{\text{M}(\text{CO})_4\}_2]^{2-}$ ; Systematic syntheses

## 1. Introduction

Transition metal–mercury complexes with a linear M–Hg–M (M = transition metal) arrangement have been studied for several decades [1–6]. These mercury bridged complexes have been utilized as synthons in organometallic syntheses [2,3,7]. The complex  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_2]^{2-}$  has been prepared by other laboratories [4,5], either under high temperature with a prolonged reaction period (Reaction (1)) or by using reducing reagents such as sodium amalgam (Reaction (2)).



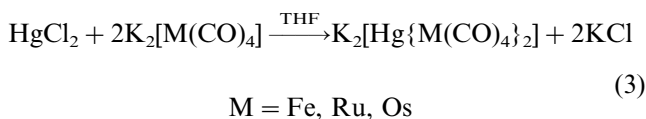
Unfortunately, these conditions are not practical for the synthesis of Ru and Os analogs since the starting materials  $\text{K}_2[\text{Ru}_2(\text{CO})_8]$  and  $\text{K}_2[\text{Os}_2(\text{CO})_8]$  are not easily prepared [8].

We describe here a simplified synthesis of  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_2]^{2-}$  and adapt this procedure to the systematic preparation of the related Group VIII dianions  $[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]^{2-}$  and  $[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]^{2-}$ , the single crystal X-ray structures of which are also reported here. Additionally we report systematic syntheses of the polymeric species  $[\text{Hg}\{\text{M}(\text{CO})_4\}]_x$  (M = Fe, Ru, Os).

\* Corresponding author. Fax: +1 614 2921685.

## 2. Results and discussion

Reactions of  $\text{HgCl}_2$  with the metal carbonylate anions,  $[\text{M}(\text{CO})_4]^{2-}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) in THF gave the desired products in yields  $> 80\%$  (Reaction 3). The reaction of  $\text{K}_2[\text{Fe}(\text{CO})_4]$  with  $\text{HgCl}_2$  was complete in 30 min at room temperature (r.t.). However, the reactions of  $\text{K}_2[\text{Ru}(\text{CO})_4]$



and  $\text{K}_2[\text{Os}(\text{CO})_4]$  with  $\text{HgCl}_2$  were slower, requiring 2 h at r.t. for the preparation of  $\text{K}_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  and 3 h at  $60^\circ\text{C}$  for the preparation of  $\text{K}_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$ . The color of  $\text{K}_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  is orange–yellow and that of  $\text{K}_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  is yellow. Both compounds are air and moisture sensitive. The IR spectra (Fig. 1) of these complexes in the CO stretching region are consistent with that of  $\text{K}_2[\text{Hg}\{\text{Fe}(\text{CO})_4\}_2]$ .

Sosinsky and co-workers found that the sodium salt,  $\text{Na}_2[\text{Hg}\{\text{Fe}(\text{CO})_4\}_2]$ , is stable up to its melting point,  $170^\circ\text{C}$  [5]. The potassium salts of the complexes,  $\text{K}_2[\text{Hg}\{\text{M}(\text{CO})_4\}_2]$  ( $\text{M} = \text{Ru}, \text{Os}$ ), are stable likewise;  $\text{K}_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  decomposed at ca.  $170^\circ\text{C}$  and  $\text{K}_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  decomposed at ca.  $220^\circ\text{C}$ .

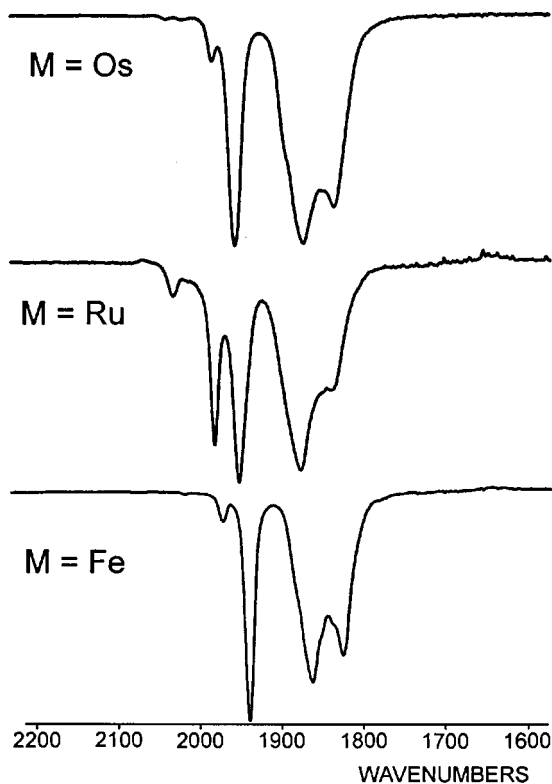


Fig. 1. IR spectra of  $\text{K}_2[\text{Hg}\{\text{M}(\text{CO})_4\}_2]$ ,  $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ , in the CO stretching region (in THF).

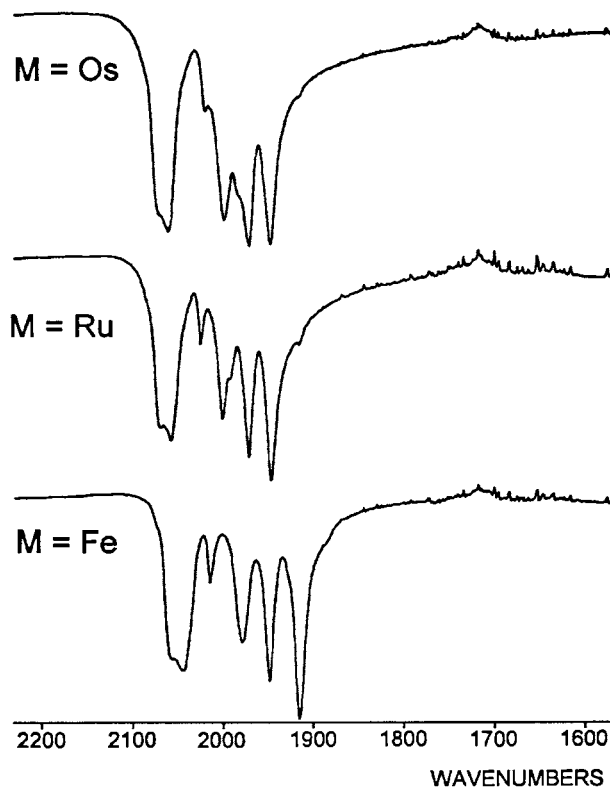
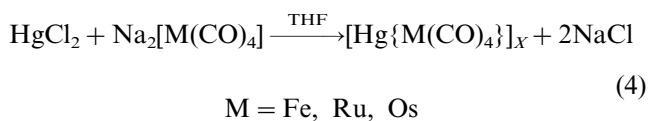


Fig. 2. IR spectra of  $[\text{Hg}\{\text{M}(\text{CO})_4\}_x]$ ,  $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ , in the CO stretching region (in nujol mull).

