

## THE SYNTHESIS OF SOME MIXED METAL CLUSTER COMPLEXES OF OSMIUM WITH COBALT AND IRON

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### Summary

The reactions of *cis*-dihydridotetracarbonylosmium,  $\text{H}_2\text{Os}(\text{CO})_4$  with both  $\text{Fe}_2(\text{CO})_9$  and  $\text{Co}_2(\text{CO})_8$  have been studied at room temperature. With  $\text{Fe}_2(\text{CO})_9$ , the major product is  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  and  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  was obtained as a minor product. With  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_2\text{Os}(\text{CO})_{11}$  and  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  are obtained, along with an unstable compound which was identified mass spectrometrically as  $\text{HOsCo}(\text{CO})_8$ .  $\text{Os}(\text{CO})_5$  reacts under UV irradiation with  $\text{Co}_2(\text{CO})_8$  to give  $\text{Co}_2\text{Os}(\text{CO})_{11}$ . The main product of the reaction of  $\text{H}_2\text{Os}_2(\text{CO})_8$  with  $\text{Fe}_2(\text{CO})_9$  is  $\text{FeOs}_2(\text{CO})_{12}$ .

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### Introduction

Some years ago we briefly described some mixed metal cluster compounds of osmium with iron and cobalt [1]. Since that time, the synthesis and study of the chemistry of mixed metal cluster compounds has received considerable attention [2]. Due to the importance of mixed metal cluster compounds, we now describe further details on the synthesis of the osmium-iron and osmium-cobalt compounds.

### Results and discussion

When a solution of  $\text{H}_2\text{Os}(\text{CO})_4$  is stirred with  $\text{Fe}_2(\text{CO})_9$ , a deep purple solution is obtained. Removal of the volatiles and subsequent chromatography yielded purple  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  (67%) and orange  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  (6%). Both these compounds have also been prepared by other routes.  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  has only been obtained in low yields by other routes [3,4], but  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  has been prepared in yields up to (95%) [4–6]. The crystal structure of  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  has also been reported [7].

TABLE 1  
IR DATA FOR THE MIXED METAL CLUSTER COMPOUNDS <sup>a</sup>

| Compound  | $\nu(\text{CO}) \text{ cm}^{-1}$  |
|---|---|
| $\text{Fe}_2\text{Os}(\text{CO})_{12}$              | 2119w, 2057s, 2043vs, 2039(sh), 2015w, 1995(sh),<br>1865vw(br), 1840vw(br).             |
| $\text{FeOs}_2(\text{CO})_{12}$ <sup>b</sup>        | 2070s, 2043vs, 2034vs, 2022m, 2003m, 1988w.   |
| $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$           | 2086s, 2072s, 2040vs, 2032m, 2025m, 2015w, 1875w<br>1848m.                              |
| $\text{Co}_2\text{Os}(\text{CO})_{11}$              | 2127w, 2069s, 2049vs, 2025m, 1823m.   |
| $\text{Co}_2\text{Os}(\text{CO})_{11}$ <sup>c</sup> | 2128m, 2078m, 2067s, 2047vs, 2034m, 2033m,<br>2004w, 1994w, 1821m, 1808m, 1801(br)(sh). |
| $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  | 2112w, 2081s, 2078s, 2057vs, 2046s, 2028m, 2015m.                                       |

<sup>a</sup> Spectra taken in n-heptane solution. sh = shoulder, br = broad. <sup>b</sup> Weak bands of  $\text{Os}_3(\text{CO})_{12}$  were also observed in this spectrum. <sup>c</sup> Nujol mull.

