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PREPARATION AND STRUCTURE OF DI-(μ-SALICYLATO-O,O′)-BIS(1,5-CYCLOOCTADIENE)DIRHODIUM(I)

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Abstract—Di-(μ-salicylato-O,O′)-bis(1,5-cyclooctadiene)dirhodium(I) complex of the formula $[Rh(HOC_6H_4CO_2)\ (COD)]_2$ (COD = 1,5-cyclooctadiene), has been obtained in the reaction of $[RhCl(COD)]_2$ with silver salicylate. It has a dimeric structure with two bridging carboxylate groups, two terminally bounded COD and Rh···Rh distance of 3.325(3) Å. The α-hydroxyl group of the salicylate ligands forms intramolecular hydrogen bonding with the nearest oxygen of carboxylate group.

The hydroformylation of olefins is one of the most important industrial processes.[1] Rhodium based catalysts of high activity and selectivity, especially homogeneous, are of particular interest. Special efforts have been directed to studies which allow the prolongation of the life time of homogeneous industrial catalysts and to understand the effect of different species decreasing the catalytic activity of rhodium. It is well known that dioxygen may be one of those substances, inhibiting the hydroformylation reaction and changing the structure of the catalytically active form. It may first oxidize triphenylphosphine to triphenylphosphine oxide and then decrease activity or totally deactivate the rhodium catalyst.[2] Additionally, oxygen present in the system facilitates aldehyde oxidation to carboxylic acid which can then interact with the rhodium complex. Carboxylic acids may also be produced in carbonylation reaction of alcohols.

The main task of this paper was the isolation and structure determination of rhodium(I) species with carboxylate ligand in the coordination sphere as a product of possible reaction in the real catalytic systems used for olefin hydroformylation.

Hydroformylation of hex-1-ene with $[Rh(acac)(CO)(PPh_3)]$ in the presence of carboxylic acids has been reported recently.[3] Several rhodium complexes, products of reaction of rhodium catalyst with propionic or salicylic acids have been identified. Reaction of $[Rh(acac)(CO)(PPh_3)]$ with salicylic acid in the presence of free triphenylphosphine leads to the formation of a mixture of two species: $[Rh(HOC_6H_4CO_2)(CO)(PPh_3)_2]$ and $[Rh(HOC_6H_4CO_2)(CO)_2]_2$ (Scheme 1). We failed to isolate $[Rh(HOC_6H_4CO_2)(CO)_2]_2$ and its formula was proposed on the basis of UV-vis and IR studies. Formation of that complex "*in situ*", in the reaction mixture in the absence of CO, was quite unexpected. To confirm its structure we tried to obtain it in another way by substitution of COD by CO in $[Rh(HOC_6H_4CO_2)(COD)]_2$. In the first step by treating the dinuclear $[Rh(Cl)(COD)]_2$ complex with silver salicylate, chloride bridges were substituted by salicylate ligands and dimeric $[Rh(HOC_6H_4CO_2)(COD)]_2$ was formed. Its structure was determined by the X-ray diffraction.

Similar syntheses were frequently used for preparation dimeric rhodium(I) complexes, i.e.: $[Rh(RCO_2)(CO)_2]_2$ (R = CF_3, CH_3, p-FC_6H_4)[4]; $[Rh(RCO_2)(COD)]_2$ (R = $C_6H_5NHC_6H_4CO_2$[5], R = H, CH_3[6]); $[Rh(RCO_2)(NBD)]_2$ (R = CH_3, CH_2Cl, CH_2F); $[Rh(CH_3CO_2)(dcpd)]_2$ (dcpd = dicyclopentadiene][7], $[Rh(CH_3CO_2)(C_3H_5)_2]_2$.[8]

Using equimolar concentrations of potassium acetate and the rhodium complex $[RhCl(COD)]_2$ the dimer with chloride and carboxylate bridges, $[(COD)Rh(\mu\text{-}Cl)(\mu\text{-}CH_3CO_2)Rh(COD)]$ have been obtained and X-ray structure determined.[9] In the reaction of sodium benzoate or acetate with $[Rh(NBD)_2]BF_4$ the complexes of formula $[Rh(NBD)(RCO_2)]_2$, (where R = CH_3, C_6H_5) were prepared.[9]