We found that the reaction of  $\text{HgCl}_2$  with  $\text{Na}_2[\text{M}(\text{CO})_4]$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) in a 1:1 molar ratio in THF produced the polymeric complexes  $[\text{Hg}\{\text{M}(\text{CO})_4\}_x]$  (Reaction 4), which are essentially



insoluble in common organic solvents [9–12]. The nujol mull IR spectra (Fig. 2) of the yellow precipitates in the CO stretching region are consistent with that reported for  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_x]$ . The iron derivative  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_x]$  was first synthesized early in the 20th century from the reaction of  $\text{Fe}(\text{CO})_5$  and  $\text{HgSO}_4$  in 10%  $\text{H}_2\text{SO}_4$  at r.t. [9]. However, there has been no report of syntheses of analogous polymeric complexes  $[\text{Hg}\{\text{M}(\text{CO})_4\}_x]$  ( $\text{M} = \text{Ru}, \text{Os}$ ). The highly unstable nature of  $\text{Ru}(\text{CO})_5$  and  $\text{Os}(\text{CO})_5$  preclude procedures that directly parallel the published synthesis of  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_x]$ .

For crystal growing purposes, potassium salts were converted to  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  and  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  through metathesis reactions in  $\text{CH}_2\text{Cl}_2$  with  $[\text{PPN}]\text{Cl}$  and  $[\text{Ph}_3\text{MeP}]\text{Br}$ , respectively. The CO stretching frequencies in the IR spectra of these complex cation salts occur at ca.  $30\text{ cm}^{-1}$  higher

values than in the potassium salts. This shift is attributed to diminished interaction (ion-pairing) of the complex positive cations with the anion's carbonyl oxygens compared with the interactions of the potassium cations with the anion's [13].

Crystals of  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]^-$  were grown in concentrated  $\text{CH}_3\text{CN}$  solution in a refrigerator at  $4^\circ\text{C}$ . Crystals of  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]^-$  were grown in a  $\text{CH}_2\text{Cl}_2$ /hexane solution in a refrigerator at  $4^\circ\text{C}$  by a vapor diffusion method. The ORTEP diagrams for  $[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]^{2-}$  and  $[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]^{2-}$  are provided in Fig. 3(a) and (b). Crystallographic data for both compounds are given in Table 1. Atomic coordinates ( $\text{\AA}$ ) and isotropic thermal displacement parameters ( $\text{\AA}^2 \times 10^3$ ) with ESD's and selected interatomic distances and interbond angles are given in Tables 2–5. Both  $[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]^{2-}$  and  $[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]^{2-}$  are isostructural with  $[\text{Hg}\{\text{Fe}(\text{CO})_4\}_2]^{2-}$ . These consist of two  $\text{M}(\text{CO})_4$  units, trigonal-bipyramidal fragments, joined at apical sites by a mercury atom in a linear  $\text{M}-\text{Hg}-\text{M}$  array with a staggered arrangement of the three equatorial COs of the  $\text{M}(\text{CO})_4$  units. The anion  $[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]^{2-}$  has a crystallographically imposed center of symmetry at the Hg position. Therefore an  $\text{Ru}-\text{Hg}-\text{Ru}$  angle of  $180^\circ$  is dictated. For the  $[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]^{2-}$  anion, the  $\text{Os}-\text{Hg}-\text{Os}$  angle is

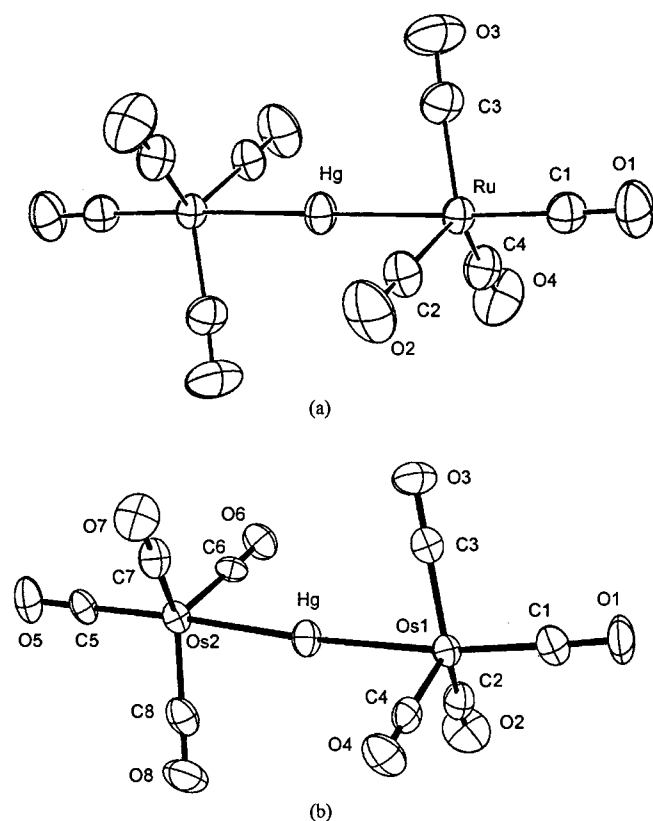


Fig. 3. (a) ORTEP diagram of  $[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]^{2-}$  showing 50% probability ellipsoids; (b) ORTEP diagram of  $[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]^{2-}$  showing 50% probability ellipsoids.

Table 1

Crystallographic data for  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2] \cdot 2\text{CH}_3\text{CN}$  (1) and  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  (2)

