Journal of Organometallic Chemistry, 59 (1973) 379–394

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NEW MIXED TETRANUCLEAR METAL CARBONYLS OF GROUP VIIIB

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(Received January 20th, 1973)

SUMMARY

The new mixed tetranuclear carbonyls $Co_3Rh(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_2Ir_2(CO)_{12}$, $Rh_3Ir(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$ are easily synthesised by reacting tetracarbonylmetallate anions with halocarbonyls or with metallic cations in aqueous solution. Infrared spectra of all these compounds reveal the presence of both terminal and bridging carbonyl groups, in most cases consistent with a $Co_4(CO)_{12}$-$Rh_4(CO)_{12}$ like structure.

Thermal stability decreases as the rhodium content increases, as shown by the facile redistribution to tetranuclear species containing less rhodium and to hexanuclear species, such as $Co_2Rh_4(CO)_{16}$. Mass spectra are generally complicated, except in the case of $Co_2Ir_2(CO)_{12}$, and parallel the thermal stability. All compounds containing cobalt react readily with Lewis bases.

Preliminary X-ray data for $Co_2Rh_2(CO)_{12}$, $Co_2Ir_2(CO)_{12}$ and $Co_2Rh_4(CO)_{16}$ are also reported.

INTRODUCTION

The tetranuclear carbonyls of cobalt, rhodium and iridium, show conspicuous differences in structure and in chemical behaviour: $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ have bridging carbonyl groups, while $Ir_4(CO)_{12}$ has not; $Co_4(CO)_{12}$ reacts easily with Lewis bases, while $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ do not; and finally $Rh_4(CO)_{12}$ is thermally unstable, being easily converted into $Rh_6(CO)_{16}$[1], while $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$ do not transform into the corresponding hexanuclear neutral species.

Hoping to further the understanding of these differences we have investigated the properties of tetranuclear carbonyls containing two such metals in the same molecule; we examined initially the synthesis of cobalt–rhodium tetranuclear mixed carbonyls[2] and then extended our studies to cobalt–iridium and iridium–rhodium containing carbonyls[3].

We detail here the synthesis and properties of these compounds. While this work was in progress, the synthesis of $Co_2Rh_4(CO)_{16}$ was reported as a preliminary communication[4].

RESULTS AND DISCUSSION

Synthesis of tetranuclear carbonyls

The tetranuclear carbonyl $Co_2Rh_2(CO)_{12}$ was first prepared, as previously reported[2], by reacting $Zn[Co(CO)_4]_2$ with $Rh_2(CO)_4Cl_2$ in toluene solution:

$$Zn[Co(CO)_4]_2+Rh_2(CO)_4Cl_2 \rightarrow Co_2Rh_2(CO)_{12}+ZnCl_2 \qquad (1)$$

This same compound was formed less quickly using a suspension of $Na[Co(CO)_4]$ in n-hexane:

$$2\,Na[Co(CO)_4]+Rh_2(CO)_4Cl_2 \rightarrow Co_2Rh_2(CO)_{12}+2\,NaCl \qquad (2)$$

These two syntheses require a hydrocarbon solvent, owing to the sensitivity of the product to Lewis bases such as ethers; behaviour which is very similar to that of $Co_4(CO)_{12}$[5].

Subsequently we found that the same reaction can be easily carried out in aqueous solution starting from $Na[Rh(CO)_2Cl_2]$ and $Na[Co(CO)_4]$:

$$2\,[Rh(CO)_2Cl_2]^-+2\,[Co(CO)_4]^- \rightarrow Co_2Rh_2(CO)_{12}+4\,Cl^- \qquad (3)$$

The starting materials are easily water-soluble while the reaction product is not, and under these conditions the product is not attacked by water, factors which result in high yields.

This type of synthesis in aqueous solution is very versatile, and is limited only by the availability of soluble reagents. It was usefully extended to the preparation of all the compounds reported here. For example, using $RhCl_3$ or K_3RhCl_6 we obtained $Co_3Rh(CO)_{12}$ in good yields:

$$3\,[Co(CO)_4]^-+RhCl_3 \rightarrow Co_3Rh(CO)_{12}+3\,Cl^- \qquad (4)$$

In this case the product was accompanied by small amounts of $Co_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$, which probably originate from slow concomitant reduction of Rh^{III} to Rh^{I} according to:

$$RhCl_3+2\,[Co(CO)_4]^- \rightarrow [Rh(CO)_2Cl_2]^-+Cl^-+\tfrac{1}{2}\,Co_4(CO)_{12} \qquad (5)$$

followed by reaction of Rh^{I} with the $[Co(CO)_4]^-$ anion as in (3).

Fortunately, $Co_2Rh_2(CO)_{12}$ was easily elimitated by heating the reaction product at 60° in n-heptane solution according to the scheme:

$$Co_2Rh_2(CO)_{12} \xrightarrow[60^\circ]{\text{n-Heptane}} Co_2Rh_4(CO)_{16}+Co_3Rh(CO)_{12} \qquad (6)$$

Heating must be discontinued as soon as all the $Co_2Rh_2(CO)_{12}$ has reacted, as shown by the disappearance of a (characteristic) IR absorption band at 1871 cm^{-1}; since prolonged heating gave a further slow reaction:

$$Co_3Rh(CO)_{12} \xrightarrow[60^\circ \text{ or more}]{\text{n-Heptane}} \text{(Hexanuclear species)}+Co_4(CO)_{12} \qquad (7)$$

Reaction (6) allows the synthesis of $Co_3Rh(CO)_{12}$ starting from $Co_2Rh_2(CO)_{12}$ but this method is inconvenient because longer heating times are required, during which, reaction (7) proceeds to some extent.

By contrast, reaction (6) is useful for preparation of the hexanuclear $Co_2Rh_4(CO)_{16}$ which is not very soluble and separates as crystals. This same compound was reported by Stone and Chaston[4] to be formed from a solution of $Co_2(CO)_8$ and $Rh_2(CO)_4Cl_2$ in hexane. Having obtained the compound in a different way, we considered it worthwhile to investigate the possible presence of $Co_2Rh_2(CO)_{12}$ and/or $Co_3Rh(CO)_{12}$ as intermediates in Stone's synthesis. We found effectively that this reaction occurred initially according to the stoichiometry:

$$3\,Co_2(CO)_8 + 2\,Rh_2(CO)_4Cl_2 \xrightarrow[25^\circ]{\text{n-Hexane}} 2\,Co_2Rh_2(CO)_{12} + 2\,CoCl_2 + 8\,CO \quad (8)$$

allowing us to prepare $Co_2Rh_2(CO)_{12}$ in a very simple way.