Dimeric rhodium(I) carboxylates, $[Rh(HCO_2)$

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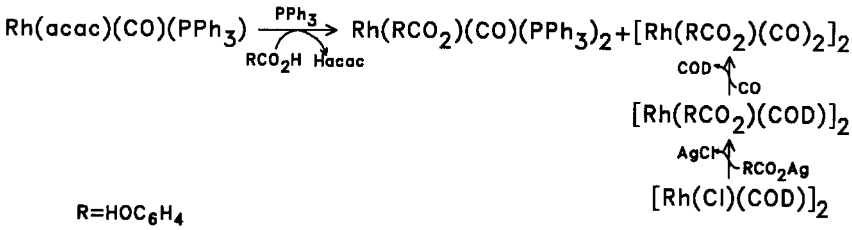

Scheme 1.

$(CO)_2]_2$ and $[Rh(CF_3CO_2)(NBD)]_2$ were obtained in reaction of rhodium(II) dimers, $[Rh_2(CH_3CO_2)_4]$[11] and $[Rh_2(CF_3CO_2)_4]$[12], respectively. Dimeric rhodium(II) oxalate, $[Rh(C_2O_4)_2(COD)]_2$, was obtained in reaction of Rh(acac)(COD) with oxalic acid.[13]

RESULTS AND DISCUSSION

The molecular structure of $[Rh(HOC_6H_4CO_2)(COD)]_2$ is shown in Fig. 1 and principal interatomic distances and angles are given in Table 1.

The Rh(1)···Rh(2) distance of 3.325(3) Å is comparable to that in dimeric rhodium(I) carboxylates with no direct metal–metal bonding: $[Rh(C_6H_5NHC_6H_4CO_2)(COD)]_2$ 3.424(3) Å[5], $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CH_3CO_2)(COD)_2]$ 3.161(1) Å[9] and $[Rh(CH_3CO_2)(NBD)]_2$ 3.1050(7) Å.[14] Shorter Rh···Rh distances were found in the dimers: $[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (R = CH_2Cl, $CHCl_2$, CCl_3, CF_3) and $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(dppm)_2]^+$ (dppm = diphenylophosphinometan) 2.784(2) Å[15] and 2.8415(7) Å.[16]

Each rhodium atom in $[Rh(HOC_6H_4CO_2)(COD)]_2$ has the coordination number four with the square planar configuration. Two coordination sites are occupied by oxygens of carboxylate ligands and two by the olefinic bonds of

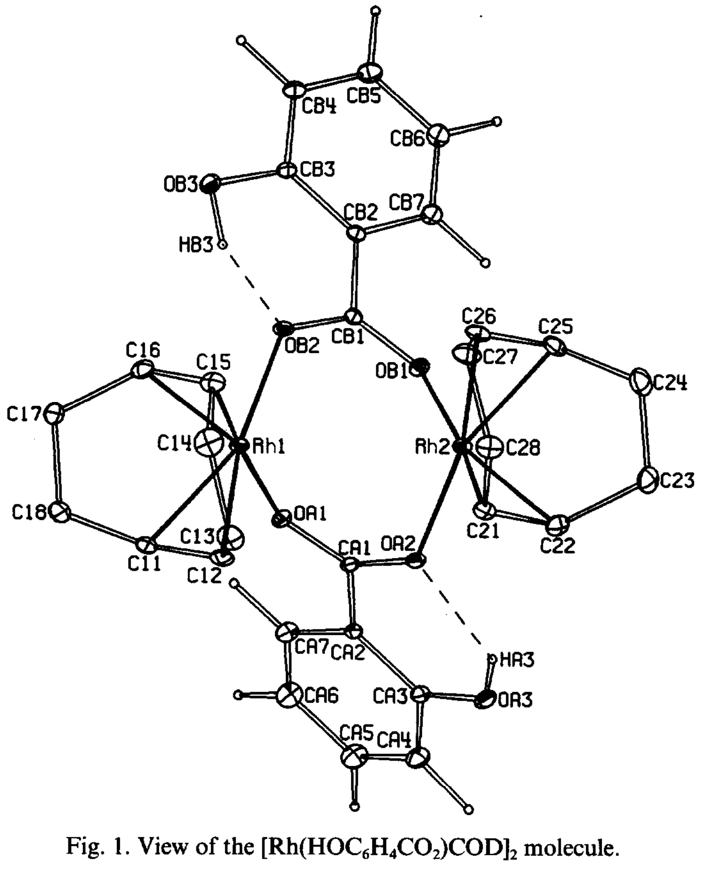

Fig. 1. View of the $[Rh(HOC_6H_4CO_2)COD]_2$ molecule.

