

## Preliminary communication

### A new route to mixed-metal carbonyls containing osmium

J.R. MOSS and W.A.G. GRAHAM

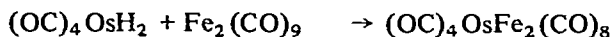
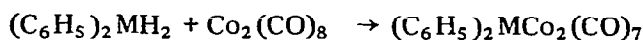
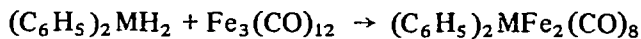
*Department of Chemistry, University of Alberta, Edmonton, Alberta (Canada)*

(Received October 14th, 1969; in revised form, April 21st, 1970)

Neutral mixed-metal carbonyls of Group VIII metals have been reported for iron and ruthenium<sup>1,2</sup>, and have been briefly mentioned for ruthenium and osmium<sup>3</sup>. These preparations involved fairly vigorous conditions; for example,  $\text{Ru}_2\text{Os}(\text{CO})_{12}$  and  $\text{RuOs}_2(\text{CO})_{12}$  were obtained by heating a mixture of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  in xylene at  $175^\circ$  for 90 hours under carbon monoxide pressure<sup>3</sup>. We now report a novel reaction by which the hitherto unknown iron-osmium dodecacarbonyls can be prepared under mild conditions.

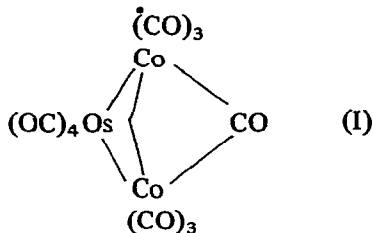
When a suspension of  $\text{Fe}_2(\text{CO})_9$  in n-heptane is stirred with  $\text{H}_2\text{Os}(\text{CO})_4$  (4/1 molar ratio) at room temperature for 3 hours, a deep purple solution and a dark solid are produced. Removal of solvent and  $\text{Fe}(\text{CO})_5$  formed in the reaction left a dark solid residue which was chromatographed on Florisil. Hexane elution afforded purple  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  (dec.  $> 130^\circ$ , 70% yield), having infrared carbonyl stretching bands in n-heptane at 2119w, 2057s, 2043vs, 2039sh, 2015w, 2004w. Additional exceedingly weak, broad bands are observed in the bridging region at 1865 and 1840  $\text{cm}^{-1}$  which are of comparable intensity to those in  $\text{Fe}_3(\text{CO})_{12}$ . Benzene elution afforded orange  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  (dec.  $> 166^\circ$ , 6% yield) having  $\nu(\text{CO})$  in n-heptane at 2086s, 2072s, 2040vs, 2032m, 2025m, 2015w, 1994w, 1875w, 1848m. Both new compounds exhibited molecular ions of the expected isotopic pattern in their mass spectra, and molecular weights were confirmed by exact mass measurement of the most abundant peaks of the molecular ions.

This synthetic approach was suggested by the facile reaction of  $(\text{C}_6\text{H}_5)_2\text{MH}_2$  (M = Si or Ge) with iron or cobalt carbonyls<sup>4</sup>, *i.e.*,



The reaction of  $\text{H}_2\text{Os}(\text{CO})_4$  with  $\text{Co}_2(\text{CO})_8$  (1/1 molar ratio, n-heptane solution) took place over 5 hours at room temperature. Chromatography (Florisil, hexane elution) of the reaction products gave  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_4(\text{CO})_{12}$ , orange  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  (dec.  $> 130^\circ$ , 10% yield,  $\nu(\text{CO})$  in hexane at 2112w, 2081s, 2078s, 2057vs, 2046s,

2028m, 2015m) and red  $\text{Co}_2\text{Os}(\text{CO})_{11}$  (dec.  $> 80^\circ$ , 20% yield,  $\nu(\text{CO})$  in heptane at 2127w, 2069s, 2049vs, 2025m, 1823m). The anticipated structure for the latter molecule is I, although the infrared spectrum exhibits a bridging carbonyl band, the terminal region is simpler than expected for I, and the structure remains in doubt. Both cobalt-osmium compounds have been characterized by analysis and mass spectrometry. We



have also observed among the products a volatile liquid, identified mass spectrometrically as  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$ .

As an extension of the above reactions, the recently reported dinuclear osmium carbonyl hydride,  $\text{H}_2\text{Os}_2(\text{CO})_8$ <sup>5</sup>, was stirred at room temperature with a suspension  $\text{Fe}_2(\text{CO})_9$  in n-heptane (1/2 molar ratio) to give an orange solution. The major product, isolated by chromatography and recrystallization, was orange  $\text{FeOs}_2(\text{CO})_{12}$  (dec.  $> 150^\circ$ , 20% yield,  $\nu(\text{CO})$  in n-heptane at 2070s, 2042vs, 2034vs, 2022m, 2008w, 2003m, 1988w), which showed a molecular ion of the expected isotope pattern in its mass spectrum.

It appears that the reaction of osmium carbonyl hydrides with carbonyls of other metals provides a useful new route to mixed polynuclear compounds. The scope of the reaction is being further investigated.

#### REFERENCES

- 1 D.B. Yawney and F.G.A. Stone, *Chem. Commun.*, (1968) 619; *J. Chem. Soc., A.*, (1969) 502.
- 2 J. Knight and M.J. Mays, *Chem. Ind.*, (1968) 1159.
- 3 B.F.G. Johnson, R.D. Johnston, J. Lewis, I.G. Williams and P.A. Kilty, *Chem. Commun.*, (1968) 861.
- 4 E.H. Brooks, M. Elder, W.A.G. Graham and D. Hall, *J. Amer. Chem. Soc.*, 90 (1968) 3587; E.H. Brooks and J. Hoyano, to be published.
- 5 J.R. Moss and W.A.G. Graham, *Chem. Commun.*, (1969) 800.