

Carbon Dioxide Activation; Formation of *trans*-(Ph₃P)₂Rh(CO)(OCO₂H) in the Reaction of CO₂ with HRh(CO)(PPh₃)₃-CO and the Determination of its Structure by X-Ray Crystallography

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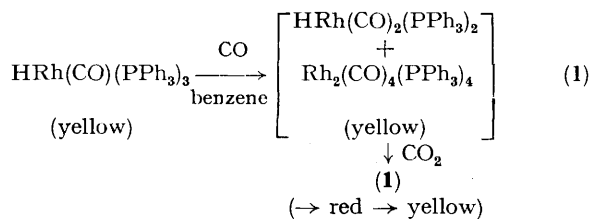
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Summary The intermediate produced from the interaction of HRh(CO)(PPh₃)₃ with CO reacts with carbon dioxide to yield a novel hydrogencarbonate complex, *trans*-(Ph₃P)₂-Rh(CO)(OCO₂H) (**1**), whose structure has been established by X-ray crystallography; (**1**) undergoes reversible loss of CO₂.

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, (Ph₃P)₂Rh(CO)(OCO₂H) (**1**), produced *via* a previously unknown pathway from the reaction of CO₂ with HRh(CO)(PPh₃)₃-CO.

When a yellow benzene solution of HRh(CO)₂(PPh₃)₂ and Rh₂(CO)₄(PPh₃)₄ [formed by pretreatment of HRh(CO)(PPh₃)₃ with CO²] was stirred for *ca.* 36 h under an atmosphere of pure CO₂ 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



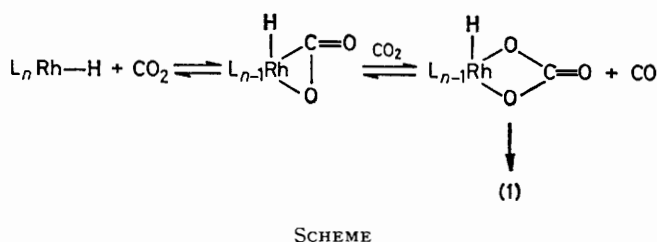
composition Rh(PPh₃)₂C₂H₄O₄, produced CO and CO₂ (*ca.* 1:1) upon pyrolysis, and exhibited the following spectroscopic properties: i.r. (KBr) ν_{max} 1970s, 1600m, 1500m, and 1350m cm⁻¹; ¹H n.m.r. (CD₂Cl₂) δ 7.25 (br. m). The structure of (**1**) was established by an X-ray study³ of single crystals grown at -10 °C from CO₂-saturated CH₂Cl₂.

Crystal data: C₃₈H₃₁O₄P₂Rh·2CH₂Cl₂, *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 Å³. All X-ray measurements were carried out on a Syntex P2₁ automatic diffractometer (Mo-K α radiation, graphite monochromator), where the crystal was maintained at -100 °C in a dry N₂ stream. The unit cell contains two molecules of CH₂Cl₂ of solvation. Using 6573 reflections with *I*₀ > 3.0σ(*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

† 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 hydrogen-carbonate hydrogen being attached to the oxygen with the longest C-O bond. ‡



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 H₂O 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)(PPh₃)₃ (*ca.* 66 atom % D), product (1) was obtained, substantially deuterium-enriched (*ca.* 33 atom %), calculated from the H₂O: D₂O ratio produced on pyrolysis).§ These results are consistent with a mechanism involving initial rhodium-promoted reductive disproportionation of CO₂,^{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-CO₂ or hydrido-carbonate species) have resulted in rapid conversion, even in the solid state, into (1).

While solutions of (1) in CO₂-saturated CH₂Cl₂ are stable at 0 °C for several hours, under an atmosphere of argon (1) is rapidly converted with loss of CO₂, PPh₃ and H₂O(?) into a new material (2) [i.r. ν_{max} 1970s, 1502s, and 1190m cm⁻¹; Ph₃P/Rh *ca.* 1.5]. Interestingly, pyrolysis of (2) still produced CO₂ (1 CO₂/2 Rh/3 PPh₃) and (2) was reconverted into (1) in the presence of CO₂, PPh₃, and H₂O (equation 2).

‡ The formation of (Ph₃P)₂Rh(CO)(OCO₂H) from (Ph₃P)₂Rh(CO)OH and CO₂ 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)(PPh₃)₃ and H₂O in benzene at 20 °C over a few hours.

¶ A similar decomposition mode has been postulated for the corresponding (R₃P)₂Rh(CO)OCO₂H complexes (R = cyclohexyl or Pr).⁵ The related perchlorinated derivative, Rh₂(PPh₃)₆(μ-CO₃), is known⁸ [ν(CO₃) 1485 and 1465 cm⁻¹].

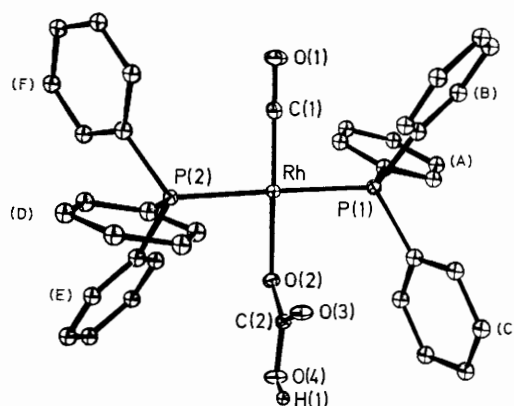
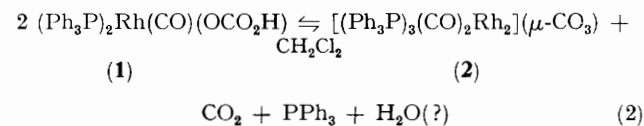


FIGURE. A view of the structure of (1). Principal bond lengths (Å): Rh-C(1) 1.798(4), Rh-P(1) 2.333(1), Rh-P(2) 2.332(1), Rh-O(2) 2.075(2), O(2)-C(2) 1.283(4), C(2)-O(3) 1.243(4), C(2)-O(4) 1.336(4). Principal bond angles (°): C(1)-Rh-P(1) 89.1(1), C(1)-Rh-P(2) 91.8(1), O(2)-Rh-P(1) 90.4(1), O(2)-Rh-P(2) 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, (PPh₃)₂(CO)Rh(μ-CO₃)Rh(CO)(PPh₃). ¶



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