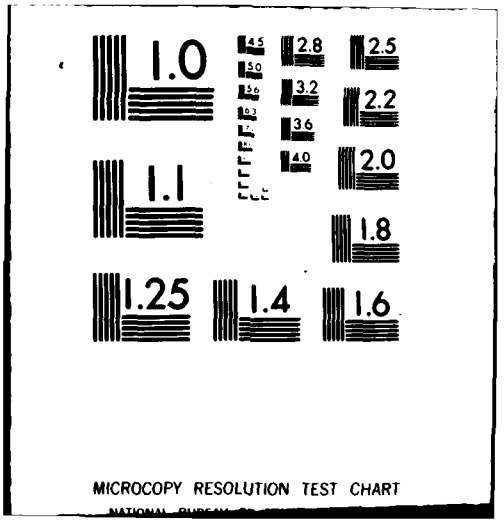
AD-A092 211 BOSTON COLL CHESTNUT HILL MASS DEPT OF CHEMISTRY F/G 7/2
CARBON DIOXIDE ACTIVATION: FORMATION OF TRANS- (PH3P) 2RH(CO) (--ETC(U)
NOV 80 S F HOSSAIN, K M NICHOLAS, C L TEAS N00014-78-C-0558
UNCLASSIFIED TR-2 NL

END
DATE FILMED
-81
DTIC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART

OFFICE OF NAVAL RESEARCH
Contract N00014-78-C-0558
Task No. NR 053-683
Technical Report No. 2

Carbon Dioxide Activation; Formation of trans-$(Ph_3P)_2Rh(CO)(OCO_2H)$ in the Reaction of CO_2 with $HRh(CO)(PPh_3)_3/CO$.

by

S. Fazley Hossain, Kenneth M. Nicholas*, Carol L. Teas and Raymond E. Davis

Boston College
Department of Chemistry
Chestnut Hill, Massachusetts 02167

Prepared for Publication
in
Chemical Communications

November 11, 1980

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2	2. GOVT ACCESSION NO. AD-A092 211	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Carbon Dioxide Activation; Formation of trans-$(Ph_3P)_2Rh(CO)(OCO_2H)$ in the Reaction of CO_2 with $HRh(CO)(PPh_3)_3/CO$		5. TYPE OF REPORT & PERIOD COVERED 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) S.F. Hossain, K.M. Nicholas*, C.L. Teas, and R.E. Davis		8. CONTRACT OR GRANT NUMBER(s) N 00014-78-C-0558
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Boston College Chestnut Hill, MA 02167		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-683
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE 11/12/80 13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Chemical Communications.

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Activation of CO_2, hydrido rhodium complexes, bicarbonate complex, reversible CO_2 fixation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The intermediate produced from the interaction of $HRh(CO)(PPh_3)_3$ with CO reacts with CO_2 to yield a novel bicarbonate complex, trans-$(PPh_3)_2Rh(CO)(OCO_2H)$ (I) whose structure has been established X-ray crystallographically. The bicarbonate complex undergoes reversible loss of CO_2. Results from the reaction of $DRh(CO)(PPh_3)_3/CO$ with CO_2 are consistent with a mechansim for formation of I involving rhodium-promoted CO_2 disproportionation followed by H transfer from Rh to O of coordinated carbonate.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Carbon Dioxide Activation; Formation of trans-$(Ph_3P)_2Rh(CO)(OCO_2H)$ in the Reaction of CO_2 with $HRh(CO)(PPh_3)_3/CO$.

By S. Fazley Hossain, Kenneth M. Nicholas*, (Department of Chemistry, Boston College, Chestnut Hill, Massachusetts, U.S.A. 02167)
Carol L. Teas, and Raymond E. Davis*(Department of Chemistry, University of Texas, Austin, Texas, U.S.A. 78712)

Summary. The intermediate produced from the interaction of $HRh(CO)(PPh_3)_3$ with CO reacts with carbon dioxide to yield a novel bicarbonate complex, trans-$(PPh_3)_2Rh(CO)(OCO_2H)$(I), whose structure has been established X-ray crystallographically; I 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 coordinated carbon monoxide, the coordination chemistry of carbon dioxide is largely unknown.[1] We report herein a novel bicarbonate complex, $(Ph_3P)_2Rh(CO)(OCO_2H)$(I), produced via a previously unrecognized 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 hr under an atmosphere of pure CO_2 at 5°C, the solution slowly

turned red then yellow again with formation of a yellow precipitate of I (70% yield, eq. 1).

$$HRh(CO)(PPh_3)_3 \xrightarrow[\text{benzene}]{CO} \left[\begin{array}{c} HRh(CO)_2(PPh_3)_2 \\ + \\ Rh_2(CO)_4(PPh_3)_4 \end{array}\right] \xrightarrow{CO_2} \underline{I} \qquad (1)$$

(yellow) (yellow) (red-yellow)

Compound I 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: IR(KBr): 1970(s), 1600(m), 1500(m), 1350(m); NMR(CD_2Cl_2,δ):7.25(bm). The structure of I was established by an X-ray study[3] of single crystals grown at -10° from CO_2-saturated CH_2Cl_2.

