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INFRARED SPECTROSCOPIC STUDY OF THE μ-LIGAND EXCHANGE REACTION OF BIS(μ-ANION)DIRHODIUM TETRACARBONYLS: EVIDENCE FOR INTERMEDIATES WITH TWO DIFFERENT BRIDGING LIGANDS

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Summary

$Rh_2(CO)_4XY$ type intermediates have been detected in the μ-ligand exchange reaction of bis(μ-anion)dirhodium(I) tetracarbonyls,

$$Rh_2(CO)_4X_2 \rightarrow Rh_2(CO)_4Y_2$$

where $X \neq Y$; X,Y = halogen, $RCOO^-$, RO^- and R = alkyl, aryl, substituted aryl.

Introduction

In the past decade considerable attention has been given to the chemistry of bis(μ-anion)dirhodium(I) tetracarbonyls [1 - 8,16]. Most preparative methods* are based on the exchange of the μ-anions:

$$Rh_2(CO)_4X_2 + 2\,MY \rightarrow Rh_2(CO)_4Y_2 + 2\,MX \qquad (1)$$

where X and Y are anions (Br^-, I^- [1]; CH_3COO^-, CF_3COO^-, p-$FC_6H_4COO^-$ [2]; CH_3S^-, $C_2H_5S^-$, $C_4H_9S^-$, $C_6H_5S^-$, $C_6F_5S^-$, p-$FC_6H_4S^-$ [3,5,8]; N_3^- [7]) but $X \neq Y$ and where M = H, Na, K, Ag or other cations. Reaction

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* With the reported exception of $Rh_2(CO)_4Cl_2$ [11], $Rh_2(CO)_4(OAc)_2$ [6,13] and some $Rh_2(CO)_4(SR)$ [6] derivatives.

(1) could hardly occur in one step, however. A schematic mechanism of the reaction could be visualised either by (2) or (3):

$$\left.\begin{aligned}
&Rh_2(CO)_4X_2 \rightarrow \underset{(Ia)}{2\,Rh(CO)_2X}\\
&Rh(CO)_2X + MY \rightarrow \underset{(Ib)}{Rh(CO)_2Y} + MX\\
&2\,Rh(CO)_2Y \rightarrow Rh_2(CO)_4Y_2
\end{aligned}\right\} \tag{2}$$

$$\left.\begin{aligned}
&Rh_2(CO)_4X_2 + MY \rightarrow \underset{(II)}{Rh_2(CO)_4XY} + MX\\
&Rh_2(CO)_4XY + MY \rightarrow Rh_2(CO)_4Y_2 + MX
\end{aligned}\right\} \tag{3}$$

A combination of mechanisms (2) and (3) cannot be excluded.

Both types of intermediates could have some interest in the interpretation of the catalytic behaviour of mono- [18] and binuclear [19] *Rh* complexes as well as of some transformations [2,3,20,22] of $Rh_2(CO)_4X_2$ compounds.

Results and discussion

If reaction (1) is carried out at a relatively low temperature by stepwise additions of MY, the infrared spectra recorded from time to time are rather rich in bands in the ν(C—O) region, and show a systematic change. As shown in Fig. 1 simultaneously with the decrease of the bands of $Rh_2(CO)_4X_2$, first an unknown band system of the same pattern develops (marked with ◑ in Fig. 1) and almost at the same time the bands of the end product also appear. After having