|   | (1)   | (2)   |
|---|---|---|
| Chemical formula                            | $\text{C}_{84}\text{H}_{66}\text{N}_4\text{P}_4\text{O}_8\text{HgRu}_2$ | $\text{C}_{46}\text{H}_{36}\text{O}_8\text{HgOs}_2\text{P}_2$ |
| Molecular weight                            | 1786.15   | 1359.68   |
| Crystal Description                         | Orange  | Light orange  |
| Crystal size (mm)                           | $0.40 \times 0.35$  | $0.35 \times 0.30 \times 0.50$                                |
|   | $\times 0.60$   |   |
| Crystal system                              | Triclinic   | Triclinic   |
| Space Group                                 | $P\bar{1}$  | $P\bar{1}$  |
| <i>a</i> ( $\text{\AA}$ )                   | 12.615(2)   | 11.437(2)   |
| <i>b</i> ( $\text{\AA}$ )                   | 13.374(2)   | 13.532(2)   |
| <i>c</i> ( $\text{\AA}$ )                   | 13.822(2)   | 14.698(2)   |
| $\alpha$ ( $^\circ$ )                       | 104.97(1)   | 83.98(2)  |
| $\beta$ ( $^\circ$ )                        | 106.18(1)   | 83.88(2)  |
| $\gamma$ ( $^\circ$ )                       | 108.92(1)   | 78.41(2)  |
| Volume ( $\text{\AA}^3$ )                   | 1956.4(6)   | 2207.5(6)   |
| <i>Z</i>                                    | 1   | 2   |
| $D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )    | 1.481   | 2.046   |
| Absorption coefficient ( $\text{cm}^{-1}$ ) | 24.6  | 93.35   |
| Wavelength ( $\text{\AA}$ )                 | Mo-K $\alpha$ (0.710 73)  | Mo-K $\alpha$ (0.710 73)                                      |
| Temperature ( $^\circ\text{C}$ )            | -60   | -60   |
| Structure solution method                   | MULTAN 11/82  | SHELXS86  |
| Data collected ( <i>h, k, l</i> )           | $+h, \pm k, \pm l$  | $+h, \pm k, \pm l$  |
| Scan type                                   | $\omega/2\theta$  | $\omega/2\theta$  |
| $2\theta$ limit ( $^\circ$ )                | $4 \leq 2\theta \leq 45$  | $4 \leq 2\theta \leq 45$                                      |
| Independent reflections                     | 5261  | 5375  |
| Data/restraints/parameters                  | 5261/0/467  | 5375/0/532  |
| $R_f$                                       | 0.022   | 0.0327  |
| $R_w/wR_2$                                  | 0.028 <sup>a</sup>  | 0.0832 <sup>b</sup>   |

$$R_f = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \quad R_w = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

<sup>a</sup> Refined on  $F$ .

<sup>b</sup> Refined on  $F^2$ .

$175.96(2)^\circ$ .  $\text{Ru}-\text{C}-\text{O}$  and  $\text{Os}-\text{C}-\text{O}$  angles are close to  $180^\circ$ ,  $\text{C}_{\text{ap}}-\text{Ru}-\text{Hg}$  or  $\text{C}_{\text{ap}}-\text{Os}-\text{Hg}$  are ca.  $176.0(1)$  and  $172.3(2)^\circ$ ; those of  $\text{C}_{\text{ap}}-\text{Ru}-\text{C}_{\text{eq}}$  and  $\text{C}_{\text{ap}}-\text{Os}-\text{C}_{\text{eq}}$  are  $97.8$  and  $97.7^\circ$  on average;  $\text{C}_{\text{eq}}-\text{Ru}-\text{C}_{\text{eq}}$  and  $\text{C}_{\text{eq}}-\text{Os}-\text{C}_{\text{eq}}$  angles are  $118.1$  and  $118.3^\circ$  on average, respectively. The  $\text{Hg}-\text{Ru}$  and  $\text{Hg}-\text{Os}$  distances are  $2.6638(3)$  and  $2.6908(3)$   $\text{\AA}$  which as expected are slightly longer than the reported  $\text{Hg}-\text{Fe}$  distance,  $2.522$   $\text{\AA}$  [5].

### 3. Experimental

All manipulations were carried out on a standard high-vacuum line or in a dry-box under an inert gas atmosphere [14]. THF and  $\text{Et}_2\text{O}$  were vacuum distilled into storage bulbs that contained sodium-benzophenone ketyl and were equipped with Kontes Teflon stopcocks.  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  were dried over  $\text{P}_4\text{O}_{10}$  with continuous stirring for 5 days followed by vacuum

Table 2

Atomic coordinates (Å) and isotropic thermal displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) with ESD's for [PPN]<sub>2</sub>[Hg{Ru(CO)<sub>4</sub>}<sub>2</sub>] · 2CH<sub>3</sub>CN