Considering the cobalt–iridium containing carbonyls, we first tried to obtain $Co_3Ir(CO)_{12}$ by reacting $K_2[Ir(CO)I_5]$ with $Na[Co(CO)_4]$ in aqueous solution, but we obtained only a mixture of $Co_2Ir_2(CO)_{12}$ and $Co_2(CO)_8$ with minor amounts of $Co_4(CO)_{12}$. Clearly this reaction involves two stages; initial reduction of Ir^{III} to Ir^{I} with formation of $Co_2(CO)_8$ probably according to:

$$[Ir(CO)I_5]^{2-} + 2\,[Co(CO)_4]^- + CO \rightarrow [Ir(CO)_2I_2]^- + Co_2(CO)_8 + 3\,I^- \quad (9)$$

followed by reaction of the Ir^{I} species with the $[Co(CO)_4]^-$ anion to give the tetranuclear carbonyl:

$$2\,[Ir(CO)_2I_2]^- + 2\,[Co(CO)_4]^- \rightarrow Co_2Ir_2(CO)_{12} + 4\,I^- \quad (10)$$

It is noteworthy that with $[IrBr_6]^{3-}$ or $[IrCl_6]^{3-}$ no reaction was observed.

Reaction (9) requires some additional carbon monoxide which may be furnished by decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ or by decarbonylation of $[Ir(CO)I_5]^{2-}$: probably both processes occur, as the reaction leaves some iridium salt unreacted.

Reaction (9) suggested a method for preparing the $[Ir(CO)_2I_2]^-$ anion: in fact, working in methanol, where the cobalt carbonyls decompose to $Co[Co(CO)_4]_2$, it was possible to rapidly convert $K_2[Ir(CO)I_5]$ into the $[Ir(CO)_2I_2]^-$ anion according to the reaction:

$$3[Ir(CO)I_5]^{2-} + 2[Co(CO)_4]^- \xrightarrow{CH_3OH} 3[Ir(CO)_2I_2]^- + 2Co^{2+} + 9I^- + 5CO$$

The compound, $Co_2Ir_2(CO)_{12}$, seems to be the most thermally stable of all the carbonyls here reported; it can be slowly sublimed without decomposition at 60° and 0.01 mmHg. It is also more stable to air than the cobalt–rhodium compounds, but like the latter is unstable to Lewis bases. Scheme (3) was applied to the synthesis of $Rh_2Ir_2(CO)_{12}$ using $Na[Ir(CO)_4]$ (Ref. 6) instead of $Na[Co(CO)_4]$:

$$2[Ir(CO)_4]^- + 2[Rh(CO)_2Cl_2]^- \rightarrow Rh_2Ir_2(CO)_{12} + 4\,Cl^- \quad (11)$$

and gave the desired compound in good yields.

The high instability of the $[Rh(CO)_4]^-$ anion in aqueous solution[7] and the great tendency of rhodium to give polynuclear anions, resulted in very low yields of the expected $Rh_3Ir(CO)_{12}$ in the reaction between $Na[Rh(CO)_4]$ and $K_2[Ir(CO)I_5]$. This same compound could also be prepared by a method similar to that used for the synthesis of Group VIIIA mixed carbonyls[8,9], by heating a mixture of $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ to 120° under CO pressure of 300 atm. The product, together with

$Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$, was obtained as little orange crystals which were sublimed onto the cold side of the autoclave, and could be separated by extraction with n-heptane. Unfortunately here the yields are also very low, so that this compound could not be obtained in amounts sufficient for complete chemical and physicochemical characterisation.

Finally, in Table 1, are summarised the analytical data of all the carbonyls reported here, which were all obtained as well shaped crystals.

Mass spectra

The mass spectrum of a mixture of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ corresponds simply to the sum of the mass spectra of the single compounds, showing only two sets of peaks appropriate to the ion series $Co_4(CO)_n^+$ and $Rh_4(CO)_n^+$ ($12 \geqslant n \geqslant 0$). This fact proves that no redistribution reactions between the pure carbonyls occur during the measurements, and allows mixed carbonyls of the two metals to be identified.

TABLE 1

ANALYTICAL DATA OF MIXED TETRANUCLEAR CARBONYLS OF GROUP VIIIB

Compound	*Analysis found (calcd.) (%)*				
	Co	*Rh*	*Ir*	*CO*	*C*
$Co_3Rh(CO)_{12}$	28.7 (28.7)	16.7 (16.7)			
$Co_2Rh_2(CO)_{12}$	17.3 (17.86)	31.6 (31.18)		47.5 (50.85)	
$Co_2Ir_2(CO)_{12}$	13.7 (14.1)		39.6[a] (45.7)		
$Rh_2Ir_2(CO)_{12}\cdot S$[b]		19.3 (18.8)	36.4 (35.2)		
$Rh_3Ir(CO)_{12}$					17.66 (17.20)
$Co_2Rh_4(CO)_{16}$	11.64 (12.05)	40.3 (42.1)			

[a] Approximate data owing to difficulty in analytical separation of cobalt and iridium. [b] S=2 C_6H_{12}.

TABLE 2

TETRANUCLEAR ION SERIES OBSERVED IN MASS SPECTRA OF MIXED CARBONYLS $M'_xM''_{4-x}(CO)_{12}$

Compound	*Observed ions*[a,b]			
$Co_3Rh(CO)_{12}$	$Co_3Rh(CO)_n^+$ (≈50%)	$Co_4(CO)_n^+$ (≈50%)	$Co_2Rh_2(CO)_n^+$ (≈1%)	
$Co_2Rh_2(CO)_{12}$	$Co_2Rh_2(CO)_n^+$ (≈60%)	$Co_3Rh(CO)_n^+$ (≈30%)	$Co_4(CO)_n^+$ (≈7%)	$CoRh_3(CO)_n^+$ (≈4%)
$Co_2Ir_2(CO)_{12}$	$Co_2Ir_2(CO)_n^+$ (≈100%)			
$Rh_3Ir(CO)_{12}$	$Rh_3Ir(CO)_n^+$ (≈50%)	$Rh_2Ir_2(CO)_n^+$ (≈25%)	$Rh_4(CO)_n^+$ (≈25%)	
$Rh_2Ir_2(CO)_{12}$	$Rh_2Ir_2(CO)_n^+$ (≈80%)	$Rh_3Ir(CO)_n^+$ (≈10%)	$RhIr_3(CO)_n^+$ (≈10%)	

[a] Relative intensities reported in brackets have only indicative value. [b] $12 \geqslant n \geqslant 0$.

Furthermore, it seems reasonable to exclude analogous redistributions between the pairs $Co_4(CO)_{12}/Ir_4(CO)_{12}$ and $Rh_4(CO)_{12}/Ir_4(CO)_{12}$, as it is well known that rupture of metal–metal bonds takes place with increasing difficulty in going from cobalt to iridium[10].

