Carbon Dioxide Activation; Formation of *trans*-$(Ph_3P)_2Rh(CO)(OCO_2H)$ in the Reaction of CO_2 with $HRh(CO)(PPh_3)_3$–CO and the Determination of its Structure by *X*-Ray Crystallography

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Summary The intermediate produced from the interaction of $HRh(CO)(PPh_3)_3$ with CO reacts with carbon dioxide to yield a novel hydrogencarbonate complex, *trans*-$(Ph_3P)_2Rh(CO)(OCO_2H)$ (**1**), whose structure has been established by *X*-ray crystallography; (**1**) undergoes reversible loss of CO_2.

THE search for alternative fuels and chemical feedstocks has stimulated considerable interest in the activation of carbon oxides by transition metals. While there exists a long-standing and rich chemistry of co-ordinated carbon monoxide, the co-ordination chemistry of carbon dioxide is largely unknown.[1] We report herein a novel hydrogencarbonate complex, $(Ph_3P)_2Rh(CO)(OCO_2H)$ (**1**), produced *via* a previously unknown pathway from the reaction of CO_2 with $HRh(CO)(PPh_3)_3$–CO.

When a yellow benzene solution of $HRh(CO)_2(PPh_3)_2$ and $Rh_2(CO)_4(PPh_3)_4$ [formed by pretreatment of $HRh(CO)(PPh_3)_3$ with CO[2]] was stirred for *ca.* 36 h under an atmosphere of pure CO_2 at 5 °C, the solution slowly turned red then yellow again with the formation of a yellow precipitate of (**1**) (70% yield, equation 1). Compound (**1**) had the composition $Rh(PPh_3)_2C_2HO_4$, produced CO and CO_2 (*ca.* 1 : 1) upon pyrolysis, and exhibited the following spectroscopic properties: i.r. (KBr) ν_{max} 1970s, 1600m, 1500m, and 1350m cm^{-1}; ^1H n.m.r. (CD_2Cl_2) δ 7·25 (br. m). The structure of (**1**) was established by an *X*-ray study[3] of single crystals grown at −10 °C from CO_2-saturated CH_2Cl_2.

$$\begin{array}{ccc} HRh(CO)(PPh_3)_3 & \xrightarrow[\text{benzene}]{\text{CO}} & \left[\begin{array}{c} HRh(CO)_2(PPh_3)_2 \\ + \\ Rh_2(CO)_4(PPh_3)_4 \\ \text{(yellow)} \end{array}\right] \\ \text{(yellow)} & & \downarrow CO_2 \\ & & (\mathbf{1}) \\ & & (\rightarrow \text{red} \rightarrow \text{yellow}) \end{array} \qquad (1)$$

Crystal data: $C_{38}H_{31}O_4P_2Rh\cdot 2CH_2Cl_2$, M = 886·4, triclinic, space group $P\bar{1}$, a = 12·702(2), b = 14·736(2), c = 11·582(2) Å, α = 99·46(1), β = 107·56(1), γ = 98·258(1)°, U = 1995·2 Å^3. All *X*-ray measurements were carried out on a Syntex $P2_1$ automatic diffractometer (Mo-K_α radiation, graphite monochromator), where the crystal was maintained at −100 °C in a dry N_2 stream. The unit cell contains two molecules of CH_2Cl_2 of solvation. Using 6573 reflections with $I_0 > 3\cdot 0\sigma(I_0)$, the structure was solved by conventional heavy-atom methods and refined to final R and R_w values of 0·040 and 0·043, respectively. Refinement included treatment of phenyl rings as rigid groups, but independent refinement of all other parameters, including those of the solvent hydrogen atoms.†

The molecular structure (Figure) consists of a square-planar arrangement of *trans*-triphenylphosphine, CO, and hydrogencarbonate ligands about Rh; the five atoms Rh, P(1), P(2), C(1), and O(2) are coplanar to within 0·01 Å. The hydrogencarbonate plane (also ± 0·01 Å) makes an angle of 85·2° with the metal co-ordination plane, compared with 73° in (hydrogencarbonato)methyl-*trans*-bis(triethylphosphine)palladium(II).[4] Pairs of molecules are hydrogen-bonded through the hydrogencarbonate ligands across crystallographic inversion centres, in a manner similar to the aforementioned Pd^{II} complex, except that in (**1**) the C–O

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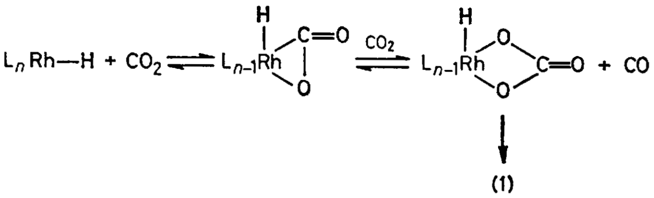
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

distances (Figure) are significantly different, the hydrogencarbonate hydrogen being attached to the oxygen with the longest C–O bond.‡



