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μ,μ-BIS(ALCOHOLATO)- AND μ,μ-BIS(PHENOLATO)DIRHODIUM(I) TETRACARBONYL COMPLEXES

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SUMMARY

$Rh_2(CO)_4(OR)_2$ complexes (R = Me, Et, Pr, i-pent, Ph, *p*-chlorophenyl) were prepared from $Rh_2(CO)_4Cl_2$ and sodium alcoholates or phenolates. They are converted by phosphines into the monomeric $Rh(CO)(PR'_3)_2(OR)$ derivatives (R' = Bu, Ph) via $Rh_2(CO)_3(PR'_3)(OR)_2$ intermediates.

INTRODUCTION

Dinuclear rhodium(I) tetracarbonyl complexes containing two μ-bridging anions of the general formula $Rh_2(CO)_4X_2$ have been described in several papers. Thus X can be halogen (Cl^-, Br^-, I^-)[1,2], RS^- (R = CH_3, C_2H_5, C_4H_9, C_6H_5, *p*-FC_6H_4, C_6F_5)[3–6], $RCOO^-$ (R = *p*-FC_6H_4, CF_3, CH_3), NO_3^-, and SCN^-, while X_2 can be *o*-phthalate or sulphate[7]. Some phosphine substituted derivatives of the general formula $Rh_2(CO)_{4-m}L_mX_2$ (L = phosphine, m = 1–4) have also been recently described[8,9,17]. The structure of some $Rh_2(CO)_4X_2$ complexes (as schematically shown in Fig. 1) has been determined by X-ray[11], IR[1,2] and other[1] methods. There is some evidence for *syn–anti*-type stereoisomers in the case of X = RS^- [3].

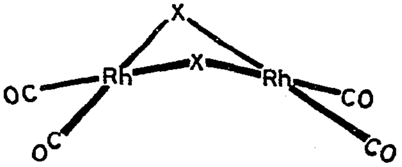

Fig. 1. Structure of $Rh_2(CO)_4X_2$ complexes.

The striking analogy between RS^- and RO^- anions as bridging ligands and the absence of data on X = RO^- complexes prompted us to study μ,μ-bis(alcoholato)-dirhodium tetracarbonyls, and we describe our results below.

RESULTS AND DISCUSSION

1. *Preparative methods*

Sodium alcoholates and phenolates (NaOR, where R = alkyl and aryl groups) react with $Rh_2(CO)_4Cl_2$ in hexane, benzene or $CHCl_3$ as solvent under argon or nitrogen at 0–30° to give good yields of $Rh_2(CO)_4(OR)_2$ complexes (I) according to eqn. (1).

$$Rh_2(CO)_4Cl_2 + 2\ NaOR \rightarrow \underset{(I)}{Rh_2(CO)_4(OR)_2} + NaCl \qquad (1)$$

The majority of these complexes were rather unstable. When handled in an atmosphere of carbon monoxide they yielded $Rh_4(CO)_{12}$, a reaction which obviously has some relevance to the synthesis of $Rh_4(CO)_{12}$ under rather similar conditions[18,19]. Upon drying or storage for longer periods in solution under nitrogen or argon a black solid was precipitated, but this did not contain Rh carbonyl entities, and was most probably metallic rhodium. Because of this instability only the *p*-chlorophenolato derivative was isolated in a pure crystalline form suitable for analysis. The phenolato complex [(I), $R = C_6H_5$] was isolated below −30° in the form of yellow needles, but its composition had to be established by indirect methods (see Experimental). The methanolato-, n-propanolato- and i-pentanolato- derivatives were prepared in hexane, and identified by their IR spectra in the solution (Table 1).