Table 1. Selected interatomic distances (Å) and angles (°)

	Interatomic distances		
Rh(1)—O(A1)	2.111(3)	Rh(2)—O(A2)	2.113(3)
Rh(1)—O(B2)	2.095(3)	Rh(2)—O(B1)	2.123(3)
Rh(1)—C(15)	2.116(6)	Rh(2)—C(21)	2.101(6)
Rh(1)—C(16)	2.100(6)	Rh(2)—C(22)	2.113(6)
Rh(1)—C(11)	2.106(6)	Rh(2)—C(25)	2.115(6)
Rh(1)—C(12)	2.111(6)	Rh(2)—C(26)	2.111(6)
O(A1)—C(A1)	1.252(6)	O(A2)—C(A1)	1.278(6)
O(B2)—C(B1)	1.277(6)	O(B1)—C(B1)	1.255(6)
O(B2)···O(B3)	2.542(5)	O(A2)···O(A3)	2.559(5)
O(B2)···H(B3)	1.62(3)	O(A2)···H(A3)	1.91(7)
	Bond angles		
O(A1)—Rh(1)—O(B2)	90.8(2)	O(A2)—Rh(2)—O(B1)	91.9(2)
Rh(1)—O(A1)—C(A1)	127.5(4)	Rh(2)—O(A2)—C(A1)	125.0(4)
Rh(1)—O(B2)—C(B1)	128.1(4)	Rh(2)—O(B1)—C(B1)	126.0(4)
O(A1)—C(A1)—O(A2)	123.6(5)	O(B2)—C(B1)—O(B1)	123.6(5)
O(A1)—C(A1)—C(A2)	118.5(5)	O(B2)—C(B1)—C(B2)	116.9(5)
O(A2)—C(A1)—C(A2)	117.9(5)	O(B1)—C(B1)—C(B2)	119.5(5)
O(B3)—H(B3)···O(B2)	157(6)	O(A3)—H(A3)···O(A2)	122(5)

COD. The rhodium–oxygen distances are equal 2.111(3), 2.095(3), 2.113(3), 2.123(3) Å and comparable to similar bonds in other rhodium dimeric carboxylates.[5,9,14,15] Rhodium–carbon (COD) distances, equal 2.100(6)–2.116(6) Å, are close to those in other complexes of that type.[5,9] Carbon–carbon bond distances (single and olefinic) and angles within the cyclooctadiene group agree with those published for coordinated cyclooctadiene in other complexes.[5,9] The α-hydroxyl group of the salicylate ligands are hydrogen bonded to the nearest carboxyl oxygen (Table 1). In both crystallographically independent salicylate ligands the carboxylate group and carbon ring are almost coplanar. The angle between planes through the salicylate ligands is 83(1)°, similarly as found for the carboxylate groups of N-phenylanthranilate ligands in [Rh($C_6H_4NHC_6H_5CO_2$)COD]$_2$.[5]

The position of rhodium atoms with respect to the carboxylate ligand planes is the most remarkable difference between complexes [Rh($C_6H_4NHC_6H_5CO_2$)COD]$_2$ and [Rh($HOC_6H_4CO_2$)COD]$_2$. In [Rh($C_6H_4NHC_6H_5CO_2$)COD]$_2$ the rhodium atoms are situated in the planes of carboxylate groups. In contrast, in [Rh($HOC_6H_4CO_2$)COD]$_2$ both rhodium atoms are located out of the O(B2)C(B1)C(B2)O(B1) plane, Rh(1) 0.49(1) and Rh(2) −0.89(1) Å and out of the O(A1)C(A1)C(A2)O(A2) plane, Rh(1) 0.51(1) and Rh(2): −0.93(1) Å. The torsion angles Rh(1)—O(B2)—C(B1)—O(B1), O(B2)—C(B1)—O(B1)—Rh(2), Rh(2)—O(A2)—C(A1)—O(A1) and O(A2)—C(A1)—O(A1)—Rh(1) are −19.8(11)°, −28.6(10)°, −33.1(10)° and −17.3(10)°, respectively.

