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# The Reactions of Bis(tricyclohexyl phosphine)rhodium(I)carbonyl Tetrahydridoborate with Carbon Dioxide and Formic Acid

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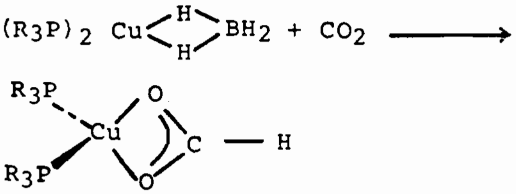
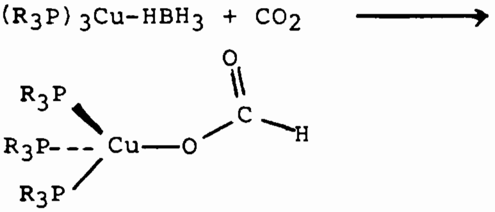
There has been considerable recent interest in the reactions of carbon dioxide with transition metal complexes no doubt stimulated by the prospects of developing useful catalytic conversions of $CO_2$ into organic compounds [1]. Towards the goal of achieving $CO_2$ reduction, a number of reports have 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, $L_nCu(O_2CH)$.


(1)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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, Tenn.

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 0.35 g (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 °C 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 (0.10–0.15 g). Spectral and analytical data are given in the text.

### *Reaction of 1 with Formic Acid*

A stirred solution of 0.145 g (0.20 mmol) **1** in 20 ml $CH_2Cl_2$ was treated with 0.09 g (2 mmol) formic acid. After 2.5 h 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 0.14 g 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 h at 20 °C 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** (eqn. 3) based on the following spectroscopic and analytical data: IR (KBr) 2935 (s, $\nu$C–H), 2850(m, $\nu$C–H), 1948(s, $\nu$ MC–O), 1634 (m, $\nu_{asy}$OCO), 1450(m, $\nu$ C–C), 1300(w, $\nu_{sym}$OCO); $^1H$ NMR ($C_6D_6$) $\delta$ 8.88 (s, $O_2C\underline{H}$), 2.12–1.23 (bm, $C_6H_{11}$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 165.9 ($O_2\underline{C}H$),

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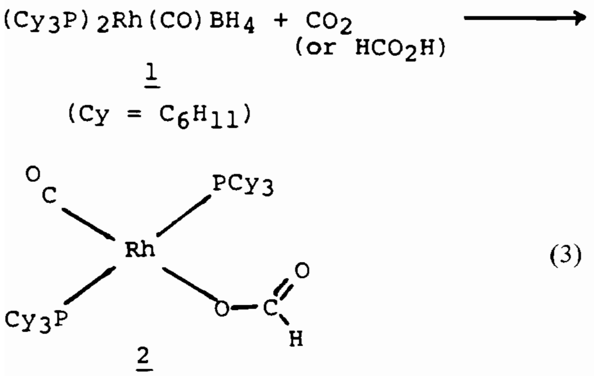
TABLE I. IR Data for Representative Formato Complexes.

| 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.

34.2–26.9 ($\underline{C}_6H_{11}$); $^{31}P$ NMR ($CH_2Cl_2$) $\delta$ 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.



(3)

The presence of the formato ligand in **2** is most clearly indicated by the IR absorption at 1634 $cm^{-1}$ ($\nu$ OCO), the $^1H$ NMR resonance at $\delta$ 8.88 ($O_2C\underline{H}$), 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 I), 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 dihydridocarbonato 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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