THE FORMATION OF A NEW MIXED COBALT RHODIUM CARBONYL FROM $Co_2(CO)_8$ AND $Rh_4(CO)_{12}$: INFRARED SPECTROSCOPIC CHARACTERIZATION UNDER CARBON MONOXIDE PRESSURE *

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Summary

The formation of a new compound, the most characteristic IR absorption bands of which appear at 2007 cm^{-1} and 1956 cm^{-1}, has been observed in the reaction between $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ under carbon monoxide pressure in a hydrocarbon medium. The same compound is also formed either by the reaction of $Co_2(CO)_8$ with $[Rh(CO)_2Cl]_2$ or by the reaction of $Co_3Rh(CO)_{12}$ with carbon monoxide. The new complex has not been isolated in a pure state, but the formula $CoRh(CO)_7$ is proposed on the basis of the stoichiometry of its formation and its physico-chemical properties. Equilibrium constants and thermodynamic parameters for the reaction $2 Co_2(CO)_8 + Rh_4(CO)_{12} \rightleftharpoons 4 CoRh(CO)_7$ have been estimated. Possible structures for the new complex are discussed on the basis of its IR spectrum.

Introduction

During the investigation of the hydrocarbonylation of diketene it was shown that mixtures of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ have higher catalytic activities than either of the two carbonyls alone [1], and this was attributed to the presence of mixed cobalt rhodium carbonyl hydrides of unknown nature.

Homometallic and mixed tetranuclear clusters of the type $Co_{4-x}Rh_x(CO)_{12}$ (x = 1, 2, 4), first synthesized under atmospheric conditions by Chini and coworkers [2], have been well characterized, along with many other neutral or anionic mixed tetrametal carbonyl clusters [3]. In contrast, only a few examples of bi- and trinuclear mixed carbonyls containing at least one cobalt or rho-

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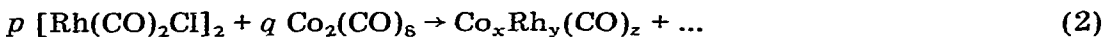* Dedicated to the memory of Professor Paolo Chini.

dium atom are known, e.g. $MnCo(CO)_9$ [4], $ReCo(CO)_9$ [5], $TcCo(CO)_9$ [6], $[FeCo(CO)_8]^-$ [7], and $Co_2Os(CO)_{11}$ [8], and none containing only rhodium and cobalt have previously been described.

In order to investigate the new catalytic species effective in the diketene hydrocarbonylation it was decided first to examine the reaction between Co_2-$(CO)_8$ and $Rh_4(CO)_{12}$. We describe below the results obtained from an IR spectroscopic study of this reaction in aliphatic hydrocarbon solvents under carbon monoxide pressure (10 to 155 bar) at temperatures between 40 and 84°C.

Results

When a mixture of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ in hexane at 25°C and under a carbon monoxide pressure of 50 bar is heated to 70°C, there are marked changes with time in the IR spectrum. New bands appear at 2134w, 2062s, 2059s, 2049s, 2007m, 1977w, and 1956ms cm^{-1} which cannot be attributed to any of the previously known cobalt or rhodium carbonyls or mixed clusters and which indicate the presence of one or more unknown species in solution (eq. 1).

The same new bands, of which the most characteristic are those at 2007 cm^{-1} and 1956 cm^{-1}, appear in the IR spectrum when $[Rh(CO)_2Cl]_2$ is treated with $Co_2(CO)_8$ (eq. 2) at 25°C and under a p_{CO} of 1 bar, and when Co_3Rh-$(CO)_{12}$ is heated in hexane at 70°C under a CO pressure of 50 bar (eq. 3).

$$a\ Co_2(CO)_8 + b\ Rh_4(CO)_{12} \rightarrow Co_xRh_y(CO)_z \tag{1}$$

$$p\ [Rh(CO)_2Cl]_2 + q\ Co_2(CO)_8 \rightarrow Co_xRh_y(CO)_z + ... \tag{2}$$

$$Co_3Rh(CO)_{12} + CO \rightarrow Co_xRh_y(CO)_z + ... \tag{3}$$

The ratio between the intensities of the two new bands at 2007 cm^{-1} and 1956 cm^{-1} is the same ($E(2007) : E(1956) \sim 0.83$) for all three reactions. This indicates that both bands belong to the same compound and that this unknown complex is the only one formed in substantial amounts. Since the new complex is not formed under the same conditions with only $Co_2(CO)_8$ or $Rh_4(CO)_{12}$ present, it is very likely to contain both metals.