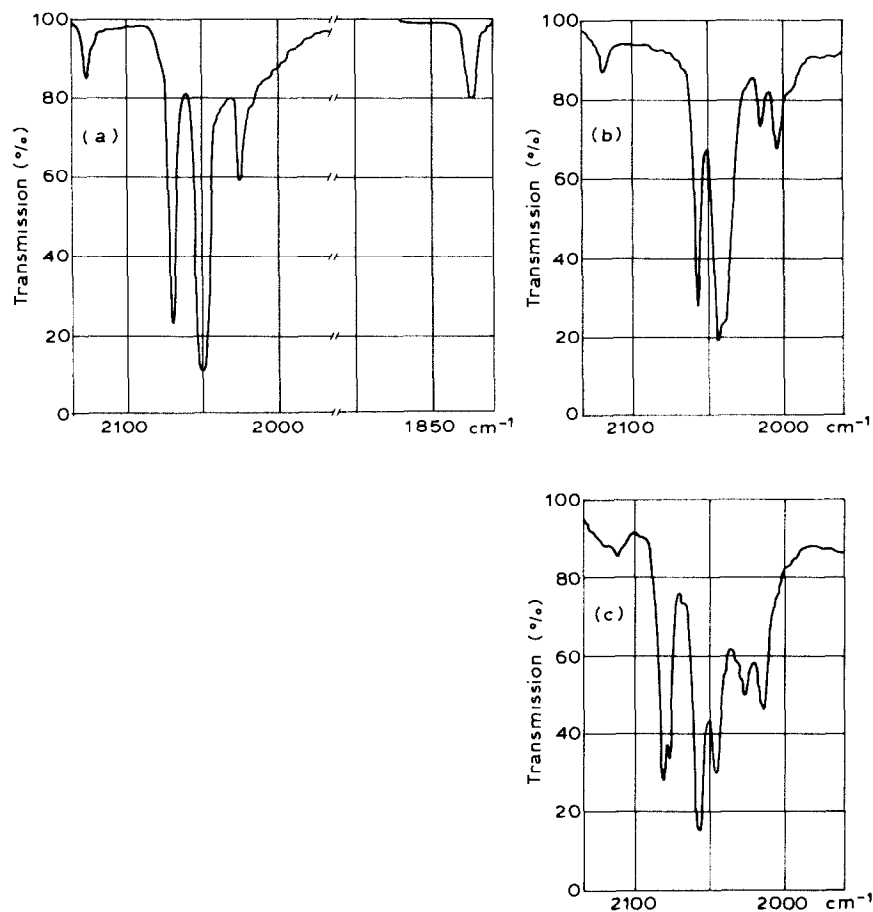
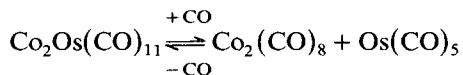


Fig. 1. Infrared spectra in the carbonyl stretching frequency regions in n-heptane solution of (a)  $\text{Co}_2\text{Os}(\text{CO})_{11}$ ; (b)  $\text{Fe}_2\text{Os}(\text{CO})_{12}$ ; (c)  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$ .

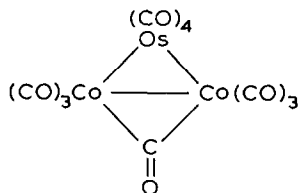
Although we obtained good yields of  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  from the reaction of  $\text{H}_2\text{Os}(\text{CO})_4$  and  $\text{Fe}_2(\text{CO})_9$ , the reaction of  $\text{H}_2\text{Os}_2(\text{CO})_8$  with  $\text{Fe}_2(\text{CO})_9$  was more complex and several products were formed. The main product was  $\text{FeOs}_2(\text{CO})_{12}$ , however, it could not be completely separated from  $\text{Os}_3(\text{CO})_{12}$ ; it was identified by its mass spectrum. Carbonyl stretching frequencies for the iron-osmium dodecacarbonyls are given in Table 1 (see also Fig. 1) These IR spectra are similar to those of the respective iron-ruthenium analogs [8] which may suggest similar structures and thus  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  may have a structure similar to that of  $\text{Fe}_3(\text{CO})_{12}$  [9] and  $\text{FeOs}_2(\text{CO})_{12}$  a structure similar to  $\text{Os}_3(\text{CO})_{12}$  [10].

The two iron-osmium dodecacarbonyls showed molecular ions in their mass spectra having the expected isotope patterns. The mass spectra are very similar to those reported for the iron-ruthenium analogs and the mass spectrum of  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  is similar to that observed for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  [8].