Table 2 summarises the tetranuclear ions observed in the mass spectra of the mixed carbonyls: the relative intensities reported have only an indicative meaning, as noticeable variations are observed with time.

The appearance of tetranuclear ions containing metal ratios different from those present in the original carbonyls, agrees with the complicated redistribution phenomena already noticed in the chemical behaviour (react. 6 and 7); in this case these reactions occur probably when the sample is introduced into the hot source ($T < 150°$) and, therefore, consideration of Table 2 gives further information on these redistributions.

The $M'_3M''(CO)_{12}$ species $Co_3Rh(CO)_{12}$ and $Rh_3Ir(CO)_{12}$ give rise to new, different ions through redistribution processes of the neutral species, because it is possible to observe the parent peaks of these new ions ($n = 12$):

$$2\,Co_3Rh(CO)_{12} \rightarrow Co_4(CO)_{12} + Co_2Rh_2(CO)_{12} \tag{12}$$

$$2\,Rh_3Ir(CO)_{12} \rightarrow Rh_4(CO)_{12} + Rh_2Ir_2(CO)_{12} \tag{13}$$

Moreover, the $Co_2Rh_2(CO)_{12}$ species formed in eqn. (12) should rapidly disappear as required by the high ratio found between the ions $Co_4(CO)_n^+$ and $Co_2Rh_2(CO)_n^+$ ($\approx 50/1$ as in Table 2); the final result being in agreement with reactions (6) and (7). On the contrary, Table 2 indicates that the reaction products in eqn. (13), $Rh_4(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$, have about the same stability.

The situation is rather similar for the $M'_2M''_2(CO)_{12}$ species, with the exception of the non-rhodium containing $Co_2Ir_2(CO)_{12}$ which, in agreement with the observed thermal stability, gives no redistribution reactions. In these cases the mass spectra indicate the probable initial redistribution reactions:

$$2\,Co_2Rh_2(CO)_{12} \rightarrow Co_3Rh(CO)_{12} + CoRh_3(CO)_{12} \tag{14}$$

$$2\,Rh_2Ir_2(CO)_{12} \rightarrow Rh_3Ir(CO)_{12} + RhIr_3(CO)_{12} \tag{15}$$

and the relative intensities require that in (14) the rhodium-rich species $CoRh_3(CO)_{12}$ should rapidly disappear; the final results reflecting reaction (6) followed to some extent by reaction (7). On the contrary the $Rh_3Ir(CO)_{12}$ and $RhIr_3(CO)_{12}$ species should have about the same stability.

The behaviour of the cobalt–rhodium mixed carbonyls of high rhodium content can be related to the very easy formation of stable hexanuclear mixed carbonyls such as $Co_2Rh_4(CO)_{16}$. This type of transformation is similar to that which leads to $Rh_6(CO)_{16}$ from $Rh_4(CO)_{12}$, and contrasts with the failure to obtain $Co_6(CO)_{16}$ and $Ir_6(CO)_{16}$ in a similar way: in fact these two carbonyls can be prepared only by other methods[6,11]. In the two-step transformation:

$$6\,M_2(CO)_8 \rightarrow 3\,M_4(CO)_{12} \rightarrow 2\,M_6(CO)_{16} \tag{16}$$

metal-to-carbon bonds are broken and metal–metal bonds are formed and an energy balance, calculated for every step, would account for the relative stabilities of the various species. Unfortunately, the metal–metal and metal–carbon bond energies are unknown, and we can only propose qualitative considerations. Experimentally, the stable species for Group VIIIB simple carbonyls are: $Co_2(CO)_8 \simeq Co_4(CO)_{12}$ for cobalt, $Ir_4(CO)_{12}$ for iridium and $Rh_4(CO)_{12} < Rh_6(CO)_{16}$ for rhodium[12,13]. From this we can deduce that the balance between the metal–metal and metal–carbon energies becomes increasingly favourable in the order Co < Ir < Rh[14]. This observation not only agrees with the instability of $CoRh_3(CO)_{12}$ and generally, of all tetranuclear carbonyls containing rhodium, but also agrees with the thermal stability of $Co_2Ir_2(CO)_{12}$.

As is known from the literature[10], the ease of formation of both M_nC^+ ions and $M_n(CO)_n^{2+}$ ions in the mass spectrometer increases with the increase in atomic

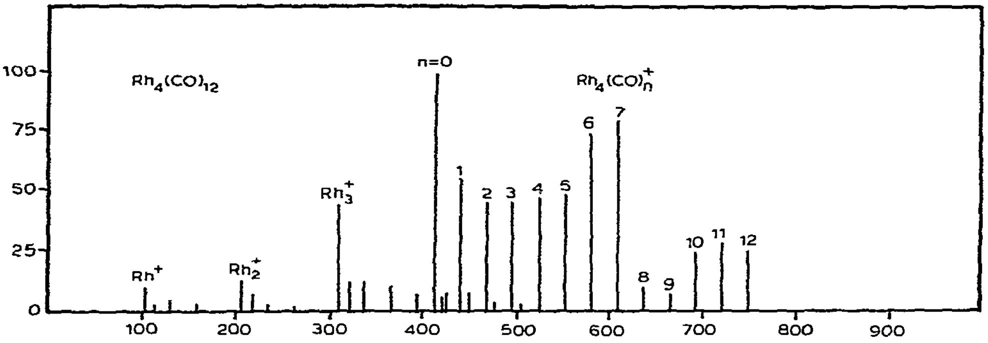

Fig. 1. Mass spectrum of $Rh_4(CO)_{12}$.

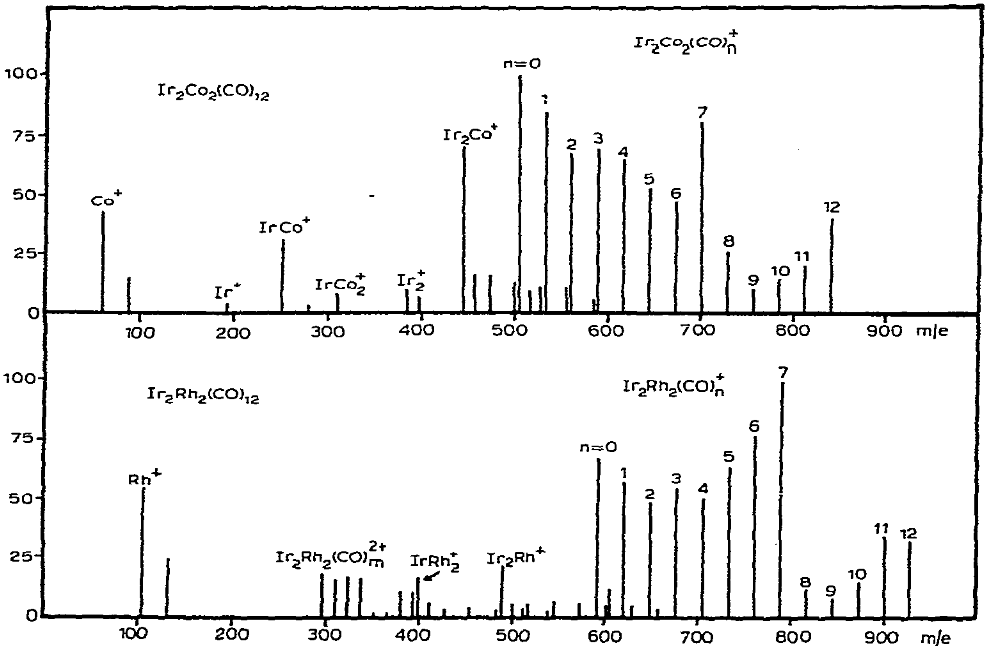

Fig. 2. Mass spectra of $Co_2Ir_2(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$ (only the ions of the ^{193}Ir isotope are reported).