In a typical experiment with a mixture of $Co_2(CO)_8$ (1.7 mmol dm^{-1}) and Rh_4-$(CO)_{12}$ (0.71 mmol dm^{-1}) corresponding to a molar ratio 2.4 : 1 in the presence of carbon monoxide (55 bar at 70°C), a decrease of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ in a molar ratio 2 to 1 was observed until about 35% and 50% of the original Co_2-$(CO)_8$ and $Rh_4(CO)_{12}$, respectively, had disappeared; at the same time the intensities of the bands assigned to the new complex increased (Fig. 1). Taking into account the small amount of $Rh_6(CO)_{16}$ which is formed as shown by the intensity of the band at 1819 cm^{-1}, with the reasonable assumption that only one new complex is formed, the ratio between Co and Rh in the new compound must be 1, and so the complex must have the formula $[CoRh(CO)_{z/m}]_m$.

Attempts to isolate the new complex formed in reactions 1, 2 or 3 have so far failed. The solutions are stable at room temperature under a p_{CO} of at least 10 bar, but they decompose, in the absence of carbon monoxide, or even under a p_{CO} of 1 bar, and $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ are formed. When the reaction solution containing the new complex is cooled to $-70°C$, $Rh_4(CO)_{12}$

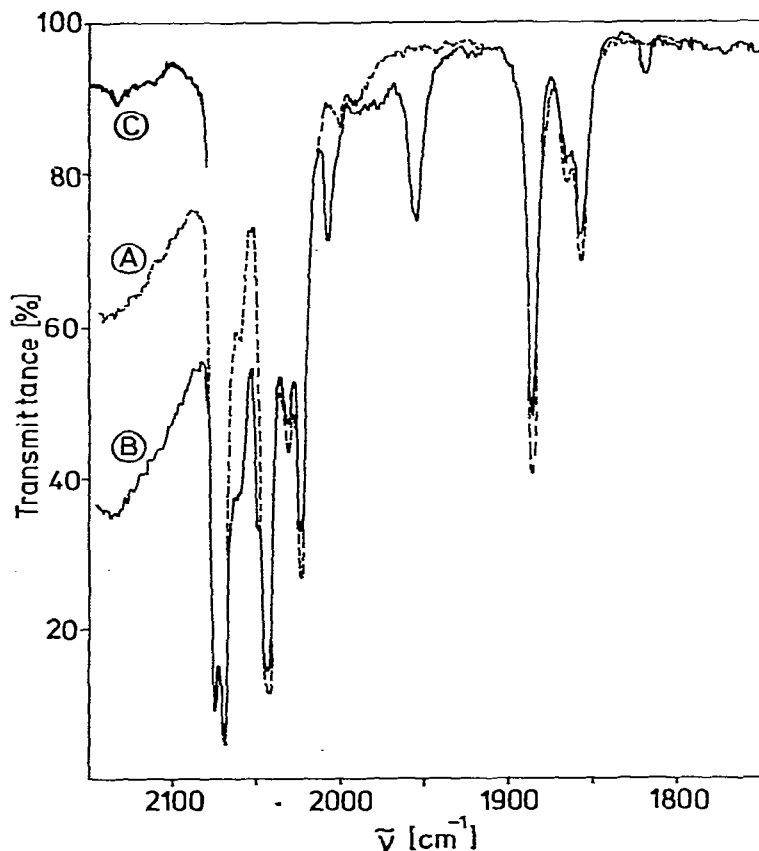Fig. 1. Spectra of the reaction mixture: 2 $Co_2(CO)_8$ + $Rh_4(CO)_{12}$. A: before starting the reaction, p_{CO} 50 bar (at 25°C); B: after 1.25 h at 70°C and 55 bar; C: high-frequency region after releasing the carbon monoxide pressure to 1 bar. The weak band at 2134 cm^{-1} was not detectable in B because of the strong absorption of dissolved carbon monoxide. Initial concentration: 1.7 mmol dm^{-3} $Co_2(CO)_8$ and 0.71 mmol dm^{-3} $Rh_4(CO)_{12}$, pathlength 0.0585 cm; the spectra were measured at instrument temperature (38°C).