TABLE 1

INFRARED SPECTRA (cm^{-1}) OF μ,μ-BIS(ALCOHOLATO)DIRHODIUM(I) TETRACARBONYL COMPLEXES IN THE CARBONYL STRETCHING REGION (HEXANE SOLUTION)

Compound	A_1	B_1	B_2	$\nu(^{13}CO)$
$Rh_2(CO)_4(OCH_3)_2$	2089.8 w	2071.4 s(br)	2008.9 s	1976.8 w
$Rh_2(CO)_4(OC_3H_7)_2$	2095.4 w	2070.5 s 2073.4 s	2003.3 s 2007.7 s	1975.7 w 1971.0 w
$Rh_2(CO)_4[OCH_2CH(CH_3)CH_2CH_3]_2$	2096.1 w	2070.6 s(br)	2003.5 s 2008.0 s	1975.2 w
$Rh_2(CO)_4(OC_6H_5)_2$	2095.4 w	2077.8 s 2080.5 s	2017.9 s	1986.0 w
$Rh_2(CO)_4(p\text{-}ClC_6H_4O)_2$	2095.8 w	2078.9 s 2082.9 s	2019.9 s	1988.2 w

Addition of triphenylphosphine in 2/1 P/Rh molar ratio solutions of the complexes obtained by reaction (1) gave the mononuclear $Rh(CO)(PPh_3)_2(OR)$ derivatives [(II), $R = n\text{-}C_3H_7$, C_6H_5, $p\text{-}ClC_6H_4$]:

$$Rh_2(CO)_4(OR)_2 + 4\ PPh_3 \rightarrow \underset{(II)}{2\ Rh(CO)(PPh_3)_2(OR)} + 2\ CO \qquad (2)$$

These compounds are more stable than the unsubstituted dimers of type (I). The formulation of complexes (II) as mononuclear derivatives was confirmed by their formation (in solution) from $Rh(CO)(PPh_3)_2Cl$ and NaOR. Some PBu_3 derivatives of type (II) were obtained in solution and identified by IR spectroscopy (Table 2).

2. *Spectroscopic investigations*

(*a*) *IR spectra.* The IR spectra of compounds (I) in the carbonyl stretching region are very similar to those of other $Rh_2(CO)_4X_2$ complexes. A typical spectrum

TABLE 2

CARBONYL STRETCHING FREQUENCIES (cm^{-1}) OF SOME PHOSPHINE DERIVATIVES OF ALCOHOLATORHODIUM CARBONYL COMPLEXES, $Rh(CO)(PR_3)_2(OR)$

Compounds	ν
$Rh(CO)(PBu_3)_2(OC_3H_7)$	1957.8[a]
$Rh(CO)(PPh_3)_2(OC_3H_7)$	1965.6[b]
$Rh(CO)(PBu_3)_2(OC_6H_5)$	1959.2[a]
$Rh(CO)(PPh_3)_2(OC_6H_5)$	1965.4[b]
$Rh(CO)(PBu_3)_2(p\text{-}ClC_6H_4O)$	1955.5[a]
$Rh(CO)(PPh_3)_2(p\text{-}ClC_6H_4O)$	1963.4[b]

[a] Hexane solution. [b] Nujol mull.

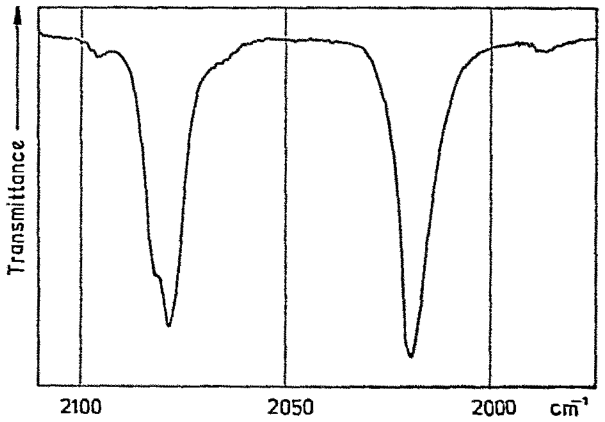

Fig. 2. IR spectrum of $Rh_2(CO)_4(p\text{-}ClC_6H_4O)_2$ in the carbonyl stretching region (in hexane).

is shown in Fig. 2, and the data for all compounds prepared are summarized in Table 1.