Crystal data: (I) $C_{38}H_{31}O_4P_2Rh \cdot 2\ CH_2Cl_2$, 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 $P2_1$ autodiffractometer (MoKα 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 6473 reflections with $I_o > 3.0\sigma_{I_o}$, the structure was solved by conventional heavy-atom methods and refined to final R and wR 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.†

† Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB11EW. Any request should be accompanied by the full literature citation for this communication.

The molecular structure (Figure) consists of a square planar arrangement of trans-triphenylphosphines, CO, and bicarbonate ligands about Rh; the five atoms Rh, P1, P2, C1, O2 are coplanar to within 0.01Å. The bicarbonate plane, (also ± 0.01Å) makes an angle of 85.2° with the metal coordination plane compared with 73° in (bicarbonato)-methyl-trans-bis(triethylphosphine)palladium(II).[4] Pairs of molecules are hydrogen bonded through the bicarbonate ligands across crystallographic inversion centers, in a manner similar to the afore-mentioned Pd(II) complex, except that in I the C-O distances (Figure) are significantly different, the bicarbonato hydrogen being attached to the oxygen with the longest C-O bond.‡

Regarding the mechanism leading to I, especially the origin of the bicarbonate ligand, the major pathway leading to I apparently does not involve adventitious moisture as demonstrated by the following observations: 1) 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 I; 2) starting with $DRh(CO)(PPh_3)_3$ (ca. 66 atom %), product I was obtained, substantially deuterium-enriched (ca. 33 atom %, calculated from H_2O/D_2O ratio produced on pyrolysis).§ These results are consistent with a mechanism

‡ 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 IR spectrum of our authentic I is identical to the compound prepared by Otsuka and Ibers,[5] but at variance with 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° over a few hours.

involving initial rhodium-promoted reductive disproportionation of CO_2[7,8] followed by H-transfer from Rh to O of coordinated carbonate (Scheme I). Our preliminary attempts to isolate the red suspected precursor to I (possibly a hydrido-CO_2 or hydrido-carbonate species) have resulted in rapid conversion, even in the solid state, to I.

While solutions of I in CO_2-saturated CH_2Cl_2 are stable at 0° for several hours, under an atmosphere of argon I is rapidly converted with loss of CO_2, PPh_3 and H_2O(?) to a new material II (IR: 1970(s), 1502(s), 1190(m) cm^{-1}; Ph_3P/Rh ca. 1.5). Interestingly, pyrolysis of II still produced CO_2 (1 CO_2/2 Rh/3 PPh_3) and II was reconverted to I in the presence of CO_2, PPh_3, and H_2O (eq. 2). Based on these results we tentatively formulate II as a binuclear carbonate complex, $(PPh_3)_2(CO)$-$Rh(\mu\text{-}CO_3)Rh(CO)(PPh_3)$.§§

$$\underset{\text{I}}{2\ (Ph_3P)_2Rh(CO)(OCO_2H)} \xrightarrow[CH_2Cl_2]{} \underset{\text{II}}{[(Ph_3P)_3(CO)_2Rh_2](\mu\text{-}CO_3)} + CO_2 + PPh_3 + H_2O(?) \qquad (2)$$

Support from the Office of Naval Research and 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

§§ A similar decomposition mode has been postulated for the corresponding $(R_3P)_2Rh(CO)OCO_2H$ complexes (R = cyclohexyl, i-propyl).[5] The related perphosphinated derivative, $Rh_2(PPh_3)_5(\mu\text{-}CO_3)$, is known[6] ($\nu_{CO_3}$ 1485, 1465 cm^{-1}).

Foundation for the purchase of the Syntex $P2_1$ diffractometer and an NSF Undergraduate Research Participation award (C.L.T.).

[1] Review: M.E. Volpin and L.S. Kolmnikov, 'Organometallic Reactions', 1975, 5,313; see also references in V.D. Bianco, S. Doronzo, and N. Gallo, Inorg. Nucl. Chem. Lett., 1979, 15, 187.

[2] D. Evans, G. Yagupsky, and G. Wilkinson, J. Chem. Soc. A, 1968, 2660.

[3] Details of the X-ray structure determination method are essentially as previously described: P.E. Riley and R.E. Davis, Acta Crystallogr., 1976, B32, 381.

[4] R.J. Crutchley, J. Powell, R. Faggiani, and C.J.L. Lock, Inorg. Chim. Acta, 1977, 24, L 15.

[5] T. Yoshida, D.L. Thorn, T. Okano, J.A. Ibers, and S. Otsuka, J. Am. Chem. Soc., 1979, 101, 4212.

