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Preliminary communication

INSERTION OF CARBON DIOXIDE INTO THE RHODIUM—CARBON BOND

THE STRUCTURE OF TRIS(TRIPHENYLPHOSPHINE)RHODIUM BENZOATE

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Summary

Carbon dioxide acts on the $(Ph_3P)_3RhPh$ with formation of $(Ph_3P)_3OOCPh$. The crystal structure of this compound has been determined by X-ray diffraction.

In the recent years considerable attention has been paid to CO_2 insertion into the transition metal—carbon σ-bond. The insertion of carbon dioxide into titanium (zirconium)—carbon [1—3], cobalt—carbon [4—6], copper—carbon [7, 8] and zinc—carbon [9, 10] bonds has been described.

We found that carbon dioxide may readily insert into the rhodium—carbon σ-bond in the monovalent rhodium triphenylphosphine complex $(Ph_3P)_3RhPh$ to give the carboxylate complex $(Ph_3P)RhOOCPh$. The initial complex was prepared by a published method [11].

Carbon dioxide reacted with tris(triphenylphosphine)phenylrhodium at room temperature under CO_2 pressure (1.2 mmole of $(Ph_3P)_3RhPh$, 12 ml of benzene, 20 atm CO_2, 24 h) to form red crystals, m.p. 135—137°. Found: C, 72.21; H, 4.68; P, 8.53. $C_{61}H_{50}P_3PO_2$ calcd.: C, 72.47; H, 4.95; P, 9.20%.

The action of mineral acid on the complex obtained yields benzoic acid, while methanol and BF_3 give methyl benzoate.

The same complex was obtained in the reaction of stoichiometric quantities of benzoic acid and $(Ph_3P)_3RhOH$, described earlier by Ugo et al. [12]. The IR spectrum of $(Ph_3P)_3RhOOCPh$ shows the absorption bands characteristic of transition metal carboxylate complexes: $\nu(OCO)_{as}$ 1608 s and 1570 s, and $\nu(OCO)_s$ 1360 vs (cm^{-1}).

According to the data of X-ray analysis tris(triphenylphosphine)rhodium benzoate crystallizes in the form of benzene solvate $(Ph_3P)_3RhOOCPh \cdot 0.5\ C_6H_6$.

The crystals are triclinic $a = 12.162(3)$, $b = 9.809(2)$, $c = 22.880(5)$ Å, $\alpha = 98.08(4)$, $\beta = 97.97(2)$, $\gamma = 75.11(3)^\circ$, $Z = 2$, space group $P1$.

The intensities of 2587 reflections with $F_2 \geqslant 5\ \sigma\ (F^2)$ were measured on an automatic Hilger Watts four-circle diffractometer. The structure was decoded by heavy atom technique and corrected by the least-square method in isotopic approximation to $R = 6.8\%$.

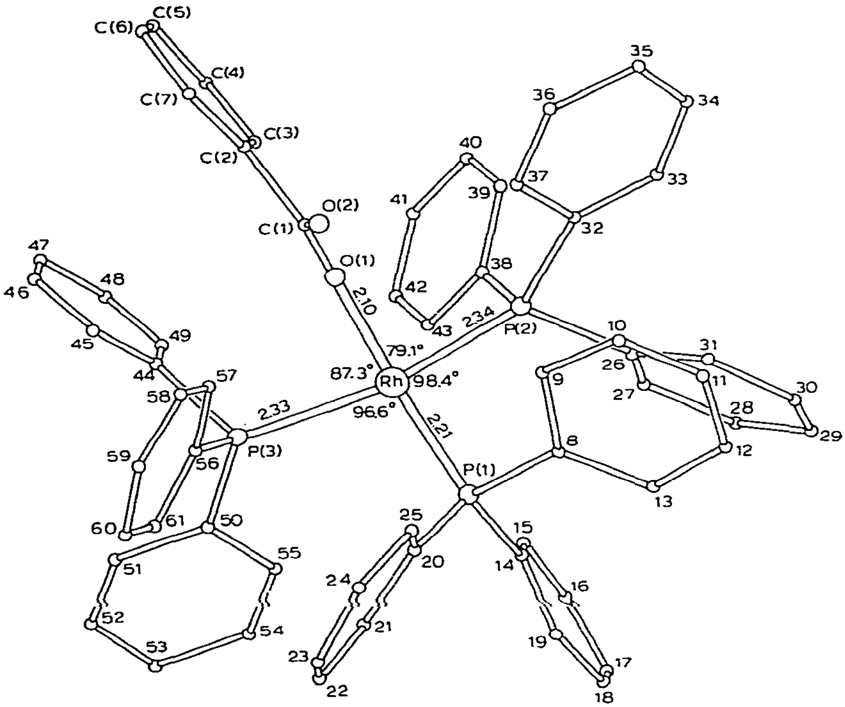

Fig. 1. The structure of $(Ph_3P)_3RhOOCPh \cdot 0.5\ C_6H_6$.

The complex is monomeric (Fig. 1) the rhodium atom being coordinated with three Ph_3P ligands and benzoate ligand by monodentate bonding, which occurs rather rarely among the transition metal carboxylate complexes. The rhodium coordination is almost square planar, somewhat distorted owing to the steric hindrance of the bulky triphenylphosphine ligands. The non-bonded distance Rh···O(2) equal to 3.230 Å shows the absence of any noticeable interaction between these atoms but does not exclude the possibility of a weak additional coordination. It can be noted that apical sites in the rhodium coordination polyhedron are shielded with hydrogen atoms bound to C(9) and C(43) (Rh···H(9), 2.79, Rh···H(43) 2.93 Å), the H positions being found from geometric considerations.

It should be noted that the insertion of carbon dioxide at the rhodium—carbon σ-bond occurs easily only for monovalent rhodium compounds. An attempt to obtain rhodium carboxylate complexes by action of carbon dioxide (pressure 30 atm, temperature 20—100°) on the complexes $L_3Rh^{III}(C_2H_5)Cl_2$ [14], $L_3Rh^{III}Cl(I)CH_3$ and $L_3Rh^{III}Cl(I)C_2H_5$ (where $L = Ph_3P$) [15] was unsuccessful.

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