An n-heptane solution of  $\text{H}_2\text{Os}(\text{CO})_4$  reacts with  $\text{Co}_2(\text{CO})_8$  to give  $\text{Co}_2\text{Os}(\text{CO})_{11}$  as the main product. Minor products also identified from this reaction are  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  and  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$ . The dinuclear compound  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$  was unstable and was not completely separated from  $\text{H}_2\text{Os}_2(\text{CO})_8$ , also formed in this reaction.  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$  was identified by the observation of a molecular ion in its mass spectrum at  $m/e$  476 with the expected isotope pattern and by the presence of a high field signal in its  $^1\text{H}$  NMR spectrum at  $\delta -5.3$  ppm (benzene solution). The species  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$  may be an intermediate in the formation of  $\text{Co}_2\text{Os}(\text{CO})_{11}$  via a second intermediate  $(\text{CO})_4\text{CoOs}(\text{CO})_4\text{Co}(\text{CO})_4$ . In an attempt to isolate this second intermediate, the reaction of  $\text{Co}_2\text{Os}(\text{CO})_{11}$  with CO was investigated. The only products identified from this reaction however were  $\text{Co}_2(\text{CO})_8$  and  $\text{Os}(\text{CO})_5$ . Others have also observed that reactions of some osmium carbonyl clusters with CO leads to the fragmentation of the clusters [11]. We have also found that the reaction of  $\text{Os}(\text{CO})_5$  with  $\text{Co}_2(\text{CO})_8$  leads to the formation of  $\text{Co}_2\text{Os}(\text{CO})_{11}$ , thus demonstrating the reversibility of the reaction



The IR spectrum of  $\text{Co}_2\text{Os}(\text{CO})_{11}$  shows a band at  $1823\text{ cm}^{-1}$  suggesting the presence of a bridging carbonyl in the compound. Thus a reasonable structure for this compound would be:



The terminal  $\nu(\text{CO})$  region in solution is more simple than expected for this structure, however extra bands are observed when the IR spectrum is recorded as a Nujol mull (see Table 1) suggesting the possibility that there are different structures in solution than in the solid state. The ruthenium analog of this compound,  $\text{Co}_2\text{Ru}(\text{CO})_{11}$  has recently been reported [12] and since the IR spectra of the osmium and ruthenium compounds are similar, they probably have similar structures. The suggested structure can be considered to be derived by replacing a bridging carbonyl

group of  $\text{Co}_2(\text{CO})_8$  by a bridging  $\text{Os}(\text{CO})_4$  group. The mass spectrum of  $\text{Co}_2\text{Os}(\text{CO})_{11}$  is given in the Experimental section. A parent molecular ion is observed at  $m/e$  618 with the expected isotope pattern. Peaks of the series  $[\text{Co}_n(\text{CO})_n]^+$  ( $n = 0-12$ ) were also observed, presumably formed by decomposition of the sample in the spectrometer. The compound  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  also showed a parent ion in the mass spectrum with the expected isotope pattern; the full spectrum is given in the Experimental section. Owing to the small amount of sample obtained, the  $^1\text{H}$  NMR spectrum was not recorded. Recently, the crystal structure of the analogous ruthenium compound  $\text{H}_2\text{Co}_2\text{Ru}_2(\text{CO})_{12}$  has been reported [13].

## Experimental

Dihydridotetracarbylosmium [14] and dihydridoctacarbyldiosmium [15] were prepared by literature methods. All reactions except the high pressure reactions were carried out under an atmosphere of nitrogen. Melting points were determined on a Kofler hot-stage apparatus. Infrared spectra were measured on a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127A recorder. Spectra were calibrated with gaseous carbon monoxide. NMR measurements were made on a Varian A56/60A instrument. Mass spectra were obtained using Associated Electrical Industries MS-9 and MS-12 instruments. Calculated mass spectra were obtained using a computer program prepared by Drs R.S. Gay and E.H. Brooks in the Chemistry Department at the University of Alberta. Exact masses were determined on the most abundant peak of the molecular ion. Relative abundancies given in the mass spectra are the heights of the most abundant peak of a particular ion relative to the most intense peak in the spectrum as 100.