SCHEME

Regarding the mechanism leading to (**1**), especially the origin of the hydrogencarbonate ligand, the *major* pathway leading to (**1**) apparently does *not* involve adventitious moisture as demonstrated by the following observations: (i) neither intentional addition of H_2O to the reaction medium nor scrupulous drying of all materials and glassware had any significant effect on the yield or rate of formation of (**1**); (ii) starting with $DRh(CO)(PPh_3)_3$ (*ca.* 66 atom % D), product (**1**) was obtained, substantially deuterium-enriched (*ca.* 33 atom %, calculated from the H_2O: D_2O ratio produced on pyrolysis).§ These results are consistent with a mechanism involving initial rhodium-promoted reductive disproportionation of CO_2[7,8] followed by H-transfer from Rh to the O of the co-ordinated carbonate (Scheme). Our preliminary attempts to isolate the red suspected precursor to (**1**) (possibly a hydrido-CO_2 or hydrido-carbonate species) have resulted in rapid conversion, even in the solid state, into (**1**).

While solutions of (**1**) in CO_2-saturated CH_2Cl_2 are stable at 0 °C for several hours, under an atmosphere of argon (**1**) is rapidly converted with loss of CO_2, PPh_3 and H_2O(?) into a new material (**2**) [i.r. ν_{max} 1970s, 1502s, and 1190m cm^{-1}; Ph_3P/Rh *ca.* 1·5]. Interestingly, pyrolysis of (**2**) still produced CO_2 (1 CO_2/2 Rh/3 PPh_3) and (**2**) was reconverted into (**1**) in the presence of CO_2, PPh_3, and H_2O (equation 2).

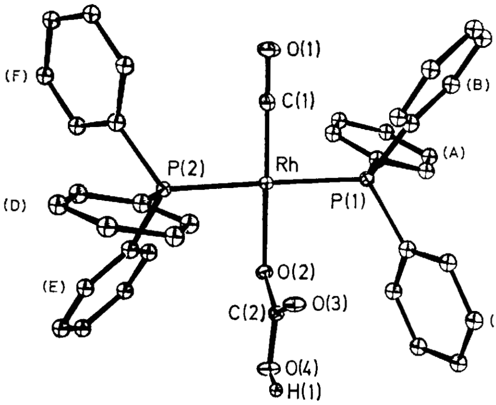


FIGURE. A view of the structure of (**1**). Principal bond lengths (Å): Rh–C(1) 1·798(4), Rh–P(1) 2·333(1), Rh–P(2) 2·332(1), Rh–O(2) 2·075(2), O(2)–C(2) 1·283(4), C(2)–O(3) 1·243(4), C(2)–O(4) 1·336(4). Principal bond angles (°): C(1)–Rh–P(1) 89·1(1), C(1)–Rh–P(2) 91·8(1), O(2)–Rh–P(1) 90·4(1), O(2)–Rh–P(2) 88·7(1), Rh–O(2)–C(2) 118·6(2), O(2)–C(2)–O(3) 124·8(3), O(2)–C(2)–O(4) 113·2(3), O(3)–C(2)–O(4) 122·0(3).

Based on these results we tentatively formulate (**2**) as a binuclear carbonate complex, $(PPh_3)_2(CO)Rh(\mu\text{-}CO_3)Rh(CO)(PPh_3)$.¶

$$\underset{(\mathbf{1})}{2\,(Ph_3P)_2Rh(CO)(OCO_2H)} \underset{CH_2Cl_2}{\leftrightharpoons} \underset{(\mathbf{2})}{[(Ph_3P)_3(CO)_2Rh_2](\mu\text{-}CO_3)} + CO_2 + PPh_3 + H_2O(?) \qquad (2)$$

Support from the Office of Naval Research and the Alfred P. Sloan Foundation (K.M.N.) and the Robert A. Welch Foundation (R.E.D.) is acknowledged. The Texas group is also grateful to the National Science Foundation for the purchase of the Syntex $P2_1$ diffractometer and an N.S.F. Undergraduate Research Participation award (C.L.T.).

(*Received, 7th November* 1980; *Com.* 1203.)

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‡ The formation of $(Ph_3P)_2Rh(CO)(OCO_2H)$ from $(Ph_3P)_2Rh(CO)OH$ and CO_2 has been mentioned in two earlier reports. The i.r. spectrum of our authentic (**1**) is identical to that of the compound prepared by Otsuka *et al.*,[5] but at variance with that of Vaska's product,[6] the formulation of which has been questioned.[5]

§ No D/H exchange was observed between $DRh(CO)(PPh_3)_3$ and H_2O in benzene at 20 °C over a few hours.

¶ A similar decomposition mode has been postulated for the corresponding $(R_3P)_2Rh(CO)OCO_2H$ complexes (R = cyclohexyl or Pr^i).[5] The related perphosphinated derivative, $Rh_2(PPh_3)_5(\mu\text{-}CO_3)$, is known[8] [$\nu(CO_3)$ 1485 and 1465 cm^{-1}].

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