The difference in arrangement of carboxylate groups in both complexes can be explained as a result of hydrogen bond formation and repulsion of cyclooctadiene ligands in [Rh($HOC_6H_4CO_2$)COD]$_2$. The engagement of carboxyl oxygen in hydrogen bonding reduces the bond angle of Rh(1)—O(B2)—C(B1) to 128.1(4)° and Rh(2)—O(A2)—C(A1) to 125.0(4)°. In [Rh($C_6H_5NHC_6H_4CO_2$)COD]$_2$, where hydrogen bonding is not present the corresponding angles are *ca* 140°. The decrease of Rh—O—C angles causes the simultaneous decrease of Rh···Rh and COD···COD distances. The way of diminishing of COD ligand repulsion is through twisting. In such a way the shortest distance between carbon atoms of different COD ligands is *ca* 3.90(1) Å and is well comparable with that of 3.82 Å in [Rh($C_6H_5NHC_6H_4CO_2$)COD]$_2$.[17]

EXPERIMENTAL

Preparation

The [Rh($HOC_6H_4CO_2$)(COD)]$_2$ complex was obtained according to the earlier described procedure.[3] 0.19 g [RhCl(COD)]$_2$ and 0.19 g [$HOC_6H_4CO_2Ag$] were added to 25 cm^3 heptane, in which both substrates are sparingly soluble. The colourless solution turned dark yellow during stirring at room temperature. After 2 h the precipitate consisting of AgCl formed and unreacted substrates were separated from the yellow solution and washed repeatedly with heptane, until a colourless filtrate was obtained. The primary yellow solution and the yellow filtrates were collected and evaporated. The light-yellow precipitate of complex $[Rh(HOC_6H_4CO_2)(COD)]_2$ formed was filtered off and dried *in vacuo*. Yield: 80%. IR (KBr) 1625(m), 1587(m), 1562(vs), 1460(m), 1380(vs), 755(s) cm^{-1}. UV-vis (toluene) 30700 cm^{-1} (17300 M^{-1} cm^{-1}), 24200 cm^{-1} (3200 M^{-1} cm^{-1}) ^1H NMR ($CDCl_3$) $\delta = 1.88$ (4H, CH_2-CH_2-$CH =$), $\delta = 2.81$ (4H, CH_2-CH_2-$CH =$), $\delta = 4.29$ (4H, -$CH = CH$-), $\delta = 6.76$ (2H, Ph), 7.26 (1H, Ph) $\delta = 7.68$ (1H, Ph), $\delta = 10.68$ (1H, O*H*) ppm.

Structure determination

Crystal data. $C_{30}H_{34}O_6Rh_2$, M = 696.4, $a = 13.258(7)$, $b = 12.984(8)$, $c = 16.352(8)$ Å, $\beta = 96.46(4)°$, $U = 2797(3)$ $Å^3$, D_m (by flotation) = 1.654 g cm^{-3}, $Z = 4$, $D_c = 1.654(3)$ g cm^{-3}, $F(000) = 1408$, space group $P2_1hc$, Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu = 101.4$ cm^{-1}, $T =$ 297(2) K.

The compound crystallized with columnar habit. A specimen of dimensions *ca* 0.1 < 2R < 0.25 mm was selected. Intensity data were recorded on a Kuma KM4 automated diffractometer using graphite monochromatized Cu-K_α radiation. Intensities were measured using 2θ-ω technique, up to $2\theta = 150°$. Intensities of three standard reflections monitored after every 100 intensity scan decreased approximately 15%. 5564 recorded data were rescaled according to the intensities of the control reflections and were corrected for Lorentz and polarization factors.

The structure was solved by direct methods and refined by the full-matrix least squares using program SHELX-76.[18] The carbon bonded H-atoms were included in geometry calculated positions with d(C-H) = 1.08 Å. The O bonded H-atoms were found from difference map and refined with constraints that d(O-H) = 0.97 Å. An absorption correction following the DIFABS[19] procedure was applied; minimal and maximal absorption corrections were 0.93 and 1.124. Least-squares refinement converged with $R = 0.0277$ and $R_w = 0.0327$, where $w = 1/\sigma^2(F_0)$, for 3688 reflections with $I > 3\sigma(I)$. Neutral-atom scattering factors were taken from ref. 20. The scattering factors for non-hydrogen atoms were corrected for real and imaginary components.

Atomic coordinates, displacement factor coefficients and the list of F_o/F_c values have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

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