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany; Pascher Microanalytisches Laboratorium, Bonn, Germany and by the microanalytical laboratory of the Chemistry Department at the University of Alberta.

### *The reaction of dihydridotetracarbylosmium with diiron enneacarbonyl*

A solution of dihydridotetracarbylosmium (0.086 g, 0.28 mmol) in n-heptane (15 ml) was stirred with finely powdered diiron enneacarbonyl (0.410 g, 1.12 mmol) at room temperature. After 3.5 h, the solution was deep purple and a dark solid had been deposited. The solvent, iron pentacarbonyl formed in the reaction, and any unreacted  $\text{H}_2\text{Os}(\text{CO})_4$  were removed under reduced pressure. The dark brown solid residue was extracted with acetone ( $2 \times 20$  ml) and centrifuged giving a deep purple solution. The acetone was removed under reduced pressure and a saturated hexane solution of the resulting purple solid was chromatographed on a Florisil column. Elution with hexane gave purple diironosmium dodecacarbonyl  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  (0.20 g, 67%) which was obtained as deep purple prisms decomposing without melting above  $130^\circ\text{C}$  after recrystallization from  $\text{CH}_2\text{Cl}_2$ /pentane. (Found: C, 22.50; Fe, 17.91; O, 28.81; Os, 30.76;  $M$  (mass spectrometrically) 639.767.  $\text{C}_{12}\text{Fe}_2\text{O}_{12}\text{Os}$  calcd.: C, 22.59; Fe, 17.50; O, 30.09; Os, 29.81%;  $M$ , 639.770). Elution with benzene gave orange  $\text{H}_2\text{FeO}_3(\text{CO})_{13}$  (0.006 g, 6%) which was recrystallized from hexane and decomposed without melting  $> 165^\circ\text{C}$ ; this product was identified by its mass spectrum. Found:  $M$ , 993.782.  $\text{C}_{13}\text{H}_2\text{FeO}_3\text{Os}_3$  calcd.:  $M$ , 993.764).

*The reaction of dihydridoosmium tetracarbonyl with diiron enneacarbonyl*

A solution of  $\text{H}_2\text{Os}_2(\text{CO})_8$  (0.109 g, 0.18 mmol) in n-heptane (15 ml) was stirred with finely powdered diiron enneacarbonyl (0.164 g, 0.45 mmol) for 3.5 h. The solvent and  $\text{Fe}(\text{CO})_5$  formed in the reaction, were removed under reduced pressure and the resulting orange-yellow residue extracted with acetone ( $3 \times 10$  ml), centrifuged, and the solvent removed under reduced pressure from the orange-brown solution. This residue was taken up in a minimum volume of hexane and chromatographed on a Florisil column. Elution with hexane gave first irondiosmium dodecacarbonyl,  $\text{FeOs}_2(\text{CO})_{12}$  (0.029 g, 21%), which was recrystallized from hexane and identified by its mass spectrum; the sample still contained traces of  $\text{Os}_3(\text{CO})_{12}$  which could not be removed. Further elution with hexane gave purple  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  (0.014 g, 6%), and benzene elution then gave orange  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  (0.017 g, 14%); the last two compounds were identified by their IR and mass spectra.