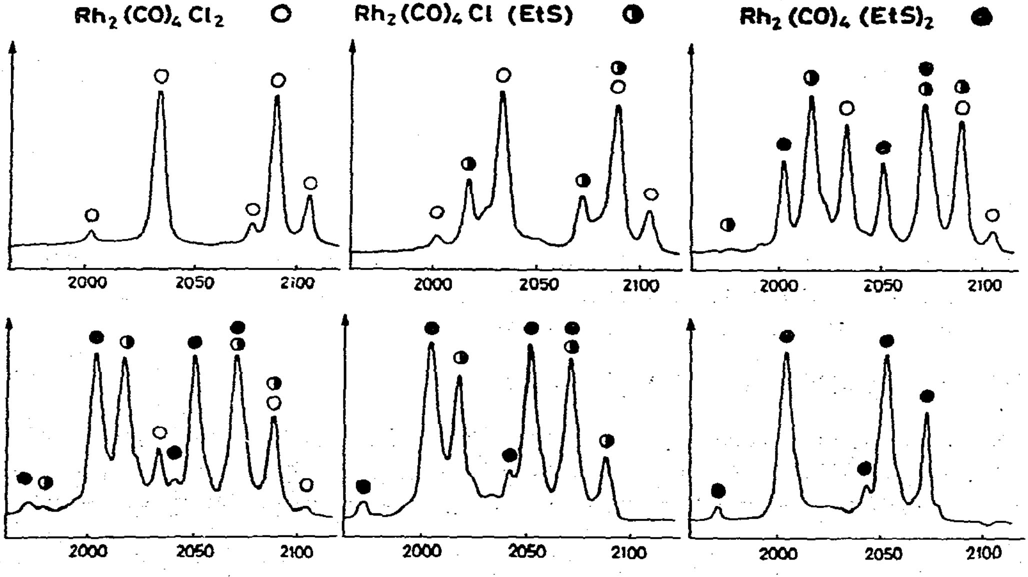


Fig. 1. Infrared spectra of reaction (1).

reached an ≈ 1/2/1 intensity ratio the band system of $Rh_2(CO)_4X_2$ gradually disappears. Upon further addition of MY (in most cases an excess is necessary) and/or by using higher temperature, or longer reaction times the unassigned band system also disappears and $Rh_2(CO)_4Y_2$ remains as the sole product as shown by the spectra and analyses of these compounds.

This phenomenon was found to be general for the systems studied, and it became evident that the observed novel band system belongs to some intermediate in reaction (1). It could be shown that the intensity of all the unknown bands in the spectra change proportionally and therefore it is reasonable to suppose that they belong to *one* novel species. Since three $\nu(^{12}C{-}O)$ bands were present, intermediates of the type (I) could be excluded. We thus suggest that these bands should be assigned to intermediates of type (II) having a molecular geometry analogous to that suggested for other anion-bridged dirhodium tetracarbonyls [1,4,14]. Similar structures were postulated recently for a "resin supported" $Rh_2(CO)_4Cl(ResS)$, which is probably a dinuclear species [21].

Attempts to isolate the intermediates using either chromatography or crystallization failed. The binuclear character of the intermediate species, however, could be proved analytically by simultaneous osmometric molarity measurements and Rh analyses on the same reaction mixtures (cf. Experimental).

In course of these experiments we observed that reactions of type (1) are not easily reversed. Thus for example $Rh_2(CO)_4I_2$ is readily formed when $Rh_2(CO)_4Cl_2$ is treated with KI (n-hexane) while a 1000 fold excess of KCl (n-hexane) caused only a very moderate transformation (≈ 10%) to $Rh_2(CO)_4ClI$ and to small amounts (≈ 1%) of $Rh_2(CO)_4Cl_2$ even after 48 h at room temperature and followed by reflux for several hours. Similarly, preference of the metal for the EtS^- rather than AcO^- ligand was observed, but reversible exchange involving different RS^- ligands could be achieved from both sides (e.g. with R = Et and Ph). On the other hand spectra recorded after chromatography (silica/hexane) of $Rh_2(CO)_4X_2 + Rh_2(CO)_4XY + Rh_2(CO)_4Y_2$ mixtures of different starting compositions suggest that a disproportionation in both directions may occur on the column. Similarly when $Rh_2(CO)_4X_2$ + $Rh_2(CO)_4Y_2$ mixtures were allowed to react in solution e.g. with X = Cl, Y = I, equilibrium was reached after 1 h (room temperature, n-hexane).

Exploratory experiments were made to decide whether product compositions obtained by reaction (1) and/or reactions (3) are controlled thermodynamically or kinetically. An equilibrium nature of the reactions was observed. For the system (4), the relationship $K_1 \cdot K_2 = K \approx 10$ was found to apply.

$$\begin{aligned} &Rh_2(CO)_4(SPh)_2 + EtSH \overset{K_1}{\rightleftharpoons} Rh_2(CO)_4(SPh)(SEt) + RhSH \\ &Rh_2(CO)_4(SPh)(SEt) + EtSH \overset{K_2}{\rightleftharpoons} Rh_2(CO)_4(SEt)_2 + PhSH \end{aligned} \qquad (4)$$

The spectra of the intermediate species could be best observed when the bands of $Rh_2(CO)_4X_2$ and $Rh_2(CO)_4Y_2$ were far enough from each other to give good resolution. Spectral data for such cases are summarized in Table 1.