and $Rh_6(CO)_{16}$ precipitate out; however, $Co_2(CO)_8$ remains in solution together with $[CoRh(CO)_{z/m}]_m$ and these cannot be separated by crystallization. The fact that the new complex has a solubility in hexane very similar to that of Co_2-$(CO)_8$ indicates that the value of m in its formula is very probably 1, for it is known that the solubility of clusters in hexane decreases with increasing number of metal atoms per molecule. We can therefore assign the formula CoRh-$(CO)_z$ to the new complex, and its formation can be represented as in eq. 4.

$$2 Co_2(CO)_8 + Rh_4(CO)_{12} \rightarrow 4 CoRh(CO)_z + (28 - 4z) CO \tag{4}$$
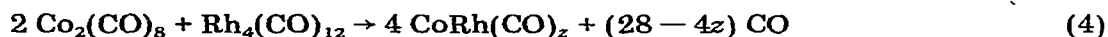
When the temperature is altered the IR spectrum changes with time, the intensities of the bands characteristic of $Co_2(CO)_8$, $Rh_4(CO)_{12}$ and $CoRh(CO)_z$ reaching practically constant values after some hours (e.g. ~4 h at 70°C) (Table 1). Only the band at 1819 cm^{-1} shows a further slight increase with time, indicating a slow decarbonylation of $Rh_4(CO)_{12}$ to $Rh_6(CO)_{16}$, while the ratio

TABLE 1

ABSORBANCE VALUES OF THE BANDS USED FOR THE ANALYSIS OF THE MIXTURE OF $CoRh(CO)_7$, $Rh_4(CO)_{12}$, $Co_2(CO)_8$ AND $Rh_6(CO)_{16}$ AND ABSORBANCE RATIO BETWEEN THE TWO CHARACTERISTIC BANDS (AT 2007 AND 1956 cm^{-1}) OF $CoRh(CO)_7$ AT VARIOUS REACTION TIMES (cell thickness: 0.585 mm)

τ (h)	p_{CO} (bar)	$\dfrac{E(2007)}{E(1956)}$	$\dfrac{CoRh(CO)_7}{E(1956)}$	$\dfrac{Rh_4(CO)_{12}}{E(1886)}$	$\dfrac{Co_2(CO)_8}{E(1858)}$	$\dfrac{Rh_6(CO)_{16}}{E(1819)}$
0	55	—	0	0.388	0.162	0.006
1		0.79	0.109	0.316	0.139	0.019
2.5		0.82	0.159	0.255	0.120	0.024
3.1		0.85	0.181	0.214	0.112	0.030
4.7		0.84	0.185	0.191	0.103	0.043
5.9		0.87	0.198	0.183	0.103	0.044
0	155	—	0	0.375	0.172	0.006
1.25		—	0.117	0.245	0.129	0.018
2.25		—	0.170	0.213	0.125	0.022
3.5		—	0.189	0.201	0.125	0.022
5.5		—	0.189	0.200	0.110	0.022
7.25		—	0.189	0.196	0.112	0.025
8.5		0.81	0.181	0.193	0.117	0.025

between the two bands at 2007 and 1956 cm^{-1} assigned to $CoRh(CO)_z$ is constant in all cases (Table 1, column 3). In similar experiments at various CO pressure in the range 55—155 bar, the intensity of the band at 1956 cm^{-1} reached the same value after 4 h independent of the pressure, indicating that the kinetics of the reaction and the final concentration of $CoRh(CO)_z$ as well as the