The mass spectrum of  $\text{Fe}_2\text{Os}(\text{CO})_{12}$  showed the following ions (relative abundancies in parentheses):  $[P]^+$  (0.96),  $[P - \text{CO}]^+$  (0.96),  $[P - 2\text{CO}]^+$  (1.69),  $[P - 3\text{CO}]^+$  (0.74),  $[P - 4\text{CO}]^+$  (2.13),  $[P - 5\text{CO}]^+$  (7.56),  $[P - 6\text{CO}]^+$  (7.50),  $[P - 7\text{CO}]^+$  (7.20),  $[P - 8\text{CO}]^+$  (14.0),  $[P - 9\text{CO}]^+$  (12.0),  $[P - 10\text{CO}]^+$  (13.5),  $[P - 11\text{CO}]^+$  (14.4),  $[P - 11\text{CO} - \text{O}]^+$  (1.32),  $[P - 12\text{CO}]^+$  (13.65),  $[P - 11\text{CO} - \text{Fe}]^+$  (2.28),  $[P - 11\text{CO} - \text{O} - \text{Fe}]^+$  (1.76),  $[P - 12\text{CO} - \text{Fe}]^+$  (7.79),  $[\text{OsCO}]^+$  (0.15),  $[\text{Fe}(\text{CO})_5]^+$  (9.56),  $[\text{Os}]^+$  (0.59),  $[\text{Fe}(\text{CO})_4]^+$  (9.10),  $[\text{Fe}(\text{CO})_3]^+$  (3.67),  $[\text{Fe}(\text{CO})_2]^+$  (26.2),  $[\text{FeCO}]^+$  (100),  $[\text{FeC}]^+$  (7.05),  $[\text{Fe}]^+$  (79.4).

The mass spectrum of  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  showed the following ions (relative abundancies in parentheses). Computer analysis indicated slight but significant hydrogen loss from the parent ion; this is expected for other ions as well but hydrogen loss is indicated only when it becomes dominant.  $[P]^+$  (21.7),  $[P - \text{CO}]^+$  (24.6),  $[P - 2\text{CO}]^+$  (26.1),  $[P - 3\text{CO}]^+$  (12.3),  $[P - 4\text{CO}]^+$  (58.0),  $[P - 5\text{CO}]^+$  (100),  $[P - 6\text{CO}]^+$  (63.7),  $[P - 7\text{CO} - 2\text{H}]^+$  (71.0),  $[P - 8\text{CO} - 2\text{H}]^+$  (38.1),  $[P - 9\text{CO} - 2\text{H}]^+$  (37.6),  $[P - 10\text{CO} - 2\text{H}]^+$  (42.0),  $[P - 11\text{CO} - 2\text{H}]^+$  (34.8),  $[P - 12\text{CO} - 2\text{H}]^+$  (30.4),  $[P - 13\text{CO} - 2\text{H}]^+$  (36.2),  $[\text{Os}_3]^+$  (13.0),  $[P - \text{CO}]^{2+}$  (1.5),  $[P - 2\text{CO}]^{2+}$  (2.2),  $[P - 3\text{CO}]^{2+}$  (7.2),  $[P - 4\text{CO}]^{2+}$  (10.0),  $[P - 5\text{CO}]^{2+}$  (14.5),  $[P - 6\text{CO} - 2\text{H}]^{2+}$  (34.8),  $[P - 7\text{CO} - 2\text{H}]^{2+}$  (34.8),  $[P - 8\text{CO} - 2\text{H}]^{2+}$  (30.4),  $[P - 9\text{CO} - 2\text{H}]^{2+}$  (27.5),  $[P - 10\text{CO} - 2\text{H}]^{2+}$  (27.5),  $[P - 11\text{CO} - 2\text{H}]^{2+}$  (26.1),  $[P - 12\text{CO} - 2\text{H}]^{2+}$  (21.7),  $[P - 13\text{CO} - 2\text{H}]^{2+}$  (15.9).

*The reaction of dihydridotetracarbylosmium with dicobalt octacarbonyl*

A solution of dihydridotetracarbylosmium (0.086 g, 0.28 mmol) in n-heptane (10 ml) was stirred at room temperature with dicobalt octacarbonyl (0.10 g, 0.29 mmol) for 6 h. The solvent was removed under reduced pressure leaving an oily red-brown residue. When this residue was sublimed ( $30^\circ\text{C}/0.01$  mmHg) an unstable red-brown oil condensed on the water-cooled probe. This oil was identified by  $^1\text{H}$  NMR and mass spectroscopy to be (hydridotetracarbylosmium)tetracarbylcobalt  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$  containing  $\text{H}_2\text{Os}_2(\text{CO})_8$  as an impurity. The residue after removal of the  $\text{HOs}(\text{CO})_4\text{Co}(\text{CO})_4$  was taken up in a minimum volume of hexane and centrifuged. The clear red-brown solution was chromatographed on a Florisil column. Elution with hexane gave in order  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_4(\text{CO})_{12}$ , and orange  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  (0.013 g, 13%), which was recrystallized from pentane and decomposes  $> 130^\circ\text{C}$ . (Found: C, 17.38; H, 0.36; *M* (mass spectrometrically) 837.740.  $\text{C}_{12}\text{H}_2\text{Co}_2\text{O}_{12}\text{Os}_2$  calcd.: C, 17.23; H, 0.24%; *M*, 837.741). Elution with benzene