| Atom | x           | y          | z           | B        |
|------|-------------|------------|-------------|----------|
| Hg   | 0.000       | 0.000      | 0.000       | 3.183(4) |
| Ru   | 0.09323(2)  | 0.10920(2) | 0.11725(2)  | 2.556(6) |
| O1   | -0.2065(2)  | 0.2180(2)  | 0.2566(2)   | 5.11(7)  |
| O2   | -0.0171(3)  | 0.2903(2)  | 0.0221(2)   | 6.09(8)  |
| O3   | 0.1020(3)   | 0.1027(3)  | 0.3020(2)   | 6.23(9)  |
| O4   | -0.3316(3)  | -0.1015(3) | -0.0337(3)  | 6.3(1)   |
| C1   | -0.1623(3)  | 0.1786(3)  | 0.2042(3)   | 3.29(8)  |
| C2   | -0.0442(3)  | 0.2216(3)  | 0.0572(3)   | 3.58(8)  |
| C3   | 0.0300(3)   | 0.1049(3)  | 0.2312(3)   | 3.81(9)  |
| C4   | -0.2399(3)  | -0.0246(3) | 0.0224(3)   | 3.81(9)  |
| P1   | -0.37596(7) | 0.31101(6) | -0.29774(6) | 2.08(2)  |
| P2   | -0.14563(7) | 0.36599(6) | -0.33213(6) | 2.10(2)  |
| N1   | -0.2368(2)  | 0.3430(2)  | -0.2732(2)  | 2.52(6)  |
| N2   | 1.2088(4)   | -0.7451(4) | -1.2986(4)  | 8.1(2)   |
| C5A  | -0.3942(3)  | 0.4339(2)  | -0.2263(2)  | 2.43(7)  |
| C5B  | -0.4936(3)  | 0.4200(3)  | -0.2000(3)  | 4.2(1)   |
| C5C  | -0.5075(4)  | 0.5144(4)  | -0.1465(4)  | 5.7(1)   |
| C5D  | -0.4226(4)  | 0.6225(3)  | -0.1194(4)  | 5.1(1)   |
| C5E  | -0.3237(4)  | 0.6372(3)  | -0.1469(3)  | 4.5(1)   |
| C5F  | -0.3085(3)  | 0.5430(3)  | -0.1998(3)  | 3.43(8)  |
| C6A  | -0.4728(3)  | 0.2584(3)  | -0.4403(2)  | 2.42(7)  |
| C6B  | -0.4850(3)  | 0.1559(3)  | -0.5102(3)  | 3.17(8)  |
| C6C  | -0.5498(4)  | 0.1169(4)  | -0.6206(3)  | 4.2(1)   |
| C6D  | -0.6032(4)  | 0.1792(4)  | -0.6625(3)  | 4.8(1)   |
| C6E  | -0.5927(4)  | 0.2801(4)  | -0.5948(3)  | 4.8(1)   |
| C6F  | -0.5277(3)  | 0.3205(3)  | -0.4830(3)  | 3.60(8)  |
| C7A  | -0.4319(3)  | 0.2021(2)  | -0.2476(2)  | 2.37(7)  |
| C7B  | -0.3498(3)  | 0.1916(3)  | -0.1644(2)  | 2.64(7)  |
| C7C  | -0.3924(3)  | 0.1154(3)  | -0.1178(3)  | 3.51(9)  |
| C7D  | -0.5151(4)  | 0.0496(3)  | -0.1540(3)  | 4.2(1)   |
| C7E  | -0.5963(3)  | 0.0592(3)  | -0.2370(3)  | 4.3(1)   |
| C7F  | -0.5551(3)  | 0.1350(3)  | -0.2839(3)  | 3.33(8)  |
| C8A  | -0.1432(3)  | 0.2354(3)  | -0.4068(2)  | 2.54(7)  |
| C8B  | -0.1957(3)  | 0.1370(3)  | -0.3880(3)  | 2.97(8)  |
| C8C  | -0.1884(3)  | 0.0377(3)  | -0.4399(3)  | 3.74(9)  |
| C8D  | -0.1300(3)  | 0.0357(3)  | -0.5102(3)  | 4.06(9)  |
| C8E  | -0.0780(3)  | 0.1316(3)  | -0.5289(3)  | 4.20(9)  |
| C8F  | -0.0844(3)  | 0.2322(3)  | -0.4784(3)  | 3.38(8)  |
| C9A  | 0.0054(3)   | 0.4524(2)  | -0.2272(2)  | 2.22(6)  |
| C9B  | 0.1011(3)   | 0.5185(3)  | -0.2461(3)  | 3.38(8)  |
| C9C  | 0.2170(3)   | 0.5766(3)  | -0.1648(3)  | 3.75(9)  |
| C9D  | 0.2387(3)   | 0.5668(3)  | -0.0652(3)  | 3.25(8)  |
| C9E  | 0.1447(3)   | 0.5020(3)  | -0.0458(3)  | 3.50(9)  |
| C9F  | 0.0275(3)   | 0.4449(3)  | -0.1258(3)  | 3.15(8)  |
| C10A | -0.1772(3)  | 0.4358(3)  | -0.4243(2)  | 2.45(7)  |
| C10B | -0.2552(3)  | 0.3707(3)  | -0.5337(2)  | 2.95(8)  |
| C10C | -0.2935(3)  | 0.4238(3)  | -0.6008(3)  | 3.96(9)  |
| C10D | -0.2531(3)  | 0.5404(3)  | -0.5615(3)  | 4.52(9)  |
| C10E | -0.1754(4)  | 0.6059(3)  | -0.4535(3)  | 4.12(9)  |
| C10F | -0.1383(3)  | 0.5541(3)  | -0.3841(3)  | 3.14(8)  |
| C11  | 1.1670(4)   | -0.7675(4) | -1.2379(4)  | 5.6(1)   |
| C12  | 1.1116(6)   | -0.7979(4) | -1.1648(4)  | 6.9(2)   |
| H5B  | -0.5530     | 0.3452     | -0.2185     | 5.4      |
| H5C  | -0.5765     | 0.5042     | -0.1283     | 7.4      |
| H5D  | -0.4320     | 0.6871     | -0.0817     | 6.7      |
| H5E  | -0.2655     | 0.7121     | -0.1295     | 5.9      |
| H5F  | -0.2393     | 0.5532     | -0.2177     | 4.5      |
| H6B  | -0.4482     | 0.1124     | -0.4813     | 4.1      |
| H6C  | -0.5576     | 0.0468     | -0.6678     | 5.4      |
| H6D  | -0.6477     | 0.1521     | -0.7388     | 6.3      |
| H6E  | -0.6300     | 0.3226     | -0.6245     | 6.3      |
| H6F  | -0.5210     | 0.3902     | -0.4361     | 4.7      |

Table 2 (Continued)

| Atom | x       | y       | z       | B   |
|------|---------|---------|---------|-----|
| H7B  | -0.2646 | 0.2365  | -0.1395 | 3.4 |
| H7C  | -0.3362 | 0.1087  | -0.0604 | 4.6 |
| H7D  | -0.5439 | -0.0025 | -0.1218 | 5.4 |
| H7E  | -0.6813 | 0.0134  | -0.2622 | 5.7 |
| H7F  | -0.6118 | 0.1409  | -0.3413 | 4.3 |
| H8B  | -0.2363 | 0.1382  | -0.3395 | 3.9 |
| H8C  | -0.2238 | -0.0292 | -0.4268 | 4.9 |
| H8D  | -0.1257 | -0.0329 | -0.5460 | 5.3 |
| H8E  | -0.0370 | 0.1294  | -0.5770 | 5.5 |
| H8F  | -0.0490 | 0.2984  | -0.4925 | 4.4 |
| H9B  | 0.0870  | 0.5238  | -0.3153 | 4.4 |
| H9C  | 0.2820  | 0.6235  | -0.1775 | 4.9 |
| H9D  | 0.3191  | 0.6050  | -0.0100 | 4.2 |
| H9E  | 0.1598  | 0.4960  | 0.0233  | 4.5 |
| H9F  | -0.0377 | 0.4007  | -0.1114 | 4.1 |
| H10B | -0.2819 | 0.2900  | -0.5620 | 3.8 |
| H10C | -0.3483 | 0.3791  | -0.6747 | 5.1 |
| H10D | -0.2784 | 0.5762  | -0.6086 | 5.9 |
| H10E | -0.1474 | 0.6867  | -0.4266 | 5.4 |
| H10F | -0.0865 | 0.5991  | -0.3094 | 4.1 |

Positional parameters for hydrogen atoms were calculated based on an average C–H distance of 0.95 Å and were not refined. Anisotropically refined atoms are given in the form as:  $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ .

distillation into storage bulbs. [PPN]Cl (Bis(*t*-triphenylphosphino)iminium chloride, Aldrich) and [Ph<sub>3</sub>MeP]Br were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane and dried at 100°C under vacuum. Potassium and sodium salts of [M(CO)<sub>4</sub>]<sup>2-</sup> (M = Fe, Ru, Os) were prepared by literature methods with minor modifications [15]. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN and by Oneida Research Services, Whitesboro, NY.

### 3.1. Preparation of [PPN]<sub>2</sub>[Hg{Fe(CO)<sub>4</sub>}<sub>2</sub>]

In a dry-box 146.9 mg (0.608 mmol) of K<sub>2</sub>[Fe(CO)<sub>4</sub>] and 82.5 mg (0.304 mmol) of HgCl<sub>2</sub> were placed in a reaction flask along with a Teflon-coated stir bar. The reaction flask was attached to a vacuum extractor, sealed, and evacuated on the vacuum line. THF (20 ml) was condensed into the reaction flask. The contents was stirred for 30 min at r.t., during which time a yellow solution and a white precipitate were produced. The white precipitate was collected by filtration and was identified as KCl by powder X-ray diffraction. THF was removed under vacuum to give an orange–yellow solid, which was washed in ether to give a yellow powder, 155.7 mg (84% yield). IR (THF, ν<sub>CO</sub>): 1974(vw), 1939(vs), 1862(s, br), 1824(m, br) cm<sup>-1</sup>.

