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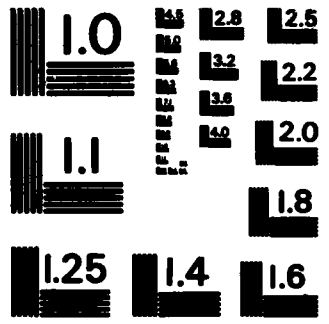

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Interaction of the title complex with CO_2 at 100°/50 atm or with HCO_2H at 20°C results in formation of the formate complex $(Cy_3P)_2(CO)Rh(O_2CH)$ whose structure is assigned on the basis of its combined spectroscopic (IR, ^1H, ^{13}C, ^{31}P NMR) properties.

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The Reactions of Bis(tricyclohexyl Phosphine)-Rhodium(I)carbonyl Tetrahydridoborate with Carbon Dioxide and Formic Acid

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William Willis and Kenneth M. Nicholas

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Chestnut Hill, Massachusetts 02167

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THE REACTIONS OF BIS(TRICYCLOHEXYL PHOSPHINE)-RHODIUM(I)CARBONYL TETRAHYDRIDOBORATE WITH CARBON DIOXIDE AND FORMIC ACID

William Willis and Kenneth M. Nicholas*†
Department of Chemistry
Boston College
Chestnut Hill, MA 02167

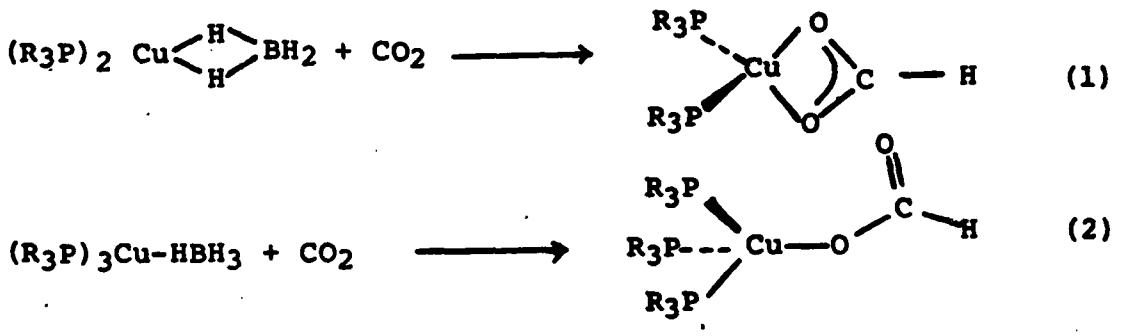
Abstract. Interaction of the title complex 1 with CO_2 at 100°C/50 atm or with HCOOH at 20° results in formation of the formate complex $(Cy_3P)_2(CO)Rh(O_2CH)$ (2) whose structure is assigned on the basis of its combined spectroscopic (IR, ^1H, ^{13}C and ^{31}P NMR) properties.

There has been considerable recent interest in the reactions of carbon dioxide with transition metal complexes no doubt stimulated by the prospects of developing useful catalytic conversions of CO_2 into organic compounds (1). Towards the goal

* Address correspondence to this author at the Department of Chemistry, University of Oklahoma, Norman, OK.

† Alfred P. Sloan Foundation Fellow, 1980-1984.

of achieving CO_2 reduction, a number of reports have appeared concerning reactions of CO_2 with metal hydride (L_nMH, 1) and, more recently, metal hydridoborate (L_nMBH_4, 2a-e) complexes. These latter compounds are of particular interest since they offer the possibility of bimetallic activation by presenting both a basic transition metal atom and a latent Lewis acidic boron center. We(2a) and others (2b-e) have described the reactions of several Cu(I) hydridoborate complexes with CO_2 and formic acid which yield formate complexes, $L_nCu(O_2CH)$.



We now report an examination of the interaction of both CO_2 and HCOOH with the complex $(Cy_3P)_2Rh(CO)BH_4$, 1 (3).

EXPERIMENTAL

IR spectra were obtained on a Perkin Elmer 599B spectrometer; NMR spectra were recorded on a Varian FT80A spectrometer. ^1H and ^{13}C spectra are referenced to TMS; ^{31}P spectra are referenced to 85% H_3PO_4. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Carbon dioxide was Linde anaerobic grade. Anhydrous formic acid was prepared by distilling commercial 96% formic acid from

a large excess of phthalic anhydride. Solvents were purified and dried by conventional methods. $(Cy_3P)_2Rh(CO)Cl$ (4) and $(Cy_3P)_2Rh(CO)BH_4$ (3) were prepared according to literature methods.

Reaction of $(Cy_3P)_2Rh(CO)BH_4$ (1) with CO_2

A suspension of 0.35g (0.50 mmol) of 1 in 30 mL of toluene was pressurized to 750 psig with CO_2 in a 125 mL stirred autoclave and then heated at 105-110° for five days. After cooling and release of pressure, the yellow-brown mixture was filtered. The solvent was removed from the filtrate in vacuo and the residue triturated with several small portions of pentane. Concentration of the pentane extracts gave $(Cy_3P)_2Rh(CO)O_2CH$ (2) as a bright yellow solid (0.10-0.15g). Spectral and analytical data are given in the text.