weight of the atoms present in the cluster. Accordingly, we found that only $Rh_2Ir_2(CO)_{12}$ exhibits a series of doubly charged tetranuclear ions. Figure 1 shows the mass spectrum of $Rh_4(CO)_{12}$, which was only qualitatively reported in the literature[15], while Fig. 2 shows the spectra of $Co_2Ir_2(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$. In order to simplify the figure, in both spectra, we report only the ions for ^{193}Ir and, for the same reason, in the $Rh_2Ir_2(CO)_{12}$ spectrum the peaks of the redistribution products are not shown. In every spectrum of these tetranuclear carbonyls the most intense peaks appear when $n = 7$–6, a kinetic behaviour which agrees with other results reported in the literature[15].

Finally, the presence of redistribution products did not allow us to compare the relative ease of bond-breaking within the original tetranuclear unity upon changing the atomic weight of metals present in the cluster, as has been reported in the literature for the trinuclear $M_3(CO)_{12}$ carbonyls[10].

Crystallographic information

Partial crystallographic information has been obtained for $Co_2Rh_2(CO)_{12}$ and for $Co_2Ir_2(CO)_{12}$. Cell constants are reported in Table 3, and are strictly comparable with those of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$[15,17]. The diffraction patterns of $Co_2Rh_2(CO)_{12}$ and $Co_2Ir_2(CO)_{12}$ are very similar to that of $Rh_4(CO)_{12}$; they exhibit the same kind of twinning* and the same distribution of the diffraction intensities**, indicating that these molecules are located in their cells in the same way as $Rh_4(CO)_{12}$, and have identical distribution of the CO ligands around the metal atom cluster. This conclusion is of particular interest for $Co_2Ir_2(CO)_{12}$ for which the CO geometry is not immediately predictable, owing to the different structures of $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$. From these data we can not draw conclusions on the relative metal atom positions because of possible disorder of these atoms. More precise positions will be obtained from a single crystal three-dimensional analysis on $Co_2Ir_2(CO)_{12}$, which is in progress.

TABLE 3

CRYSTALLOGRAPHIC DATA[a]

Compound	*a* (*Å*)	*b* (*Å*)	*c* (*Å*)	*β*	*Space group*
(1) $Co_4(CO)_{12}$	8.99	11.70	17.28	90°	*Pccn*
(2) $Rh_4(CO)_{12}$	9.24	12.02	17.74	90°	$P2_1/c$
(3) $Co_2Rh_2(CO)_{12}$	9.11(2)	11.69(2)	17.53(3)	90°0′(6′)	$P2_1/c$
(4) $Co_2Ir_2(CO)_{12}$	9.11(2)	11.62(2)	17.31(3)	90°0′(6′)	$P2_1/c$
(5) $Co_6(CO)_{16}$	16.54(2)	9.45(1)	16.41(2)	118°6′(9′)	$C2/c$
(6) $Co_2Rh_4(CO)_{16}$	16.72(2)	9.67(1)	16.65(2)	118°1′(8′)	$C2/c$
(7) $Rh_6(CO)_{16}$	16.81	9.78	17.00	118°15′	$C2/c$

[a] The data of compounds (1), (2), (5) and (7) have been reported for comparison.

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* The diffraction patterns have D_{2h} Laue symmetry, while the systematic absence of reflections, $h0l$ for l odd and $0k0$ for k odd, are those of the monoclinic space group $P2_1/c$. This inconsistency, as for $Rh_4(CO)_{12}$, can be explained only in terms of a monoclinic cell with $\beta = 90°$ and incoherent twinning along a plane parallel to the *b* axis and perpendicular to either the *a* or *c* axis.

** *hkl* Reflections with *l* odd are systematically weak.

In order to obtain information on the structure of the metal skeleton in $Co_2Rh_4(CO)_{16}$, some single crystal photographs of the compound have been recorded. The cell constants of this mixed hexanuclear complex are reported in Table 3. It is isomorphous with $Co_6(CO)_{16}$[18] and $Rh_6(CO)_{16}$[19] and all the cell edges are intermediate between those of the pure complexes. The diffraction patterns of $Co_6(CO)_{16}$ and $Co_2Rh_4(CO)_{16}$ have been compared for various crystal orientations, and show identical molecular transform for the two compounds. These facts indicate that the crystal structure of $Co_2Rh_4(CO)_{16}$ has a disordered distribution for the different metal atoms.

This disorder can be caused by random packing of the two possible isomers of the compound.

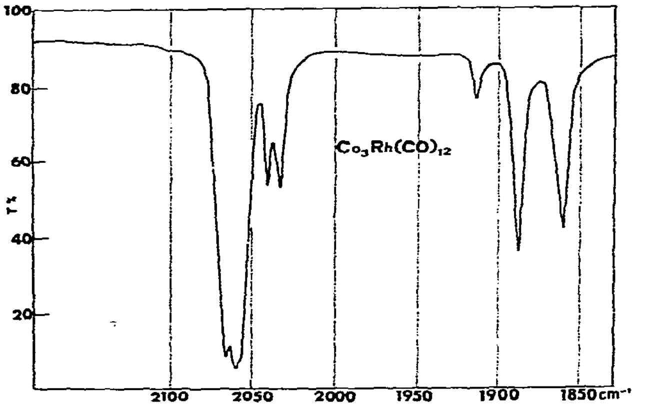
Infrared spectra

The structure of $Co_4(CO)_{12}$ in the solid state[14] and the presence of two ^{59}Co signals with a 3/1 ratio in the NMR spectra of its solutions[20,21], agree with Peraldo's interpretation of infrared spectra[22], more recently also applied to $Rh_4(CO)_{12}$[15,23].