In a dry-box, 69.6 mg (0.113 mmol) of K<sub>2</sub>[Hg{Fe(CO)<sub>4</sub>}<sub>2</sub>] and 129.5 mg (0.226 mmol) of [PPN]Cl were placed in a flask with a stir-bar. The flask

Table 3

Atomic coordinates (Å) and isotropic thermal displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) with ESD's for [Ph<sub>3</sub>MeP]<sub>2</sub>[Hg{Os(CO)<sub>4</sub>}<sub>2</sub>]

| Atoms  | x          | y          | z          | U     |
|--------|------------|------------|------------|-------|
| Hg     | 0.1986(1)  | −0.2428(1) | −0.2504(1) | 35(1) |
| Os(1)  | −0.0078(1) | −0.1639(1) | −0.1565(1) | 29(1) |
| Os(2)  | 0.3990(1)  | −0.3335(1) | −0.3456(1) | 27(1) |
| P(1)   | −0.1055(2) | −0.2995(2) | 0.2196(2)  | 30(1) |
| P(2)   | 0.6399(2)  | 0.2103(2)  | −0.2810(2) | 31(1) |
| O(1)   | −0.2469(6) | −0.0528(5) | −0.0717(5) | 57(2) |
| O(2)   | 0.1479(7)  | −0.0227(5) | −0.1033(6) | 66(2) |
| O(3)   | −0.1193(7) | −0.1692(6) | −0.3365(4) | 56(2) |
| O(4)   | 0.0264(6)  | −0.3698(5) | −0.0443(5) | 49(2) |
| O(5)   | 0.6094(6)  | −0.4656(6) | −0.4478(6) | 66(2) |
| O(6)   | 0.3937(6)  | −0.1347(4) | −0.4652(5) | 48(2) |
| O(7)   | 0.2117(6)  | −0.4502(5) | −0.3921(5) | 49(2) |
| O(8)   | 0.5121(8)  | −0.3427(6) | −0.1641(5) | 68(2) |
| C(1)   | −0.1563(8) | −0.0942(6) | −0.1031(6) | 33(2) |
| C(2)   | 0.0897(9)  | −0.0762(6) | −0.1248(6) | 44(2) |
| C(3)   | −0.0735(8) | −0.1672(6) | −0.2701(6) | 38(2) |
| C(4)   | 0.0165(8)  | −0.2931(6) | −0.877(5)  | 32(2) |
| C(5)   | 0.5308(9)  | −0.4152(6) | −0.4072(6) | 41(2) |
| C(6)   | 0.3945(7)  | −0.2070(6) | −0.4187(6) | 32(2) |
| C(7)   | 0.2842(8)  | −0.4066(6) | −0.3724(5) | 32(2) |
| C(8)   | 0.4678(8)  | −0.3401(7) | −0.2321(7) | 43(2) |
| C(9A)  | −0.0086(7) | −0.4105(6) | 0.2640(6)  | 33(2) |
| C(9B)  | 0.0257(9)  | −0.4929(6) | 0.2120(7)  | 46(2) |
| C(9C)  | 0.1095(10) | −0.5755(7) | 0.2433(8)  | 60(3) |
| C(9D)  | 0.1542(10) | −0.5757(8) | 0.3259(9)  | 67(3) |
| C(9E)  | 0.1202(10) | −0.4947(9) | 0.3775(8)  | 63(3) |
| C(9F)  | 0.0393(9)  | −0.4112(7) | 0.3473(7)  | 48(2) |
| C(10A) | −0.2072(7) | −0.3315(6) | 0.1480(5)  | 29(2) |
| C(10B) | −0.2314(8) | −0.2748(7) | 0.0657(6)  | 40(2) |
| C(10C) | −0.3167(9) | −0.2966(8) | 0.0132(6)  | 46(2) |
| C(10D) | −0.3774(9) | −0.3727(7) | 0.0427(6)  | 43(2) |
| C(10E) | −0.3530(8) | −0.4295(7) | 0.1253(6)  | 41(2) |
| C(10F) | −0.2675(8) | −0.4095(6) | 0.1783(6)  | 36(2) |
| C(11A) | −0.1902(7) | −0.2318(6) | 0.3115(5)  | 28(2) |
| C(11B) | −0.2317(8) | −0.2811(7) | 0.3928(6)  | 40(2) |
| C(11C) | −0.2988(9) | −0.2265(8) | 0.4604(7)  | 48(2) |
| C(11D) | −0.3283(9) | −0.1230(8) | 0.4465(7)  | 47(2) |
| C(11E) | −0.2917(9) | −0.0740(7) | 0.3660(7)  | 50(2) |
| C(11F) | −0.2218(8) | −0.1277(7) | 0.2979(6)  | 44(2) |
| C(12)  | −0.0130(8) | −0.2219(7) | 0.1531(6)  | 43(2) |
| C(13A) | 0.7761(7)  | 0.1793(6)  | −0.3510(5) | 29(2) |
| C(13B) | 0.8664(7)  | 0.0970(6)  | −0.3205(6) | 33(2) |
| C(13C) | 0.9718(8)  | 0.0740(6)  | −0.3730(6) | 37(2) |
| C(13D) | 0.9946(8)  | 0.1291(7)  | −0.4557(6) | 42(2) |
| C(13E) | 0.9078(9)  | 0.2101(7)  | −0.4848(6) | 43(2) |
| C(13F) | 0.8007(8)  | 0.2340(7)  | −0.4328(5) | 35(2) |
| C(14A) | 0.5778(8)  | 0.0986(6)  | −0.2443(6) | 36(2) |
| C(14B) | 0.6139(8)  | 0.0109(7)  | −0.2913(7) | 44(2) |
| C(14C) | 0.5639(9)  | −0.0716(7) | −0.2618(8) | 53(3) |
| C(14D) | 0.4785(10) | −0.0683(8) | −0.1885(8) | 62(3) |
| C(14E) | 0.4419(9)  | 0.0189(8)  | −0.1413(8) | 57(3) |
| C(14F) | 0.4919(8)  | 0.1017(7)  | −0.1704(6) | 43(2) |
| C(15A) | 0.6657(7)  | 0.2678(6)  | −0.1817(5) | 28(2) |
| C(15B) | 0.6904(8)  | 0.2099(6)  | −0.0998(6) | 36(2) |
| C(15C) | 0.7133(9)  | 0.2546(8)  | −0.0254(7) | 49(2) |
| C(15D) | 0.7135(9)  | 0.3556(8)  | −0.0318(7) | 51(3) |
| C(15E) | 0.6914(9)  | 0.4147(7)  | −0.1139(8) | 52(3) |
| C(15F) | 0.6681(8)  | 0.3702(6)  | −0.1885(6) | 40(2) |
| C(16)  | 0.5338(9)  | 0.2982(7)  | −0.3454(7) | 49(2) |
| H(9B)  | −0.0069(9) | −0.4930(6) | 0.1567(7)  | 70    |
| H(9C)  | 0.1349(10) | −0.6304(7) | 0.2082(8)  | 89    |