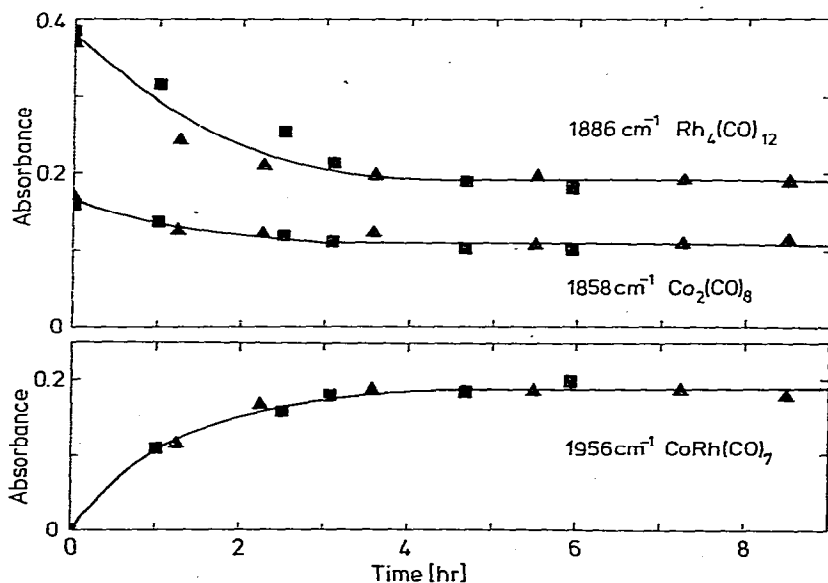Fig. 2. Variation with time of the characteristic absorbances at 1886 cm^{-1} for $Rh_4(CO)_{12}$, at 1858 cm^{-1} for $Co_2(CO)_8$, and at 1956 cm^{-1} for $CoRh(CO)_7$. Reaction temperature: 70°C. CO pressure: ■ 55 bar and ▲ 155 bar; initial concentrations and pathlength as reported in the caption of Fig. 1.

TABLE 2

EQUILIBRIUM VALUES FOR THE MOLAR CONCENTRATIONS OF $CoRh(CO)_7$, $Co_2(CO)_8$ AND $Rh_4(CO)_{12}$ AT VARIOUS TEMPERATURES AND CARBON MONOXIDE PRESSURES

T ($^\circ$C)	p_{CO} (bar)	$[CoRh(CO)_7]$ (mmol dm^{-3})	$[Co_2(CO)_8]$ (mmol dm^{-3})	$[Rh_4(CO)_{12}]$ (mmol dm^{-3})	$10^3 \times \dfrac{[CoRh(CO)_7]^4}{[Co_2(CO)_8]^2 [Rh_4(CO)_{12}]}$ (mol dm^{-3})
40	140	1.08	2.30	1.03	0.255
47	148	1.32	2.22	0.92	0.66
55	140	1.50	2.28	0.70	1.4
70	55	1.01	1.08	0.34	2.6
70	155	0.99	1.10	0.37	2.1
84	140	1.26	1.23	0.48	3.5

final concentrations of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ are not detectably influenced by p_{CO} in the temperature and p_{CO} range investigated (Fig. 2). The ratio between metal atoms and carbon monoxide must therefore be the same in the mixed complex as in a 2 $Co_2(CO)_8$ + $Rh_4(CO)_{12}$ mixture, namely 3.5, and we therefore propose for the new complex the formula $CoRh(CO)_7$ ($z = 7$ in eq. 4). The concentrations of the species $Co_2(CO)_8$, $Rh_4(CO)_{12}$ and $CoRh(CO)_7$ were calculated from the absorbance values as described in the Experimental section. The ratio $K = [CoRh(CO)_7]^4/[Co_2(CO)_8]^2[Rh_4(CO)_{12}]$ was evaluated at various temperatures after periods long enough to reach equilibrium and the values found are shown in Table 2.

The variation of ln K with $1/T$ (Fig. 3) supports the hypothesis that the reaction reported in eq. 4 ($z = 7$) corresponds to an equilibrium, the equilibrium constant at various temperature corresponding to the values of K in Table 2. A
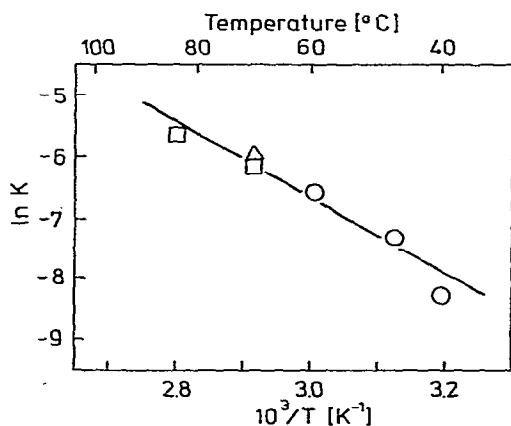

Fig. 3. A ln K vs $1/T$ plot for equilibrium reaction 5. □ 55 bar and △ 155 bar CO pressure, initial concentrations as given for Fig. 1; ○ 140—148 bar CO pressure, initial concentrations: $Co_2(CO)_8$: 3.4 mmol dm^{-3}; $Rh_4(CO)_{12}$: 1.4 mmol dm^{-3}.