In both cases the basal plane, which contains the three bridging carbonyl groups, has an approximate local D_{3h} symmetry and, assuming terminal and bridging carbon monoxide vibrations to be independent, one can foresee the appearance in the IR spectra of a weak A_1 band, due to real deviation from D_{3h} symmetry, and a strong E' band in the bridging carbonyl region. Effectively, the IR spectra of both these compounds, (for example those published by Bor in 1963), show two bands of this type[23,24].

It seems, therefore, reasonable to attempt a similar interpretation for the IR spectra of the tetranuclear mixed carbonyls. This would require that the $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ structures be maintained in the mixed metal carbonyls. This hypothesis seems reasonable, as it agrees with the constant presence of carbon monoxide bridging groups in the IR spectra, and with the preliminary X-ray data.

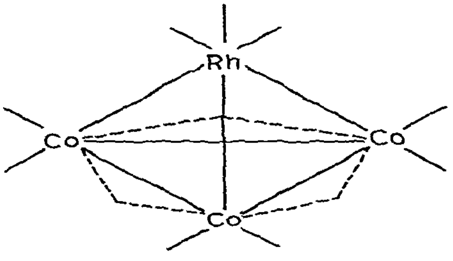
The introduction into the basal plane of one different atom, would lead to a local C_{2v} symmetry, for which three absorption bands would be expected $(2A_1+B_1)$. Figure 3 illustrates the spectrum of $Co_3Rh(CO)_{12}$ in the carbonyl stretching region.



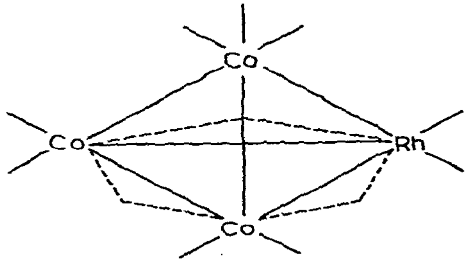
$\bar{\nu}(CO)$
2066m, 2059s, 2056(sh),
2037m, 2031m, 1909w,
1882s, 1856s

Fig. 3. IR spectrum of $Co_3Rh(CO)_{12}$ (in n-pentane).

The lack of a band at 1860 cm^{-1} proves that $Co_4(CO)_{12}$ is absent, as is also confirmed by the appearance of this band on addition of this carbonyl. The presence of $Rh_4(CO)_{12}$ can be excluded by mass spectral results. Moreover, the IR spectrum at −40° is unchanged, proving that if a mixture of isomers was present they would not be in equilibrium. Although one cannot exclude the proposition that the 1856 cm^{-1} band could be due to an isomer containing the three cobalt atoms in the basal plane, which therefore, should give rise to one band of the E' species in a position similar to that of $Co_4(CO)_{12}$ (structure A), clearly the IR spectrum requires preponderance of a structure with a rhodium atom lying on the basal plane, with local C_{2v} symmetry (structure B).

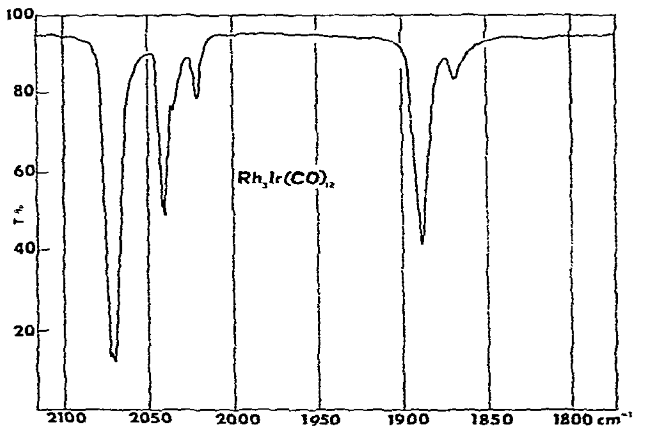


(A)



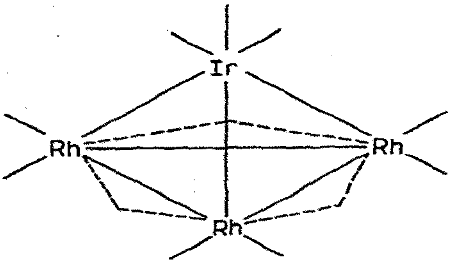
(B)

Figure 4 shows the IR spectrum of $Rh_3Ir(CO)_{12}$, which is practically identical to the product of the high pressure synthesis and that obtained in aqueous solution. Although we have not obtained this compound in amounts sufficient for a complete purification, it seems probable that the band at 1867 cm^{-1} is due to the presence of small amounts of $Rh_2Ir_2(CO)_{12}$ (1923 w, 1887 s, 1867 s cm^{-1}). We can exclude the presence of $Rh_4(CO)_{12}$ on chemical grounds as $Rh_4(CO)_{12}$ decomposes completely to give $Rh_6(CO)_{16}$ under the conditions of high pressure synthesis. Also in this case, the existence of two isomers C and D may be proposed, however the infrared spectrum agrees with a preponderance of structure (C), with all three rhodium atoms lying on

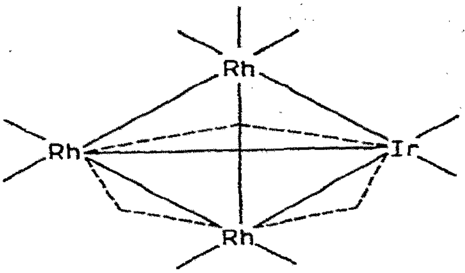


$\bar{\nu}$(CO)
2073m, 2070s, 2041.5s,
2034w, 2021m, 1886.5s,
1867.5m

Fig. 4. IR spectrum of $Rh_3Ir(CO)_{12}$ (in n-neptane).



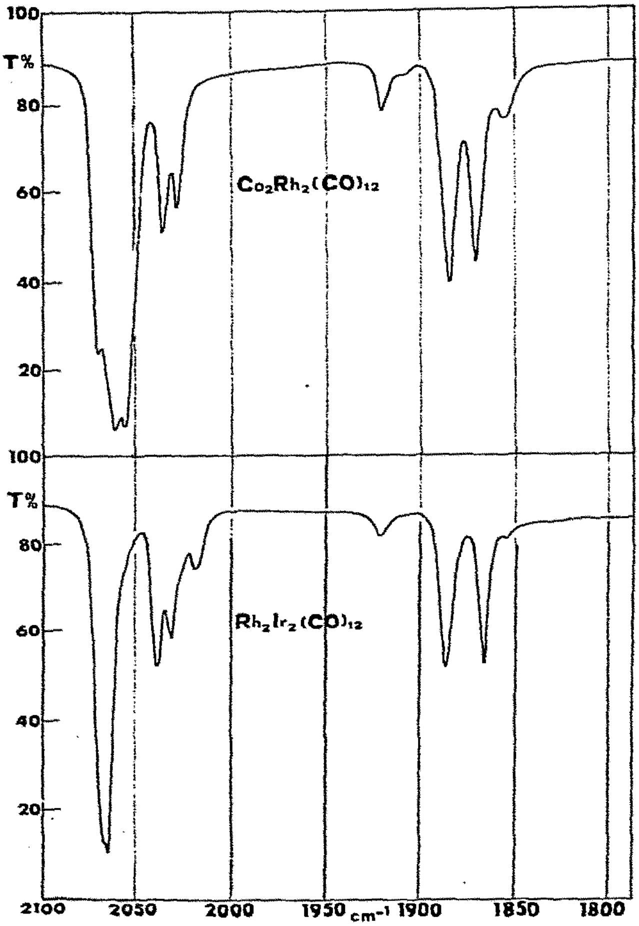
(C)



(D)

the basal plane; because, not only would this structure require only one strong band in the bridging carbonyl region, but its absorption frequency would also be almost identical to that of $Rh_4(CO)_{12}$ (1887 cm^{-1}).