Table 3 (Continued)

| Atoms  | x          | y          | z          | U   |
|--------|------------|------------|------------|-----|
| H(9D)  | 0.2087(10) | −0.6318(8) | 0.3473(9)  | 101 |
| H(9E)  | 0.1520(10) | −0.4960(9) | 0.4334(8)  | 94  |
| H(9F)  | 0.0169(9)  | −0.3558(7) | 0.3822(7)  | 72  |
| H(10B) | −0.1910(8) | −0.2223(7) | 0.0454(6)  | 60  |
| H(10C) | −0.3322(9) | −0.2589(8) | −0.0423(6) | 69  |
| H(10D) | −0.4346(9) | −0.3865(7) | 0.0079(6)  | 65  |
| H(10E) | −0.3942(8) | −0.4815(7) | 0.1456(6)  | 62  |
| H(10F) | −0.2513(8) | −0.4481(6) | 0.2333(6)  | 54  |
| H(11B) | −0.2138(8) | −0.3514(7) | 0.4014(6)  | 59  |
| H(11C) | −0.3243(9) | −0.2596(8) | 0.5154(7)  | 72  |
| H(11D) | −0.3736(9) | −0.0860(8) | 0.4924(7)  | 70  |
| H(11E) | −0.3139(9) | −0.0040(7) | 0.3567(7)  | 75  |
| H(11F) | −0.1963(8) | −0.0939(7) | 0.2433(6)  | 66  |
| H(12A) | −0.0623(8) | −0.1613(7) | 0.1281(6)  | 65  |
| H(12B) | 0.0319(8)  | −0.2583(7) | 0.1040(6)  | 65  |
| H(12C) | 0.412(8)   | −0.2044(7) | 0.1916(6)  | 65  |
| H(13B) | 0.8532(7)  | 0.594(6)   | −0.2650(6) | 49  |
| H(13C) | 0.10301(8) | 0.0201(6)  | −0.3529(6) | 56  |
| H(13D) | 1.0668(8)  | 0.1120(7)  | −0.4912(6) | 63  |
| H(13E) | 0.9222(9)  | 0.2483(7)  | −0.5397(6) | 65  |
| H(13F) | 0.7434(8)  | 0.2884(7)  | −0.4532(5) | 52  |
| H(14B) | 0.6707(8)  | 0.0091(7)  | −0.3417(7) | 65  |
| H(14C) | 0.5880(9)  | −0.1306(7) | −0.2917(8) | 79  |
| H(14D) | 0.4444(10) | −0.1249(8) | −0.1698(8) | 93  |
| H(14E) | 0.3847(9)  | 0.0205(8)  | −0.0913(8) | 86  |
| H(14F) | 0.4680(8)  | 0.1605(7)  | −0.1402(6) | 65  |
| H(15B) | 0.6915(8)  | 0.1407(6)  | −0.0952(6) | 55  |
| H(15C) | 0.7287(9)  | 0.2155(8)  | 0.0295(7)  | 73  |
| H(15D) | 0.7284(9)  | 0.3854(8)  | 0.0189(7)  | 77  |
| H(15E) | 0.6924(9)  | 0.4836(7)  | −0.1184(8) | 78  |
| H(15F) | 0.6541(8)  | 0.4092(6)  | −0.2437(6) | 59  |
| H(16A) | 0.4600(9)  | 0.3151(7)  | −0.3077(7) | 73  |
| H(16B) | 0.5194(9)  | 0.2680(7)  | −0.3984(7) | 73  |
| H(16C) | 0.5651(9)  | 0.3585(7)  | −0.3647(7) | 73  |

Positional parameters for hydrogen atoms were calculated based on an average C–H distance of 0.93 Å and were not refined. Anisotropically refined atoms are given in the form as:  $\exp(-2\pi^2[h^2(a^*)^2U(11) + K^2(b^*)^2U(22) + l^2(c^*)^2U(33) + 2klb^*c^*U(23)$

$+ 2hla^*c^*U(13) + 2hka^*b^*U(12)]$ .  $a^*$ ,  $b^*$ , and  $c^*$  are reciprocal lattice parameters.

was attached to a vacuum extractor and evacuated. CH<sub>2</sub>Cl<sub>2</sub> (20ml) was condensed into the reaction flask. An orange–yellow solution and a white precipitate were obtained after 20 min of stirring. The precipitate was isolated by filtration and identified as KCl by X-ray diffraction. The CH<sub>2</sub>Cl<sub>2</sub> was removed under vacuum to give an orange–yellow powder, which was washed in ether to yield 136.1 mg (75% yield) of [PPN]<sub>2</sub>[Hg{Fe(CO)<sub>4</sub>}<sub>2</sub>]. IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{\text{CO}}$ ): 2018(vw), 1969(w), 1934(s), 1853(vs, br) cm<sup>−1</sup>. Anal. Found: C, 60.6; H, 4.22%. C<sub>80</sub>H<sub>60</sub>N<sub>2</sub>O<sub>8</sub>P<sub>4</sub>HgFe<sub>2</sub> ([PPN]<sub>2</sub>[Hg{Fe(CO)<sub>4</sub>}<sub>2</sub>]) Calc.: C, 59.6; H, 3.75%.