gave red  $\text{Co}_2\text{Os}(\text{CO})_{11}$  (0.026 g, 18%). Recrystallisation of this product from pentane gave pure product as dark red needles which decompose  $> 80^\circ\text{C}$ . (Found: C, 21.43; Co, 19.50; O, 28.82; Os, 32.44;  $M$  (mass spectrometrically) 617.771.  $\text{C}_{11}\text{Co}_2\text{O}_{11}\text{Os}$  calcd.: C, 21.44; Co, 19.14; O, 28.77; Os, 30.87%;  $M$ , 617.772). The mass spectrum of  $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$  showed the following ions (relative abundances in parentheses). Computer analysis indicated slight but significant hydrogen loss from the parent ion; this is expected for other ions as well but hydrogen loss is indicated only when it becomes dominant. Fragments of the  $[\text{Co}_4(\text{CO})_n]^+$  series are presumed to arise from decomposition of the sample in the mass spectrometer.  $[P]^+$  (19.0),  $[P - \text{CO}]^+$  (32.0),  $[P - 2\text{CO}]^+$  (18.0),  $[P - 3\text{CO}]^+$  (12.0),  $[P - 4\text{CO}]^+$  (22.0),  $[P - 5\text{CO}]^+$  (100),  $[P - 6\text{CO}]^+$  (60.0),  $[P - 7\text{CO} - 2\text{H}]^+$  (75.0),  $[P - 8\text{CO} - 2\text{H}]^+$  (56.0),  $[P - 9\text{CO} - 2\text{H}]^+$  (56.0),  $[\text{Co}_4(\text{CO})_{12}]^+$  (7.5),  $[P - 10\text{CO} - 2\text{H}]^+$  (41.0),  $[\text{Co}_4(\text{CO})_{11}]^+$  (5.5),  $[P - 11\text{CO} - 2\text{H}]^+$  (35.0),  $[P - 11\text{CO} - \text{O} - 2\text{H}]^+$  (5.0),  $[P - 12\text{CO} - 2\text{H}]^+$  (43.0),  $[\text{Co}_4(\text{CO})_8]^+$  (9.0),  $[P - 12\text{CO} - 2\text{H} - \text{Co}]^+$  (18.0),  $[\text{Co}_4(\text{CO})_7]^+$  (19.0),  $[\text{Co}_4(\text{CO})_6]^+$  (7.0),  $[P - 12\text{CO} - 2\text{H} - 2\text{Co}]^+$  (7.5),  $[\text{Co}_4(\text{CO})_5]^+$  (7.0),  $[\text{Co}_4(\text{CO})_4]^+$  (8.5),  $[\text{Co}_4(\text{CO})_3]^+$  (12.5),  $[\text{Co}_4(\text{CO})_2]^+$  (9.0),  $[\text{Co}_4\text{CO}]^+$  (21.0),  $[\text{Co}_4]^+$  (12.5). The mass spectrum of  $\text{Co}_2\text{Os}(\text{CO})_{11}$  showed the following ions (relative abundances in parentheses):  $[P]^+$  (2.4),  $[P - \text{CO}]^+$  (10.2),  $[\text{Co}_4(\text{CO})_{12}]^+$  (6.9),  $[P - 2\text{CO}]^+$  (5.9),  $[\text{Co}_4(\text{CO})_{11}]^+$  (4.8),  $[P - 3\text{CO}]^+$  (2.0),  $[\text{Co}_4(\text{CO})_{10}]^+$  (1.2),  $[P - 4\text{CO}]^+$  (4.3),  $[\text{Co}_4(\text{CO})_9]^+$  (1.0),  $[P - 5\text{CO}]^+$  (14.4),  $[\text{Co}_4(\text{CO})_8]^+$  (9.0),  $[P - 6\text{CO}]^+$  (9.9),  $[\text{Co}_4(\text{CO})_7]^+$  (13.6),  $[P - 7\text{CO}]^+$  (14.9),  $[\text{Co}_4(\text{CO})_6]^+$  (5.2),  $[P - 8\text{CO}]^+$  (9.9),  $[\text{Co}_4(\text{CO})_5]^+$  (4.9),  $[P - 9\text{CO}]^+$  (8.4),  $[\text{Co}_4(\text{CO})_4]^+$  (7.3),  $[P - 10\text{CO}]^+$  (6.7),  $[\text{Os}(\text{CO})_5]^+$  (40.0),  $[\text{Co}_4(\text{CO})_3]^+$  (10.0),  $[P - 11\text{CO}]^+$  (7.1),  $[\text{Os}(\text{CO})_4]^+$  (41.0),  $[\text{Co}_4(\text{CO})_2]^+$  (6.2),  $[\text{Os}(\text{CO})_3]^+$  (41.0),  $[\text{Co}_4\text{CO}]^+$  (5.1),  $[\text{Os}(\text{CO})_2]^+$  (100),  $[\text{Co}_4]^+$  (8.0),  $[\text{Os}(\text{CO})\text{C}]^+$  (4.0),  $[\text{OsCO}]^+$  (62.0),  $[\text{OsC}]^+$  (19.5),  $[\text{Os}]^+$  (46.6),  $[\text{Co}_3]^+$  (6.8),  $[\text{Co}(\text{CO})_4]^+$  (1.3),  $[\text{Os}(\text{CO})_5]^{2+}$  (1.6),  $[\text{Os}(\text{CO})_4]^{2+}$  (7.3),  $[\text{Co}(\text{CO})_3]^+$  (3.8),  $[\text{Os}(\text{CO})_3]^{2+}$  (15.3),  $[\text{Os}(\text{CO})_2]^{2+}$  (22.9),  $[\text{Co}_2]^+$  (8.2),  $[\text{Co}(\text{CO})_2]^+$  (9.8),  $[\text{OsCO}]^{2+}$  (12.2),  $[\text{CoCO}]^+$  (10.0),  $[\text{Co}]^+$  (11.3).