Figure 5 shows the IR spectra of $Co_2Rh_2(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$ which are



$\bar{\nu}(CO)$
2074w, 2064s, 2059s,
2038m, 2030m, 1920w,
1910(sh), 1885s, 1871s, 1855w

$\bar{\nu}(CO)$
2071s, 2042m, 2034m,
2022w, 1923w, 1887s,
1867s, 1855w

Fig. 5. IR spectra of $Co_2Rh_2(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$ (in n-pentane).

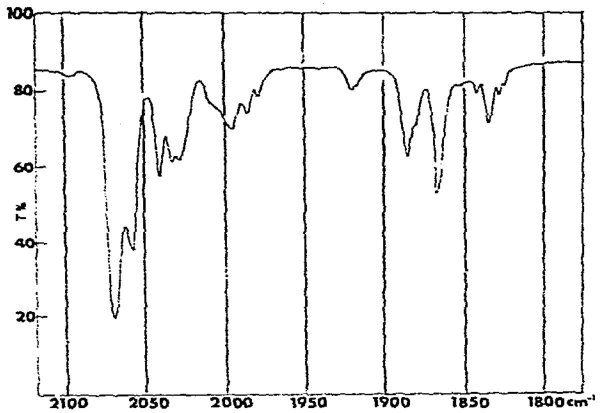
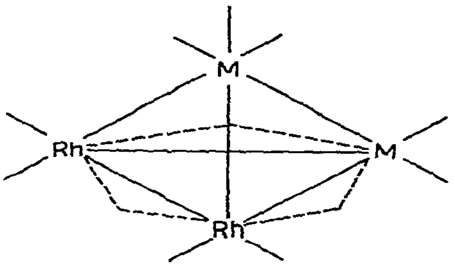


Fig. 6. IR spectrum of $Rh_2Ir_2(CO)_{12}$ about 20% enriched in ^{13}CO (n-hexane).

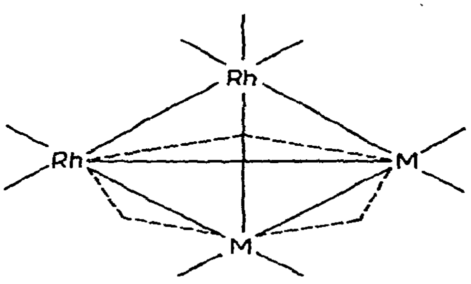
very similar in the bridging carbonyl region. This similarity argues for the presence of similar isomers. Also in this case, the IR spectrum at −40° remains unchanged, proving that if some isomers are present, they are not in equilibrium.

All four bridging absorptions (Fig. 5) are authentic. This has been shown by synthesising $Rh_2(CO)_4Cl_2$ ca. 60% enriched in ^{13}CO and then converting it to $Rh_2Ir_2(CO)_{12}$ according to eqn. (11). The IR spectrum of this species (about 20% ^{13}CO enriched) is shown in Fig. 6; all four carbonyl stretching bands of the bridging zone are still present requiring the presence of minor amounts of an isomeric species or the assignment of the fourth band to a combination (or overtone) frequency.

For the compounds $M_2Rh_2(CO)_{12}$, one can draw only two structures having bridging groups on the basal plane: in the first (structure E) the two rhodium atoms lie in the basal plane, while in the second (structure F) the two cobalt or iridium atoms lie in this plane:



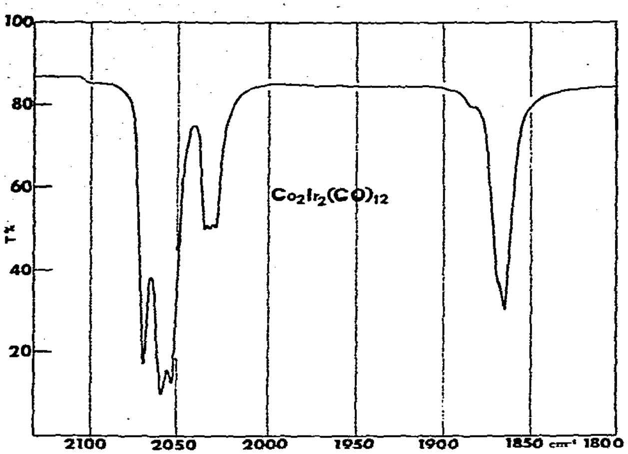
(E)



(F)

(M = Co, Ir)

Both structures are expected to give three absorption bands in the bridging region, so that the IR spectra of both isomers agree, but the comparison of the observed absorption frequencies with those of $Co_3Rh(CO)_{12}$ allow us to choose the predominant isomer. In fact, $Co_3Rh(CO)_{12}$ shows bridging absorption bands at 1909 w, 1882 s and 1856 s cm^{-1}, while $Co_2Rh_2(CO)_{12}$ shows bands at 1920 w, 1885 s and 1871 s cm^{-1}.



$\bar{\nu}$(CO)
2072s, 2061s, 2055s,
2036–2033–2030m,
1885w, 1867(sh), 1865s

Fig. 7. IR spectrum of $Co_2Ir_2(CO)_{12}$ (in n-pentane).

Assuming that in $Co_3Rh(CO)_{12}$ the basal plane contains a Co_2Rh arrangement, the differences in the absorption frequencies favour a Co–Rh_2 arrangement in the second case. For this reason it seems logical to assign structure E to $Co_2Rh_2(CO)_{12}$ and to $Rh_2Ir_2(CO)_{12}$.

Figure 7 shows the IR spectrum of $Co_2Ir_2(CO)_{12}$ in the carbonyl group stretching region. A comparison of this spectrum with those in Fig. 5 shows that this compound is rather different both in the terminal and in the bridging group region.