### 3.2. Preparation of [PPN]<sub>2</sub>[Hg{Ru(CO)<sub>4</sub>}<sub>2</sub>]

This compound was prepared and isolated by a procedure similar to that described above. The reaction

Table 4

Selected bond distances (Å) and angles (°) with ESD's for  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2] \cdot 2\text{CH}_3\text{CN}$

|          |           |          |          |
|----------|-----------|----------|----------|
| Hg–Ru    | 2.6638(3) | Ru–C1    | 1.897(4) |
| Ru–C2    | 1.913(4)  | Ru–C3    | 1.908(4) |
| Ru–C4    | 1.906(4)  | O1–C1    | 1.154(5) |
| O2–C2    | 1.147(5)  | O3–C3    | 1.148(5) |
| O4–C4    | 1.146(5)  | P1–N1    | 1.576(3) |
| Hg–Ru–C1 | 176.0(1)  | Hg–Ru–C2 | 84.8(1)  |
| Hg–Ru–C3 | 80.1(1)   | Hg–Ru–C4 | 81.9(1)  |
| Ru–C1–O1 | 178.2(4)  | Ru–C2–O2 | 178.0(4) |
| Ru–C3–O3 | 177.7(4)  | Ru–C4–O4 | 176.3(4) |
| C1–Ru–C2 | 99.2(2)   | C1–Ru–C3 | 97.9(2)  |
| C1–Ru–C4 | 96.3(2)   | C2–Ru–C3 | 118.0(2) |
| C2–Ru–C4 | 115.4(2)  | C3–Ru–C4 | 121.1(2) |

of 188.4 mg (0.694 mmol) of  $\text{K}_2[\text{Ru}(\text{CO})_4]$  with 87.8 mg (0.323 mmol) of  $\text{HgCl}_2$  in THF for 2 h produced  $\text{K}_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$ , 207.2 mg (91% yield). IR (THF,  $\nu_{\text{CO}}$ ): 1981(vw), 1952(vs), 1874(s), 1834(m, br)  $\text{cm}^{-1}$ . Metathesis with  $[\text{PPN}]\text{Cl}$  produced  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  (78% Yield). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\nu_{\text{CO}}$ ): 2034(vw), 2008(vw), 1980(w), 1949(s), 1867(vs)  $\text{cm}^{-1}$ . Anal. Found: C, 56.7; H, 3.56%.  $\text{C}_{84}\text{H}_{66}\text{N}_4\text{P}_4\text{O}_8\text{HgRu}_2$  ( $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2] \cdot 2\text{CH}_3\text{CN}$ ) Calc.: C, 56.5; H, 3.72%.

### 3.3. Preparation of $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$

This compound was prepared and isolated by a procedure similar to that described above. The reaction of 189.3 mg (0.497 mmol) of  $\text{K}_2[\text{Os}(\text{CO})_4]$  with 67.5 mg (0.249 mmol) of  $\text{HgCl}_2$  in THF for 3 h at 60°C produced 190.8 mg (87% yield) of  $\text{K}_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$ . IR (THF,  $\nu_{\text{CO}}$ ): 1983(vw), 1956(vs), 1872(s), 1834(m, br)  $\text{cm}^{-1}$ . Metathesis with  $[\text{Ph}_3\text{MeP}]\text{Br}$  produced  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$  (84% Yield). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\nu_{\text{CO}}$ ): 2043(vw), 1983(m), 1955(s), 1863(vs)  $\text{cm}^{-1}$ . Anal. Found: C, 40.6; H, 2.60%.  $\text{C}_{46}\text{H}_{36}\text{P}_2\text{O}_8\text{HgOs}_2$  ( $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$ ) Calc.: C, 40.6; H, 2.67%.

### 3.4. Preparation of $[\text{Hg}\{\text{M}(\text{CO})_4\}_x]$

Reaction of 214.5 mg (1.0 mmol) of  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  with 277.0 mg (1.0 mmol) of  $\text{HgCl}_2$  in THF for 1 h at r.t. produced yellow solution with yellow precipitate. The precipitate was isolated by filtration and washed in water and THF. The yellow precipitate, 346.8 mg (94% yield) was identified to be  $[\text{HgFe}(\text{CO})_4]_x$  by nujol mull IR spectroscopy. IR (nujol mull,  $\nu_{\text{CO}}$ ): 2058(sbr, sh), 2045(s), 2015(m), 1979(m), 1949(s), 1916(vs)  $\text{cm}^{-1}$ .

$[\text{HgRu}(\text{CO})_4]_x$  and  $[\text{HgOs}(\text{CO})_4]_x$  were prepared by the same method as described above, except that 0.686 mmol of  $\text{Na}_2[\text{Ru}(\text{CO})_4]$  and 0.686 mmol of  $\text{HgCl}_2$  were used to prepare  $[\text{HgRu}(\text{CO})_4]_x$ ; and 0.3 mmol of  $\text{Na}_2[\text{Os}(\text{CO})_4]$  and 0.3 mmol of  $\text{HgCl}_2$  were used to

Table 5

Selected bond distances (Å) and angles (°) with ESD's for  $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$

|                 |           |                 |           |
|-----------------|-----------|-----------------|-----------|
| Hg–Os(1)        | 2.6871(8) | Hg–Os(2)        | 2.6945(8) |
| Os(1)–C(1)      | 1.902(8)  | Os(1)–C(2)      | 1.905(10) |
| Os(1)–C(3)      | 1.911(9)  | Os(1)–C(4)      | 1.911(8)  |
| Os(2)–C(5)      | 1.888(9)  | Os(2)–C(6)      | 1.918(9)  |
| Os(2)–C(7)      | 1.889(9)  | Os(2)–C(8)      | 1.905(10) |
| O(1)–C(1)       | 1.149(10) | O(2)–C(2)       | 1.162(11) |
| O(3)–C(3)       | 1.161(11) | O(4)–C(4)       | 1.150(10) |
| O(5)–C(5)       | 1.165(11) | O(6)–C(6)       | 1.132(10) |
| O(7)–C(7)       | 1.184(10) | O(8)–C(8)       | 1.162(11) |
| Os(1)–Hg–Os(2)  | 175.96(2) | Hg–Os(1)–C(1)   | 172.3(2)  |
| Hg–Os(1)–C(2)   | 81.3(3)   | Hg–Os(1)–C(3)   | 83.3(3)   |
| Hg–Os(1)–C(4)   | 83.4(3)   | Hg–Os(2)–C(5)   | 171.5(3)  |
| Hg–Os(2)–C(6)   | 86.8(2)   | Hg–Os(2)–C(7)   | 77.7(2)   |
| Hg–Os(2)–C(8)   | 83.7(3)   | Os(1)–C(1)–O(1) | 178.9(8)  |
| Os(1)–C(2)–O(2) | 178.3(9)  | Os(1)–C(3)–O(3) | 176.3(8)  |
| Os(1)–C(4)–O(4) | 177.1(8)  | Os(2)–C(5)–O(5) | 177.4(9)  |
| Os(2)–C(6)–O(6) | 176.9(7)  | Os(2)–C(7)–O(7) | 177.5(7)  |
| Os(2)–C(8)–O(8) | 178.1(9)  | C(1)–Os(1)–C(2) | 97.1(4)   |
| C(1)–Os(1)–C(3) | 92.1(4)   | C(1)–Os(1)–C(4) | 104.0(3)  |
| C(2)–Os(1)–C(3) | 129.2(4)  | C(2)–Os(1)–C(4) | 113.4(3)  |
| C(4)–Os(1)–C(3) | 112.4(3)  | C(5)–Os(2)–C(6) | 100.7(3)  |
| C(5)–Os(2)–C(7) | 95.4(4)   | C(5)–Os(2)–C(8) | 96.7(4)   |
| C(6)–Os(2)–C(7) | 113.6(3)  | C(6)–Os(2)–C(8) | 114.3(4)  |
| C(7)–Os(2)–C(8) | 127.1(4)  |                 |           |