The infrared spectra of the intermediate species require further comment.

TABLE 1

CARBONYL FREQUENCIES (cm^{-1}) FOR THE $Rh_2(CO)_4XY$ TYPE COMPLEXES IN HEXANE SOLUTION^a

X	Y	A_1	B_1	B_2	$\nu(^{13}CO)$
Cl	I	2099.3(m)	2083.7(s)	2031.7(s)	2000.5(w)
Cl	CH_3COO	2105 (w)	2081.9(s)	2031 (s)	1996.0(w)
Cl	$S(C_2H_5)$	2087.9(m)	2071.5(s)	2018.0(s)	1992.5(w)
Cl	$S(C_4H_9)$	2090.1(m)	2072.6(s)	2018.8(s)	1980.0(w)
Cl	$S(C_6H_5)$	2091.1(m)	2075.3(s)	2024.6(s)	1990.0(w)
Cl	$S(C_6F_5)$	2103 (w) 2099 (m)	2084 (s)	2030 (s)	^{b}
Cl	S(*p*-tolyl)	2093 (m)	2076 (s)	2025 (s)	1998 (w) 1990 (w)
Cl	$O(C_3H_7)$	2101.8(vw)	2077.9(s) 2081.0(s)	2019.2(s) 2021.9(s)	1990.0(w)
Cl	$O(C_6H_5)$	2099.1(vw)	2084.9(s)	2025.1(s)	1993.5(w)
Cl	O(*p*-ClC_6H_4)	2100.5(vw)	2086.9(s)	2027 (s)	1995.0(w)
I	CH_3COO	2097.3(m)	2082.8(s)	2029 (s)	1999.0(w)
I	$S(C_2H_5)$	2084.7(m)	2067.4(s)	2016.9(s)	1990.0(vw)
CH_3COO	$S(C_2H_5)$	2090.9(m)	2073.1(s)	2018.0(s)	1979.5(vw)
$S(C_2H_5)$	$S(C_6H_5)$	2077.3(m)	2059.6(s)	2012.0(s)	1985.5(w)

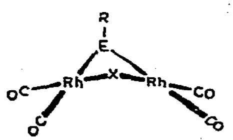
^{a}For experimental error see text. ^{b}Could not be observed.

In the initial and final stage of the reaction it was conceivable that either the final or the starting complex was not present in the solution in quantities over the IR detection limits. Spectra recorded under such conditions clearly showed that only the aforesaid three $\nu(^{12}C{-}O)$ bands plus one or two $\nu(^{13}C{-}O)$ absorptions (cf. Table 1) have detectable intensity in the spectrum of the $Rh_2(CO)_4XY$ species. This would mean that in spite of the apparent C_s symmetry of the $Rh_2(CO)_4XY$ complexes with the above suggested structure, the vibrations of the coordinated carbonyl groups apparently obey the selection rules for the point group C_{2v}. This behavior is not unexpected since very drastic changes in the molecular geometry are needed to lend a detectable intensity to the vibrational modes which under the selection rules for point group C_{2v} belong to species A_2 and hence should be inactive. Similar behaviour has been observed for the C—O stretching frequencies in the $Co_2(CO)_6(RC_2R')$ complexes with asymmetric acetylenes, and in the case of these complexes, also, the spectra can be explained on the basis of C_{2v} symmetry [9,15] while the sixth band required by the real C_s point group was observed only in the case of the "lactone" [9,10] derivatives $Co_2(CO)_7RR'C_4O_2$, in which the bridging μ-CO and μ-lactone groups are very different both in bond type and size. We thus made the assignments of the bands in Table 1 on the basis of symmetry C_{2v} in the light of the results of Lewis et al. [4].

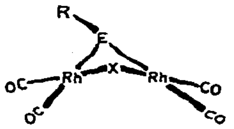
Another common feature of the IR spectra is that all bands assigned to $Rh_2(CO)_4XY$ complexes are almost exactly midway between the corresponding bands of $Rh_2(CO)_4X_2$ and $Rh_2(CO)_4Y_2$ complexes. The spectra were recorded with simultaneous DCl calibration, which usually allows the band positions to be given with a mean error of ± 0.2 cm^{-1}. In the cases studied the bands overlapped, which may increase the error to about ± 1,0 - 1.5 cm^{-1} for $\nu(^{12}C{-}O)$ bands and to about ± 2 - 3 cm^{-1} for the weak $\nu(^{13}C{-}O)$ bands. At the same time the average deviations of the $Rh_2(CO)_4XY$ band position from the midpoint were as follows: A_1 ± 2.5; B_1 ± 3.3; B_2 ± 1.7 and $\nu(^{13}C{-}O)$ ±

4.5 cm^{-1} *. These values are slightly above the probable experimental error, and the difference may be attributed to the different bonding geometries of the bridging ligands.