The presence of three bands in the bridging carbonyl region is in agreement with a structure of type E or F. Moreover, preliminary X-ray studies indicate that the $Rh_4(CO)_{12}$ structure is present[20]. In this case also, additional considerations allow us to choose between the two possible isomers: the slight tendency of iridium to promote carbon monoxide bridges and the position of the two strong absorption bands in the bridging region, which are very near to those of $Co_4(CO)_{12}$, indicate a structure having a Co_2–Ir arrangement in the basal plane as the most probable.

Finally we can advance a tentative explanation to account for the disposition of rhodium to favour carbon monoxide bridges. For the dodecacarbonyls it has been previously pointed out that the formation of carbon monoxide bridges can be rationalised as a compromise between the tendency to optimize the spatial arrangement of the carbonyl groups (icosahedral conformation) and the tendency to use less electron density originating from the metal for bonding with the carbonyl groups (truncated tetrahedron conformation)[1,25]. In fact, bridging decreases the electron density on the metal atoms (proved by lowering of the IR absorption frequencies of such carbonyl groups)[1,25] and contrasts with the metal electronegativity. It is, therefore, expected that rhodium should possess a lower electronegativity in the 0 oxidation state, a conclusion which agrees with the values of the first ionisation potentials of these metals (Rh=7.46, Co=7.86 and Ir=9 eV)[34].

Properties of the Group VIIIB tetranuclear mixed carbonyls

Table 4 summarises some properties of Group VIIIB tetranuclear carbonyls. The colour of these compounds lightens going down the subgroup, as is also true in

TABLE 4

SOME PROPERTIES OF GROUP VIIIB TETRANUCLEAR CARBONYLS

Compound	*Colour*	λ_{max}[a] *(nm)*	*Dec. temp. (°C)*	*Volatility (60°/0.01 mmHg)*	*Reactivity*	
					Air	*THF*
$Co_4(CO)_{12}$	Dark brown	375	100	+	+	+
$Co_3Rh(CO)_{12}$	Brown	365	130 (60)[d]	Dec.	+	+
$Co_2Rh_2(CO)_{12}$	Brown	348	120 (60)[d]	Dec.	+	+
$Co_2Ir_2(CO)_{12}$	Dark-red	[b]	190	+	–[e]	+
$Rh_4(CO)_{12}$	Red	300	130 (25)[d]	Dec.	–	–
$Rh_3Ir(CO)_{12}$	Orange	300	130 (85)[d]	Dec.	–	–
$Rh_2Ir_2(CO)_{12}$	Orange	310	≈150	Dec.	–	–
$Ir_4(CO)_{12}$	Yellow	319[c]	210	–	–	–

[a] n-Hexane solution. [b] No observed maximum. [c] Chloroform solution. [d] Temperatures in parenthesis refer to decomposition in solution to give $M_6(CO)_{16}$ species. [e] Stable during several days in solid state, less so in solution.

Group VIIIA[9]. In agreement with this behaviour, the UV spectra show a rough tendency to develop maximum absorbance at lower and lower wavelengths, [the inversion with $Ir_4(CO)_{12}$ is probably related to structural differences].

A rigorous comparison of the ultraviolet spectra is difficult, as it requires the knowledge of energy level order. Assuming that this order would remain fundamentally similar on changing the metal, only the relative separation value would change, and in this case the observed UV spectral change would correspond to a progressive increase in the relative separation. This behaviour is similar to that observed in Group VIIIA[9] and can be ascribed to a continuous decrease in the metallic bond order, that is, to a progressive localisation of such bonds[25].

Equally difficult is the discussion of the decomposition temperature reported in Table 4. It is important first of all to point out that in many cases they refer to different processes, and that decomposition to metal or partial decomposition with formation of hexanuclear clusters are not directly comparable. Secondly, the temperatures reported in Table 4 are those at which it is possible to observe visually evolution of carbon monoxide, so that information about possible slower decompositions occurring at lower temperatures is not available. For example, a thermogravimetric analysis of $Rh_4(CO)_{12}$ in a nitrogen atmosphere, shows that this carbonyl begins to decompose at ca. 90°, carbon monoxide evolution becoming faster at ca. 115°. After this point carbon monoxide evolution ceases, until the temperature of 160° is reached, when the $Rh_6(CO)_{16}$ formed in the first stage begins to decompose, leaving the metal at ca. 200°.

The possible transformation into hexanuclear clusters has great influence on the volatility of these carbonyls, the only compounds unambiguously volatile without decomposition being $Co_4(CO)_{12}$ and $Co_2Ir_2(CO)_{12}$.

With the exception of $Ir_4(CO)_{12}$, which probably has a particularly high lattice energy, all these tetranuclear carbonyls are soluble in hydrocarbons (≈0.5–2% by weight at 25°).

All the compounds containing cobalt are sensitive to air and to basic solvents, behaviour which can be explained on the basis of a higher affinity of cobalt towards oxygen, probably related to the lower second ionisation potential and to the smaller size of the corresponding ion.

Finally $Co_2Rh_2(CO)_{12}$ in n-heptane solution reacts with carbon monoxide at room temperature, slowly at atmospheric pressure and rapidly at 100 atm, to give a mixture of $Co_2(CO)_8$, $Rh_4(CO)_{12}$ and a new unstable compound as yet uncharacterised. Work on the chemical characterisation of the compounds is in progress.

EXPERIMENTAL

All operations were carried out under nitrogen, unless otherwise specified, using redistilled solvents stored under nitrogen. The carbonyl reagents were prepared as described in the literature: $Rh_2(CO)_4Cl_2$[26], $Rh_4(CO)_{12}$[27], $Na[Co(CO)_4]$[28], $Co_2(CO)_8$[29], $Zn[Co(CO)_4]_2$[30], $K_2[Ir(CO)I_5]$[31], $Ir_4(CO)_{12}$[32], $Na[Ir(CO)_4]$[6], $Na[Rh(CO)_4]$[7].

The analytical separation of Rh from Co was attained by precipitating rhodium as its sulphide in an acid medium, then weighing the metal after decomposition of the sulphide; cobalt was titrated with EDTA in the mother liquor. Ir and Co were separated by heating the nitrates until red hot and dissolving the cobalt oxide in hydrochloric acid. Iridium was determined by atomic absorption spectroscopy[33].

Infrared spectra were recorded on a Perkin–Elmer model 621 spectrophotometer. Mass spectra were recorded with an LKB 9000 spectrometer with an ionising potential of 70 eV and a source temperature below 150°.

(*a*). *Synthesis of* $Co_2Rh_2(CO)_{12}$ *from* $Zn[Co(CO)_4]_2$ *and* $Rh_2(CO)_4Cl_2$

On treating a solution of $Zn[Co(CO)_4]_2$ (1.041 g) in toluene (60 ml) with a solution of $Rh_2(CO)_4Cl_2$ (0.99 g) in toluene (25 ml) the brown colour rapidly appeared and $ZnCl_2$ precipitated as a white solid. After 15 min the solution was filtered, then cooled to −70° giving a crystalline product which was separated at −70° and washed with n-pentane at the same temperature. The product was crystallised from n-pentane at −50°. (Yield ≈70–80%).