ΔH^0 of ~50 kJ mol^{-1} and a ΔS^0 of ~100 J mol^{-1} K^{-1} can be calculated for this equilibrium from the values of K reported in Table 2 *.

Discussion

Although we have not isolated the new mixed carbonyl, we think that the various experiments indicate unequivocally that $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ react slowly at 40°C ($\tau_{1/2} \cong 14$ h) and rather rapidly at 70°C ($\tau_{1/2} \cong 1$ h) to give the dinuclear complex CoRh(CO)$_7$ in the reversible reaction shown in eq. 5:

$$2\ Co_2(CO)_8 + Rh_4(CO)_{12} \overset{K}{\rightleftharpoons} 4\ CoRh(CO)_7 \tag{5}$$
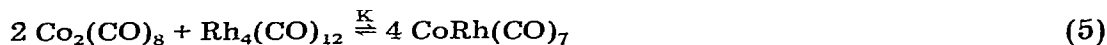
The value of 100 J mol^{-1} K^{-1} estimated for ΔS^0 corresponds to the value expected for a reaction in which the number of molecules increases from 3 to 4, and is therefore in agreement with the stoichiometry of the reaction shown in eq. 5 and with the dinuclear formula proposed for the new compound. Although CO is not involved in the equilibrium 5, its presence is necessary to stabilize the starting complexes and also the product, which in the absence of CO decomposes according to eq. 6.

$$2\ CoRh(CO)_7 \rightarrow Co_2Rh_2(CO)_{12} + 2\ CO \tag{6}$$

Various structures can be proposed for CoRh(CO)$_7$. From the IR spectrum, it seems that there are no bridging CO groups. In the experiments performed with a carbon monoxide pressure of about 150 bar, there is a weak shoulder at ca. 1851 cm^{-1} emerging from the wing of the bridging $Co_2(CO)_8$ band. Since this frequency is at half way between those of $Co_2(CO)_8$ at 1857 cm^{-1} and Rh$_2$-(CO)$_8$ at 1945 cm^{-1} [9] we tentatively assign it to a bridging band of CoRh-(CO)$_8$, assuming that this unknown complex is formed in low concentration when the carbon monoxide pressure is at or above 100 bar, as in the equilibrium eq. 7:

$$CoRh(CO)_7 + CO \rightleftharpoons CoRh(CO)_8 \tag{7}$$

We did not observed this band when the pressure was lower than 100 bar, even though the bands characteristic of CoRh(CO)$_7$ were fairly intense. This suggests that the equilibrium 7 is greatly shifted to the left when $p_{CO} \leqslant 50$ bar in the temperature range studied (25—84°C).

The IR spectrum shows no evidence of free or ion-pair bonded [Co(CO)$_4$]$^-$ [10,11]. A strong interaction between the two halves of the molecule is reflected at the high-energy end of the spectrum by the large separation (72 cm^{-1}) between the highest (all-in-phase C—O stretch) and the second band, which can be assigned with confidence to the out-of-phase coupling between the locally in-phase Rh(CO)$_v$ and Co(CO)$_w$ (v and w being 3 and 4, or 4 and 3,

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respectively) C—O vibrations. A similar large separation between the analogous vibrational frequencies was observed previously e.g. for $CoRe(CO)_9$ (74 cm^{-1}) [12] and $CoTc(CO)_9$ (77 cm^{-1}) [6]. In the absence of CO bridges this suggests that $CoRh(CO)_7$ contains a single metal—metal bond [13], and two alternative ways for the distribution of the CO groups among the metal atoms, a and b, can be proposed

$$(CO)_4Co\text{—}Rh(CO)_3 \qquad (CO)_3Co\text{—}Rh(CO)_4$$

(a) (b)

The most characteristic band is that at 1956 cm^{-1}. A similar frequency, ca. half-way between the terminal and bridging region of unsubstituted neutral metal carbonyls does not appear in the spectra of mixed carbonyls of the type $M_3M'(CO)_{12}$ or $M_2M'_2(CO)_{12}$ (M = Co; M' = Rh). In our opinion, in the case of $CoRh(CO)_7$ this frequency is associated with coordinative unsaturation in the molecule. Indeed, the spectrum shows a marked similarity to that reported by Sweany and Brown [14] for $Co_2(CO)_7$ generated photochemically in inert gas matrices (Fig. 4). In that case the coordinative unsaturation is clearly responsible for the unusually low frequency ($\sim 1950 \text{ cm}^{-1}$) of the lowest terminal C—O stretching modes.