The A_1 (total symmetric) absorption bands are much less intense than those of the other $Rh_2(CO)_4X_2$ compounds. This can be attributed to the fact that the intensity of this band is the most sensitive to the "bridge geometry", *i.e.*, to the bending angle of the two $(CO)_2RhX_2$ planes. This latter is strongly influenced by the position of those orbitals of the bridging ligands which are able to interact with the two metal atoms. Thus in the case of the carboxylato derivatives, for example, this is the most intense band of the ν(C–O) spectrum[7], while with other bridging ligands it is much less intense than the B_1 and B_2 bands[1-4].

Another particular feature of the spectrum is that the B_1 band almost always appears as a doublet, the intensity ratio of the two bands changing with time and temperature. We attribute this to a *syn–anti* equilibrium, such as that which has been clearly demonstrated for analogous bridged iron carbonyls[11,12,15,16] and tentatively suggested for $Rh_2(CO)_4(RS)_2$ complexes[3]. The free energy change in such equilibria is always very low, and so the individual isomers could be separated only in a very few cases[11,12]. We assume that all other bands of the two forms are coincident and cannot be resolved under the conditions of our measurements.

(*b*). *^{1}H NMR spectra.* The ^{1}H NMR spectra of the complexes (I) were much less informative. The spectrum of the phenolato derivative showed a multiplet centered at δ 6.9 ppm (n-hexane, TMS), while the spectrum of the methyl derivative consisted of two peaks [intensity $\approx 1/1.5$ at δ 3.53 and 3.60 ppm ($CHCl_3$, TMS)]. The "splitting" of the methyl signal can be attributed to the *syn–anti* isomerism suggested above. We were not able to study the temperature dependence of this effect which could have been decisive on this point. Neither $^1H-^1H$ coupling between the two ligands nor $^1H-^{103}Rh$ coupling (*cf. e.g.*, ref. 13) was observed.

The ^{1}H NMR spectrum of the *p*-chlorophenolato derivatives shows an ill-shaped doublet at δ 6.7 and 6.9 ppm (n-hexane, TMS). The less intense bands of the A_2B_2 spectrum of the free ligand could not be observed because of the low solubility of this complex.

(*c*). An IR study of the reaction of complexes of type (I) with phosphines* revealed the appearance of bands characteristic of binuclear $Rh_2(CO)_3(PR_3)X_2$[9,17] species (in our case X = OR). Such complexes could not be isolated pure, but the circumstances of their formation, their spectra (Table 3) and their dark brown colour favour the suggested formulation.

TABLE 3

INFRARED SPECTRA (cm^{-1}) IN THE CARBONYL STRETCHING REGION FOR THE COMPLEXES $Rh_2(CO)_3(PBu_3)(OR)_2$ (HEXANE SOLUTION)

Compounds	*ν(CO)*		
$Rh_2(CO)_3(PBu_3)(OC_6H_5)_2$	2069.6 m	2007.1 s	1976.7 m
$Rh_2(CO)_3(PBu_3)(p\text{-}ClC_6H_4O)_2$	2070.7 m	2009.2 s	1979.3 m

EXPERIMENTAL

All reactions were carried out under argon or nitrogen. Molecular weights were measured with a Knauer vapour tension osmometer in hexane or benzene.

Infrared spectra were run on a UR 20 (VEB Carl Zeiss Jena) spectrometer with an LiF prism and NaCl cells. Wavenumber calibration was performed by simultaneous recording of DCl spectra. $[Rh(CO)_2Cl]_2$ was prepared by the established method[20]. ^{1}H NMR measurements were carried out on a Varian T-60 spectrometer, with an internal standard.