prepare  $[\text{HgOs}(\text{CO})_4]_x$ . 187.8 mg (66.2% yield) of a light brown precipitate of  $[\text{HgRu}(\text{CO})_4]_x$  and 77.0 mg (51.0%) of a light brown precipitate of  $[\text{HgOs}(\text{CO})_4]_x$  were obtained. The IR (nujol mull,  $\nu_{\text{CO}}$ ) spectrum of  $[\text{HgRu}(\text{CO})_4]_x$ : 2069(sbr, sh), 2058(s), 2026(m), 2001(m), 1991(m, sh), 1972(s), 1947(vs)  $\text{cm}^{-1}$ . Anal. Found: C, 12.28, Ru, 22.93%.  $[\text{C}_4\text{O}_4\text{HgRu}]_x$  Calc.: C, 11.61; Ru, 24.43%. The IR (nujol mull,  $\nu_{\text{CO}}$ ) spectrum of  $[\text{HgOs}(\text{CO})_4]_x$ : 2072(sbr, sh), 2061(s), 2019(w), 1999(m), 1984(m, sh), 1971(vs), 1948(vs)  $\text{cm}^{-1}$ . Anal. Found: C, 9.62, Hg, 38.72%.  $[\text{C}_4\text{O}_4\text{HgOs}]_x$  Calc.: C, 9.55; Hg, 39.90%.

### 3.5. X-ray structure determination of $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$ and $[\text{Ph}_3\text{MeP}]_2[\text{Hg}\{\text{Os}(\text{CO})_4\}_2]$

Single crystals were mounted and sealed inside glass capillaries of 0.5 mm diameter. X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo– $\text{K}_\alpha$  radiation. Unit cell parameters were obtained by a least-square refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in the  $2\theta$  range of 24–30°. The diffraction data were corrected for Lorentz and polarization effects, decay, and absorption (empirically from  $\psi$ -scan data). Computations were performed on a VAX station 3100 computer using MOLEN [16] for  $[\text{PPN}]_2[\text{Hg}\{\text{Ru}(\text{CO})_4\}_2]$  and an IBM compatible PC using SHELXL 93 [17] for

[Ph<sub>3</sub>MeP]<sub>2</sub>[Hg{Os(CO)<sub>4</sub>}]<sub>2</sub>. Structures were solved using the direct method MULTAN 11/82 and difference Fourier synthesis with analytical scattering factors used throughout the structure refinement [18] for [PPN]<sub>2</sub>[Hg{Ru(CO)<sub>4</sub>}]<sub>2</sub> and SHELXS86 [19] for [Ph<sub>3</sub>MeP]<sub>2</sub>[Hg{Os(CO)<sub>4</sub>}]<sub>2</sub>. After all of the non-hydrogen atoms were located and refined, hydrogen atoms on the cations were placed at calculated positions by assuming ideal geometries with C–H distances of 0.95 Å for [PPN]<sub>2</sub>[Hg{Ru(CO)<sub>4</sub>}]<sub>2</sub> and 0.93 Å for [Ph<sub>3</sub>MeP]<sub>2</sub>[Hg{Os(CO)<sub>4</sub>}]<sub>2</sub>. The thermal parameters of the hydrogen atoms were set to  $B(H) = 1.3 B(C) \text{ \AA}^2$  for [PPN]<sub>2</sub>[Hg{Ru(CO)<sub>4</sub>}]<sub>2</sub> and  $B(H) = 1.5 B(C) \text{ \AA}^2$  for [Ph<sub>3</sub>MeP]<sub>2</sub>[Hg{Os(CO)<sub>4</sub>}]<sub>2</sub>. Then, with the positional and thermal parameters of all the hydrogen atoms fixed, the non-hydrogen atoms were refined anisotropically. New hydrogen positions were calculated, and this procedure was repeated until the parameters of the non-hydrogen atoms were refined to convergence (final shift/error ≤ 0.03).

#### Acknowledgements

This work was supported by the National Science Foundation through Grant CHE 94-0123 and CHE 97-00394.

#### References

- [1] S.V. Dighe, M. Orchin, *J. Am. Chem. Soc.* 86 (1964) 3895.
- [2] J.M. Burlitch, A. Ferrari, *Inorg. Chem.* 9 (1970) 563.
- [3] M.L. Katcher, G.L. Simon, *Inorg. Chem.* 11 (1972) 1651.
- [4] H. Behrens, H.D. Feilner, E. Lindner, D. Uhlig, *Z. Naturforsch.* b26 (1971) 990.
- [5] B.A. Sosinsky, R.G. Shong, B.J. Fitzgerald, N. Norem, C. O'Rourke, *Inorg. Chem.* 22 (1983) 3124.
- [6] P. Braunstein, M. Knorr, A. Tiripicchio, M.T. Camellin, *Inorg. Chem.* 31 (1992) 3685.
- [7] M.N. Bochkarev, N.L. Ermolaev, L.N. Zakharov, Yu. N. Saf'yanov, G.A. Razuvaev, Yu. T. Struchkov, *J. Organomet. Chem.* 270 (1984) 289.
- [8] N.K. Bhattacharyya, T.J. Coffy, W. Quintana, et al., *Organometallics* 9 (1990) 2368.
- [9] H. Hock, H. Stuhlmann, *Ber.* 62 (1929) 431.
- [10] D.M. Adams, D.J. Cook, R.D.W. Kemmitt, *Nature* 205 (1965) 589.
- [11] W. Beck, K. Noack, *J. Organomet. Chem.* 10 (1967) 307.
- [12] T. Takano, Y. Sasaki, *Bull. Chem. Soc. Jpn.* 44 (1971) 431.
- [13] K.E. Inkrott, S.G. Shore, *Inorg. Chem.* 18 (1979) 2817.
- [14] D.F. Shriver, M.A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed, Wiley, New York, 1969.
- [15] R.M. Sweet, C.J. Fritchie, R.A. Shunn, *Inorg. Chem.* 6 (1967) 749.
- [16] MOLEN, an interactive structure solution procedure was used to process X-ray data, to apply corrections, and to solve and refine structures, Enraf-Nonius, Delft, The Netherlands, 1990.
- [17] G.M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structure, University of Göttingen, Göttingen, Germany, 1993.
- [18] Atomic scattering factors from: *International Tables for X-ray Crystallography*, Kynoch, Birmingham, UK, 1974, Vol IV.
- [19] G.M. Sheldrick, *Acta Crystallogr.* A46 (1990) 467.