For the mononuclear series $Rh(CO)_n$ ($n = 1$—4), obtained by matrix isolation, there is a very narrow frequency range (12 cm^{-1}) [15] within which there are the C—O stretching modes for all the $Rh(CO)_n$ molecules, whereas the frequencies of the analogous $Co(CO)_n$ ($n = 1$—4) molecules [16] are spread out over a range of ca. 100 cm^{-1}; however, we still favour structure a, because rhodium carbonyl derivatives (e.g. $[Rh(CO)_2Cl]_2$) often assume the 16 electron configuration, which is not common in carbonyl derivatives of cobalt. In structure a, as in several $(CO)_4Co\text{—}ML_x$ complexes [17], the ligands around the cobalt atom are likely to be in a trigonal bipyramidal configuration. The ligands around the rhodium atom should have a square planar arrangement as in other rhodium or iridium complexes of the type XML_3 (L = CO, PR_3) [18].

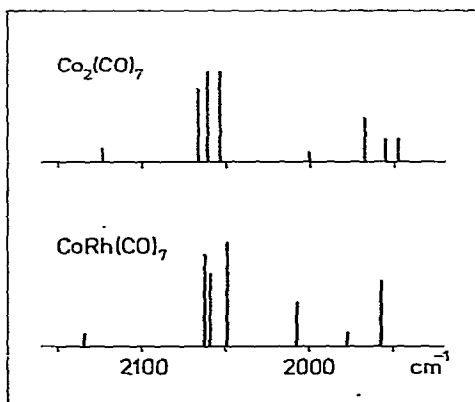Further investigations of the properties of $CoRh(CO)_7$ and related heterometal complexes are in progress.

Fig. 4. Schematic comparison of the C—O absorption spectra of $Co_2(CO)_7$ (generated photochemically from $Co_2(CO)_8$ in argon matrix [14]) and $CoRh(CO)_7$.

Experimental

Co$_2$(CO)$_8$ was prepared by the method of Szabó et al. [19], Rh$_4$(CO)$_{12}$ by the procedure given by Chini et al. [2b] and Cattermole et al. [20], and [Rh(CO)$_2$Cl]$_2$ from RhCl$_3 \cdot$ 3 H$_2$O as reported by McCleverty and Wilkinson [21]. High-purity carbon monoxide was prepared by catalytic dehydration of formic acid at 280°C, and stored in aluminum cylinders under pressure. The solvents (products of Fluka AG) were purified and dried by the usual methods. Solutions of the metal carbonyls were prepared and handled under N$_2$ or CO.

High pressure experiments were carried out in a 250 cm^3 stainless steel rocking autoclave heated in an oil bath. Samples were withdrawn under pressure directly into a high-pressure IR cell [22].

IR spectra were scanned with a Perkin-Elmer Model 325 spectrometer with a spectral slit width of 0.8 to 0.9 cm. The scanning speed was between 6 and 30 cm^{-1}/min, depending on the scale expansion. Solvent absorption was compensated by the use of a variable path cell.

The following molar extinction coefficients ϵ_M were used for the calculation of the equilibrium shown in eq. 5: Bridging band of Rh$_4$(CO)$_{12}$: $\epsilon_M(1886)$ = 9030 dm^3 mol^{-1} cm^{-1}. Bridging band of Co$_2$(CO)$_8$: $\epsilon_M(1858)$ = 1735 ± 20 dm^3 mol^{-1} cm^{-1} [23]. This value is about 15% lower than that reported in the literature [24]. The ϵ_M of the bridging band of Rh$_6$(CO)$_{16}$ at 1819 cm^{-1} was estimated ($\epsilon_M(1819)$ = 22 200 dm^3 mol^{-1} cm^{-1}) in a separate experiment, in which the increase of this band in a closed system was related to the decrease of the Rh$_4$(CO)$_{12}$ band at 1886 cm^{-1} during several hours.