(*b*). *Synthesis of* $Co_2Rh_2(CO)_{12}$ *from* $Co_2(CO)_8$ *and* $Rh_2(CO)_4Cl_2$

A solution of $Co_2(CO)_8$ (1.408 g) in n-hexane (50 ml) was stirred with $Rh_2(CO)_4Cl_2$ (1.061 g). After three days the reaction was complete, as shown by IR spectra. The solution was filtered and the solid extracted with n-pentane until the extract was colourless (≈150 ml). The original and extracted solutions were combined and cooled to −70° giving the crystalline product (Yield 80–90%).

The residual extracted solid which was dissolved in water and titrated with EDTA contained 0.1482 g of cobalt [calcd. for eqn. (6) 0.1456 g].

(*c*). *Synthesis of* $Co_2Rh_2(CO)_{12}$ *from* $Na[Co(CO)_4]$ *and* $Rh_2(CO)_4Cl_2$

A solution of $Na[Rh(CO)_2Cl_2]$, prepared by dissolving $Rh_2(CO)_4Cl_2$ (0.2 g) in an aqueous saturated solution of NaCl (15 ml), was treated dropwise with a solution of $Na[Co(CO)_4]$ (0.2 g) in water (10 ml) with stirring. After one hour the solid product was separated by filtration, washed with water and vacuum dried. The solid was extracted in n-pentane and the filtered solution was cooled to −70° to give the crystalline compound in 70–80% yield.

(d). Synthesis of $Co_3Rh(CO)_{12}$ from $Na[Co(CO)_4]$ and $RhCl_3 \cdot 3H_2O$ or $K_3[RhCl_6]$.

A solution of $RhCl_3 \cdot 3H_2O$ (1.360 g) in water (20 ml) was added dropwise with stirring to a solution of $Na[Co(CO)_4]$ (3.60 g) in water (25 ml). After half an hour the resulting precipitate was separated by filtration, washed with water and vacuum dried. It was crystallised from CH_2Cl_2 by addition of cyclohexane and concentrating in vacuum. (Yield 70–80%). The product, which contained traces of $Co_2Rh_2(CO)_{12}$, was purified by heating a solution in n-heptane until the IR absorption band at 1871 cm^{-1} disappeared. The filtered solution yielded a pure crystalline product by cooling in a dry ice/acetone bath.

This synthesis was also carried out using an equivalent amount of $K_3[RhCl_6]$ instead of $RhCl_3 \cdot 3H_2O$.

(e). Synthesis of $Co_3Rh(CO)_{12}$ and $Co_2Rh_4(CO)_{16}$ from $Co_2Rh_2(CO)_{12}$

A saturated solution of $Co_2Rh_2(CO)_{12}$ in n-heptane ($\approx 1\%$ in weight) was heated to 60° until the infrared absorption bands at 1920 w and 1871 s cm^{-1} had disappeared. The hexanuclear $Co_2Rh_4(CO)_{16}$ separated into crystals which were filtered, while the tetranuclear $Co_3Rh(CO)_{12}$ was recovered by cooling the solution in a dry ice/acetone bath. The latter was purified by several crystallisations from CH_2Cl_2/cyclohexane.

(f). Synthesis of $Co_2Ir_2(CO)_{12}$ from $Na[Co(CO)_4]$ and $K_2[Ir(CO)I_5]$

A solution of $Na[Co(CO)_4]$ (0.83 g) in water (20 ml) was treated dropwise with stirring with a solution of $K_2[Ir(CO)I_5]$ (1.340 g) in water (20 ml). After three hours the precipitate was separated by filtration, washed with water and vacuum dried. The dried product was extracted with CH_2Cl_2 and crystallised by adding cyclohexane. (Yield 60–70%).

(g). Synthesis of $Rh_3Ir(CO)_{12}$ from $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$

A mixture of $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ was heated for 24 h in an autoclave at 120° under an atmosphere of carbon monoxide (300 atm). The reaction product, which consisted of a mixture of $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$ and $Rh_3Ir(CO)_{12}$ ($\approx 3\%$), was sublimed as little orange crystals in the cold side of the autoclave and was easily separated by extraction with the minimum amount of n-heptane and by cooling the resulting orange solution in a dry ice/acetone bath.

(h). Synthesis of $Rh_3Ir(CO)_{12}$ from $Na[Rh(CO)_4]$ and $K_2[Ir(CO)I_5]$

A solution of $Na[Rh(CO)_4]$ in water was treated with stirring under carbon monoxide with an excess of solid $K_2[Ir(CO)I_5]$. The reaction mixture was immediately extracted with n-heptane, and the orange solution, dried by anhydrous sodium sulphate, was cooled in a dry ice/acetone bath to give orange crystals of the product. (Yield $\approx 10\%$ based upon Rh).

(i). Synthesis of $Rh_2Ir_2(CO)_{12}$

An aqueous solution of $Na[Rh(CO)_2Cl_2]$, prepared by dissolving $Rh_2(CO)_4Cl_2$ (0.11 g) in a saturated aqueous solution of NaCl (10 ml), was treated under carbon monoxide with a solution of $Na[Ir(CO)_4]$ (0.165 g) in water (5 ml). After half an hour the orange precipitate was extracted from the water using dichloromethane (20 ml), and the solution, dried on anhydrous sodium sulphate, was filtered. The compound was precipitated by adding cyclohexane, the orange crystals were quickly dried in a nitrogen stream. The solid product crystallises with two moles of clathrate cyclohexane, which is gradually lost on prolonged exposure to vacuum. Concentration of the mother liquor gave another less-pure crop of crystals. The yield is about 60%.

(*j*). *Synthesis of* $Rh_2(CO)_4Cl_2$ *(about 60% enriched in* ^{13}CO*)*

A solution of $RhCl_3 \cdot 3H_2O$ (0.610 g) in 2 *M* aqueous HCl (10 ml) was stirred with silver powder (1.5 g) under an atmosphere of carbon monoxide (about 60% enriched in ^{13}CO). After 48 h the yellow solution was evaporated to dryness *in vacuo*, and the solid residue was extracted with n-pentane (in 5 ml portions) until the solution was colourless. The combined extracts were evaporated to dryness *in vacuo* to give $Rh_2(CO)_4Cl_2$ (0.36 g, 80% yield).

The IR spectrum in n-pentane exhibits the following absorptions in the carbonyl stretching region: 2100 m, 2090 (sh), 2085 (sh), 2080 ms, 2050 ms, 2045 (sh), 2038 m, 2008 s and 1987 s cm^{-1}.

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