μ,μ-Bis(p-chlorophenolato)dirhodium(I) tetracarbonyl, $Rh_2(CO)_4(p\text{-}ClC_6H_4O)_2$

Rhodium carbonyl chloride (26 mg; 0.065 mmol) was stirred in hexane (10 ml) with an excess of sodium *p*-chlorophenolate (as a suspension) at 5° for 4 h. Filtration gave a clear yellow solution which on cooling to −30° deposited orange needles. These were filtered off and dried in vacuum. Yield: 19 mg. [Found: Rh, 36.4. Mol. wt. (in hexane), 584 ± 15. $C_{16}H_8Cl_2O_6Rh_2$ calcd.: Rh, 35.9%. Mol. wt., 572.8.]

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* PBu_3 was especially advantageous since its derivatives were readily soluble in hexane.

μ,μ-Bis(phenolato)dirhodium(I) tetracarbonyl, $Rh_2(CO)_4(OPh)_2$

Rhodium carbonyl chloride (26 mg) and a suspension of an excess of NaOPh were stirred in hexane (10 ml) for 3 h at room temperature. Filtration gave a light yellow solution. The rhodium content of this solution was 0.0128 g-atom Rh/l, while the molarity of the solution determined by osmometric method was 0.0062 mol/l. This corresponds to two Rh atoms per molecule. Cooling the filtrate to −30° gave yellow needles, which decomposed on drying even at −30°.

Phenolatobis(triphenylphosphine)carbonylrhodium(I), $Rh(CO)(PPh_3)_2(OPh)$

The hexane solution of μ,μ-bis(phenolato)dirhodium(I) tetracarbonyl was refluxed with an excess of triphenylphosphine for 3 h. Carbon monoxide was evolved. The complex separated as a yellow solid and was recrystallized from benzene. [Found: P, 7.8; Rh, 13.1. Mol. wt. (in benzene), 757±15. $C_{43}H_{35}O_2P_2Rh$ calcd.: P, 8.4; Rh, 13.8%. Mol. wt., 747.9.]

(p-Chlorophenolato)bis(triphenylphosphine)carbonylrhodium(I), $Rh(CO)(PPh_3)_2(p\text{-}ClC_6H_4O)$

This compound was prepared as described for the phenolato complex from μ,μ-bis(*p*-chlorophenolato)dirhodium(I) tetracarbonyl. (Found: P, 7.9; Rh, 13.4. Mol. wt., 794±15. $C_{43}H_{34}ClO_2P_2Rh$ calcd.: P, 7.9; Rh, 13.2%. Mol. wt., 782.4.)

Phenolatobis(triphenylphosphine)carbonylrhodium(I), preparation from $Rh(CO)(PPh_3)_2Cl$

$Rh(CO)(PPh_3)_2Cl$ (15 mg) in benzene solution was refluxed with an excess of NaOPh for 2 h. $Rh(CO)(PPh_3)_2(OPh)$ was identified by the IR spectrum of the solution.

n-Propylatobis(triphenylphosphine)carbonylrhodium(I), $Rh(CO)(PPh_3)_2(OPr)$

This complex was prepared as described for the phenolato complex from μ,μ-bis(n-propylato)dirhodium(I) tetracarbonyl. [Found: P, 8.0; Rh, 14.6. Mol wt. (in benzene), 745±15. $C_{40}H_{37}O_2Rh_2$ calcd.: P, 8.7; Rh, 14.4%. Mol. wt., 713.8.]

μ,μ-Bis(alcoholato)dirhodium(I) tributylphosphine tricarbonyl complexes

A dilute hexane solution of PBu_3 was added dropwise to a hexane solution of μ,μ-bis(alcoholato)dirhodium(I) tetracarbonyl complexes. At a Rh/PBu_3 2/1 ratio the colour of the reaction mixture was red-brown. The formation of the $Rh_2(CO)_3(PBu_3)(OR)$ complexes was monitored by the IR spectral change.

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