The approximate molar extinction coefficient of the most characteristic band of CoRh(CO)$_7$ at 1956 cm^{-1} was estimated indirectly to be 3270 dm^3 mol^{-1} cm^{-1} from the concentration decrease of the starting compounds in reaction 5, taking into account the fraction of Rh$_4$(CO)$_{12}$ converted into Rh$_6$-(CO)$_{16}$.

Reaction between Co$_2$(CO)$_8$ and Rh$_4$(CO)$_{12}$ (p_{CO} 55 to 155 bar)

In a typical experiment a solution of 87.5 mg (2.56 × 10^{-4} mol) of Co$_2$(CO)$_8$ and 79.4 mg (1.07 × 10^{-4} mol) Rh$_4$(CO)$_{12}$ (corresponding to a Co/Rh atomic ratio of 1.2) in 150 cm^3 of hexane was placed into a 250 cm^3 autoclave. After pressurization with carbon monoxide (50 bar) a reference sample was transferred into the high-pressure cell for IR analysis (cf. curve A in Fig. 1). The autoclave was then placed in an oil bath preheated to 70°C, and rocking was started. The pressure increased to 55 bar. After 1 h samples were taken at regular intervals and analyzed by IR spectroscopy (cf. curve B in Fig. 1). After sampling the pressure in the autoclave was restored immediately. The equilibrium of the reaction was reached after 4 h, and from the absorbance values the equilibrium concentrations of Co$_2$(CO)$_8$, Rh$_4$(CO)$_{12}$, and CoRh(CO)$_7$ were calculated, and are shown in Table 2.

In analogous experiments the temperature (40—84°C) and/or carbon monoxide pressure (10—155 bar) and reaction time were varied. In one experiment the concentrations of the starting products were doubled.

Reaction between Co$_2$(CO)$_8$ and [Rh(CO)$_2$Cl]$_2$ in hexane (p_{CO} ~ 1 bar)

Under an atmosphere of carbon monoxide, 2.8 g (8.2 mmol) of Co$_2$(CO)$_8$

and 1.061 g (2.7 mmol) of $[Rh(CO)_2Cl]_2$ (corresponding to an atomic ratio Co : Rh of 3.0) were each dissolved in 30 cm^3 of hexane, and the solutions were transferred to a 100 cm^3 glass vessel. The mixture was stirred at room temperature, and samples were withdrawn at intervals of 5 min to 1 h, diluted in 10 cm^3 of hexane (to give suitable absorbance values in the IR spectrum), and the IR spectrum recorded. The two characteristic absorption bands of $CoRh(CO)_7$ at 1956 cm^{-1} and 2007 cm^{-1} appeared even after 8 min and reached maximum intensities after 21 h. The concentration of $CoRh(CO)_7$ reached a maximum of about 1 mmol dm^{-3}. During the reaction a hexane-insoluble brownish yellow layer gradually formed on the walls of the glass vessel and also on the rock salt windows of the IR cell. This deposit , which showed two broad C—O absorptions centered at ca. 2088 and 2010 cm^{-1}, was not identified.

Similar experiments were carried out using the same conditions, but with varying concentrations of the reactants ($[Co_2(CO)_8]$ 0.004 to 0.44 mol dm^{-3}; $[Rh(CO)_2Cl]_2$ 0.002 to 0.078 mol dm^{-3}; Co : Rh ratios 1.8 to 5.6).

Reaction of $Co_3Rh(CO)_{12}$ with carbon monoxide (p_{CO} 50 bar)

$Co_3Rh(CO)_{12}$ was prepared as described by Chini et al. [2a]. A solution of 26 mg of a recrystallized sample in 20 cm^3 of hexane was placed in a 250 cm^3 autoclave, pressurized with 50 bar of carbon monoxide, and heated to 70°C. The bands at 2007 cm^{-1} and 1956 cm^{-1} characteristic of $CoRh(CO)_7$ were observed after a reaction time of 90 min. At the same time a decrease of the intensity of the band at 1913 cm^{-1} corresponding to $Co_3Rh(CO)_{12}$ and increases were observed in the bands at 2074 cm^{-1}, corresponding to $Rh_4(CO)_{12}$, and at 1858 cm^{-1} and 1867 cm^{-1}, corresponding to $Co_2(CO)_8$.

Acknowledgment

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