[6] B.R. Flynn and L. Vaska, J. Am. Chem. Soc., 1973, 95, 5081.

[7] T. Herskovitz, J. Am. Chem. Soc., 1977, 99, 2391; J. Chatt, M. Kubota, G. Leigh, F.C. March, R. Mason, and D.J. Yarrow, J. Chem. Soc. Chem. Commun., 1974, 1033; G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, J. Am. Chem. Soc., 1979, 101, 1767; G.O. Evans, W.F. Walter, D.R. Mills, and C.A. Streit, J. Organometal. Chem., 1978, 144, C 34; K.M. Nicholas, ibid, 1980, 188, C 10.

[8] S. Krogsrud, S. Komiya, T. Ito, J.A. Ibers, and A. Yamamoto, Inorg. Chem., 1976, 15, 2798.

Scheme I

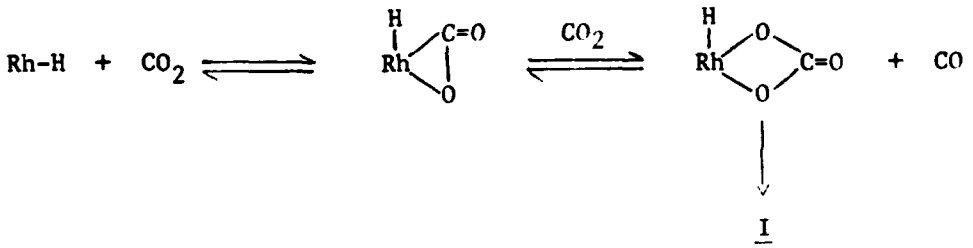
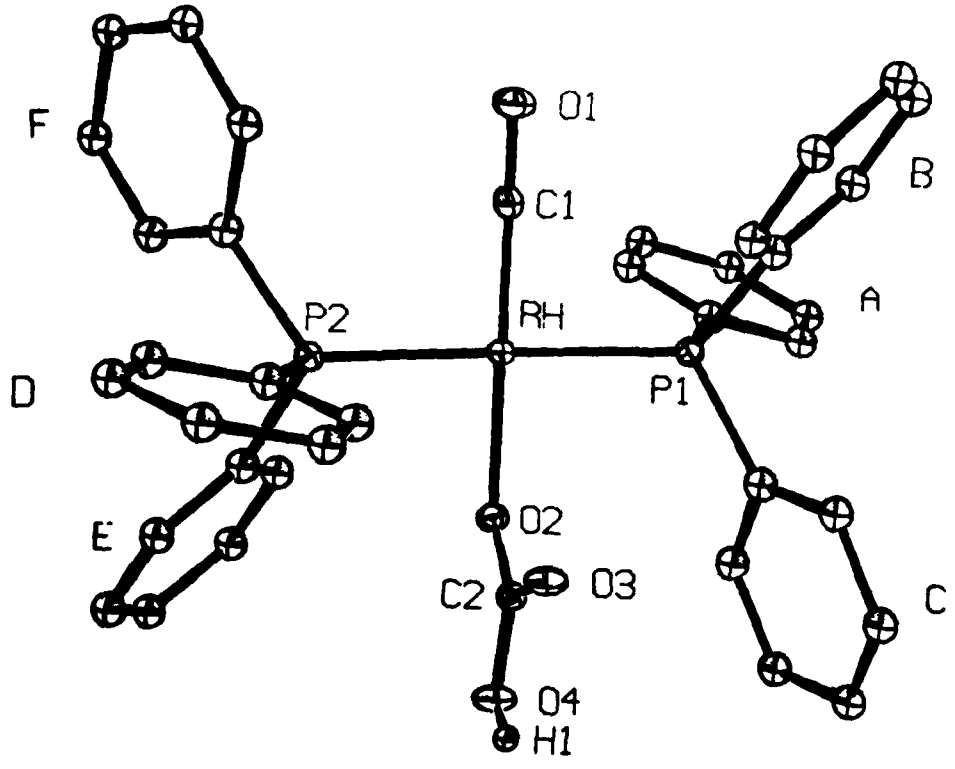


Figure Caption:

A view of the structure of I. Principal bond lengths (Å): Rh-C1 = 1.798(4), Rh-P1 = 2.333(1), Rh-P2 = 2.332(1), Rh-O2 = 2.075(2), O2-C2 = 1.283(4), C2-O3 = 1.243(4), C2-O4 = 1.336(4). Principal bond angles (°): C1-Rh-P1 = 89.1(1), C1-Rh-P2 = 91.8(1), O2-Rh-P1 = 90.4(1), O2-Rh-P2 = 88.7(1), Rh-O2-C2 = 118.6(2), O2-C2-O3 = 124.8(3), O2-C2-O4 = 113.2(3), O3-C2-O4 = 122.0(3).


F
O1
B
C1
A
P2
RH
D
P1
E
O2
C2
O3
C
O4
H1