Reaction of 1 with Formic Acid

A stirred solution of 0.145g (0.20 mmol) 1 in 20 mL CH_2Cl_2 was treated with 0.09g (2 mmol) formic acid. After 2.5 hr the solvent was removed in vacuo and the resulting yellow solid triturated with several small portions of pentane. The combined pentane extracts were concentrated to leave 0.14g of bright yellow 2, identical in all respects to that prepared from the reaction of 1 with CO_2.

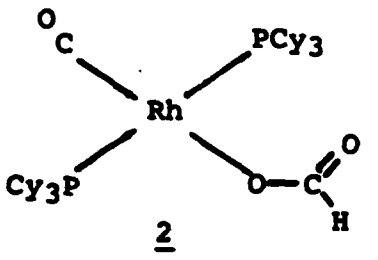
RESULTS AND DISCUSSION

Heating a toluene solution of $(Cy_3P)_2Rh(CO)BH_4$ (1) at 100-110°C under 50 atm of CO_2 results in the gradual appearance of prominent new IR absorptions at 1946 and 1634 cm^{-1} over the course of 5 days. The same absorptions are produced within 2.5 hr at 20° upon treatment of 1 with excess anhydrous formic acid. The pentane soluble species responsible for these absorptions was isolated (ca. 30-50% from CO_2 and >95% from HCOOH) as a yellow solid and is assigned structure 2 (eq. 1) based on the following spectroscopic and analytical data: IR(KBr) 2935(s, ν C-H), 2850(m, ν C-H), 1948(s, ν MC-O), 1634(m, ν_{asy}OCO), 1450(m, ν C-C), 1300(w, ν_{sym}OCO); ^{1}H NMR(C_6D_6) δ 8.88(s, $O_2C\underline{H}$), 2.12-1.23(bm, C_6H_{11}); ^{13}C NMR(C_6D_6)δ165.9($O_2\underline{C}H$), 34.2-26.9($\underline{C}_6H_{11}$); ^{31}P NMR (CH_2Cl_2) δ 37.5(d, J_{Rh-P}=121 Hz); Anal. Calcd for $C_{38}H_{67}O_3P_2Rh$: C,62.0; H,9.1; P,8.4. Found: C,62.5; H,9.6; P,8.4.

$(Cy_3P)_2Rh(CO)BH_4$ + CO_2 (or HCO_2H) ⟶ 2 (3)

1

(Cy = C_6H_{11})



2

The presence of the formato ligand in 2 is most clearly indicated by the IR absorption at 1634cm^{-1} (νOCO), the ^{1}H NMR resonance at δ8.88 ($O_2C\underline{H}$), and the ^{13}C NMR resonance of 165.9 ppm ($O_2\underline{C}H$). Considering the general preference of Rh(I) for square planar coordination geometry and the high value of

$\Delta\nu_{(asy-sym)}$ OCO (see Table 1), we propose a unidentate coordination mode for the formato ligand in 2 (5). The equivalence of the two P nuclei in the NMR spectrum of 2 supports the assigned trans geometry. Compound 2 appears to be identical to that obtained from the reaction of CO_2 with $(Cy_3P)_2RhH_2(O_2CH)$ (6). In contrast to the corresponding reactions of $(Ph_3P)_2CuBH_4$ with CO_2 and HCOOH (2a), no B-containing formate derivative was observed in the present reaction.

Although we know little about the mechanisms of the reactions between borohydride complex 1 and CO_2 and HCOOH, it appears that they follow a different pathway than the corresponding reactions of the hydride species $(R_3P)_2RhH(CO)$. The latter complexes react with CO_2 to produce dihydridobicarbonato derivatives, $(R_3P)_2RhH_2(CO)O_2COH$, and with formic acid to afford dihydridoformato derivatives, $(R_3P)_2RhH_2(CO)O_2CH$ (6).

Continued efforts are underway to explore the generality and the mechanisms of these reactions between carbon dioxide and metal tetrahydridoborate complexes.

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Table. IR Data for Representative Formato Complexes

Complex	Dentation	OCO	Ref.
$(Ph_3P)_2Cu(O_2CH)$	bi-[a]	1585,1330	2a,c
$(Ph_3P)_2RuMe(CO)(O_2CH)$	bi-[b]	1548,1360	7
(diphos)$Re(O_2CH)$	bi-[b]	1555,1356	8
(triphos)$Cu(O_2CH)$	uni-[a]	1620,1320	2d
$(C_5H_5)Fe(CO)_2(O_2CH)$	uni-[a]	1620,1293	9
$(Ph_3P)_2(CO)_2Os(O_2CH)_2$	uni-[b]	1630,1280	10
$(Ph_3P)_3Rh(O_2CH)$	uni-[b]	1615	11
$(Cy_3P)_2Rh(CO)(O_2CH)$	uni-[b]	1634,1300	this work

(a) proven by X-ray structure determination; (b) assigned on the basis of IR data and typical coordination numbers.

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