A *syn—anti* isomerism was suggested for some $Rh_2(CO)_4X_2$ compounds containing polyatomic μ-ligands with non-planar bridgehead atoms [5,16,17]. Such isomerism is also possible with $Rh_2(CO)_4XY$ complexes if at least one of the bridging ligands is able to occupy two steric positions (see structures A and E), but in this case the two conformers are better described as *axial* and *equatorial* forms. In three cases, a doubling of bands was in fact observed (cf. Table 1): with X = Cl and Y = OC_3H_7 the B_1 and B_2 bands, and with X = Cl, Y = SC_6F_5 the A_1 bands were split. *Syn—anti* isomerism was observed also with the corresponding $Rh_2(CO)_4Y_2$ complexes [16,17] in these cases.



AXIAL (A)



EQUATORIAL (E)

X = Cl
E = O, R = n-Pr
E = S, R = Ph_F

Experimental

The starting complexes $Rh_2(CO)_4Cl_2$ [11], $Rh_2(CO)_4I_2$ [1], $Rh_2(CO)_4(CH_3COO)_2$ [2] and $Rh_2(CO)_4(SPh)_2$ [8] were prepared by published procedures and identified by their IR spectra.

Silver acetate, sodium iodide, ethyl mercaptan, butyl mercaptan, thiophenol, pentafluorothiophenol, and *p*-tolyl mercaptan were of commercial origin, used without further purification. Propylate, phenolate and *p*-chlorophenolate anions were used as Na salts.

All operations were carried out under dinitrogen, IR spectra were run either on a UR-20 (Carl Zeiss Jena) or on a Perkin—Elmer 621 infrared spectrophotometer using LiF prism and NaCl cells. The calibration of the spectra was performed with simultaneous recording of DCl using an expanded wave number scale [12]. The molarities were measured by the Knauer vapour tension osmometer.

Preparation of the $Rh_2(CO)_4XY$ type complexes was usually carried out by dissolving 15 - 20 mg of $Rh_2(CO)_4X_2$ in hexane, adding stepwise 5 - 10 mg

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* In the case of compounds showing a doublet of one or more bands in the spectra due to *syn—anti* isomerism, the mean values of the two components of a given band were used for the calculations.

of the compound containing the Y anion, and stirring the solution at room temperature. The IR spectra of the reaction mixtures were recorded from time to time.

In the case of reaction mixtures containing $Rh_2(CO)_4ClI$, and $Rh_2(CO)_4Cl(CH_3COO)$, the rhodium content and the molarity of the solution was determined. The rhodium content of the solution containing $Rh_2(CO)_4ClI$ complex was 0.0246 g atom Rh/l and the molarity of the same solution was found to be 0.012 mole/l, while in the case of $Rh_2(CO)_4Cl(CH_3COO)$ containing solution the rhodium content was 0.009 g atom Rh/l and the molarity 0.0046 mole/l. This corresponds to two Rh atoms per molecule.

Experiments concerning the equilibrium nature of reaction (4) were performed by treating $\approx 10^{-3}$ molar solutions of $Rh_2(CO)_4(SPh)_2$ and of $Rh_2(CO)_4(SEt)_2$ (both prepared from $Rh_2(CO)_4Cl_2$ by the reaction with the appropriate RSH compound in hexane solution, then recrystallysed from hexane; Rh analyses were correct) with 0.1 - 1 equivalent portions of EtSH and PhSH respectively. IR spectra were recorded from time to time, and the Rh content of the samples taken for spectroscopy was determined. The spectra were evaluated quantitatively using the molar extinction coefficients for $Rh_2(CO)_4(SPh)_2$ and $Rh_2(CO)_4(SEt)_2$ determined with pure compounds and the average of these extinctions for $Rh_2(CO)_4(SPh)(SEt)$. $K_1 \cdot K_2 = K$ values obtained for this system ranged from 3 to 20. This uncertainly is due to the approximate nature of the calculations, as well as to the strong overlapping of the ν(C—O) bands.

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