#### *The reaction of carbon monoxide with $\text{Co}_2\text{Os}(\text{CO})_{11}$*

A red, n-heptane solution (10 ml) of  $\text{Co}_2\text{Os}(\text{CO})_{11}$  (0.030 g) was stirred magnetically at room temperature in a stainless steel autoclave (volume 200 ml) under pressure of CO (100 atm) for 3 h. The gases were vented and the IR spectrum of the yellow solution in the autoclave showed this to contain only  $\text{Co}_2(\text{CO})_8$  and  $\text{Os}(\text{CO})_5$ .

#### *The reaction of osmium pentacarbonyl with dicobalt octacarbonyl*

A solution of osmium pentacarbonyl (0.164 g, 0.50 mmol) and dicobalt octacarbonyl (0.25 g, 0.73 mmol) in n-heptane (20 ml) was irradiated in a quartz vessel, equipped with a water-cooled probe for 1.5 h. The IR spectrum of the reaction solution then showed that all the osmium pentacarbonyl had reacted. The solvent was removed under reduced pressure and the red-brown solid residue taken up in a minimum of hexane. This solution was chromatographed on a Florisil column. Elution with hexane gave a yellow band which was mainly  $\text{Co}_2(\text{CO})_8$ . Elution with benzene gave a red solid (0.102 g, 33%) which was purified by recrystallization from pentane and identified by its IR spectrum as  $\text{Co}_2\text{Os}(\text{CO})_{11}$ .

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