

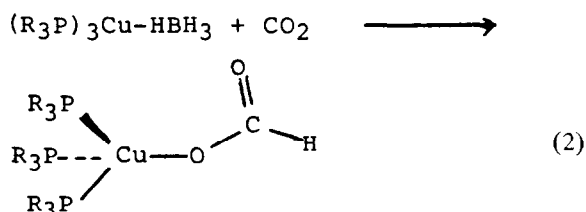
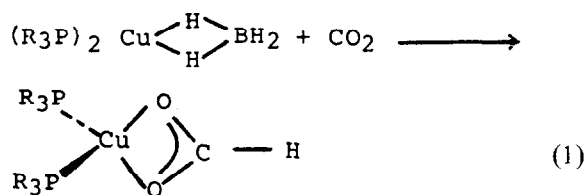
The Reactions of Bis(tricyclohexyl phosphine)-rhodium(I)carbonyl Tetrahydridoborate with Carbon Dioxide and Formic Acid

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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 CO₂ into organic compounds [1]. Towards the goal of achieving CO₂ reduction, a number of reports have appeared concerning reactions of CO₂ with metal hydride (L_nMH, [1]) and, more recently, metal hydridoborate (L_nMBH₄ [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 CO₂ and formic acid which yield formate complexes, L_nCu(O₂CH).



We now report an examination of the interaction of both CO₂ and HCOOH with the complex (Cy₃P)₂Rh(CO)BH₄, **1** [3].

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Experimental

IR spectra were obtained on a Perkin Elmer 599B spectrometer; NMR spectra were recorded on a Varian FT80A spectrometer. ¹H and ¹³C spectra are referenced to TMS; ³¹P spectra are referenced to 85% H₃PO₄. 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. (Cy₃P)₂Rh(CO)Cl [4] and (Cy₃P)₂Rh(CO)BH₄ [3] were prepared according to literature methods.

Reaction of (Cy₃P)₂Rh(CO)BH₄ (**1**) with CO₂

A suspension of 0.35 g (0.50 mmol) of **1** in 30 ml of toluene was pressurized to 750 psig with CO₂ 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 (Cy₃P)₂Rh(CO)O₂CH (**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 CH₂Cl₂ 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 CO₂.

Results and Discussion

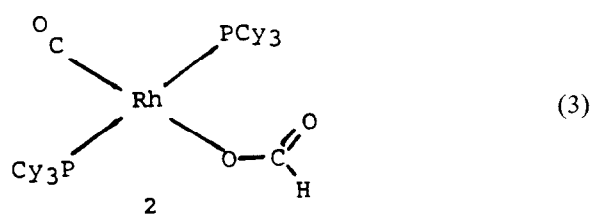
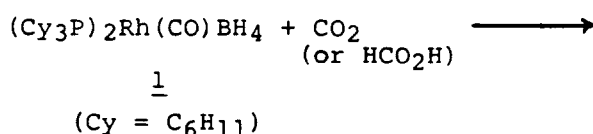
Heating a toluene solution of (Cy₃P)₂Rh(CO)BH₄ (**1**) at 100–110 °C under 50 atm of CO₂ results in the gradual appearance of prominent new IR absorptions at 1946 and 1634 cm⁻¹ over the course of 5 days. The same absorptions are produced within 2.5 h at 20 °C upon treatment of **1** with excess anhydrous formic acid. The pentane soluble species responsible for these absorptions was isolated (ca. 30–50% from CO₂ 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, νC–H), 2850(m, νC–H), 1948(s, νMC–O), 1634 (m, ν_{asy}OCO), 1450(m, νC–C), 1300(w, ν_{sym}OCO); ¹H NMR (C₆D₆) δ 8.88 (s, O₂CH), 2.12–1.23 (bm, C₆H₁₁); ¹³C NMR (C₆D₆) δ 165.9 (O₂CH),

TABLE I. IR Data for Representative Formate Complexes.

Complex	Dentation	OCO	Ref.
(Ph ₃ P) ₂ Cu(O ₂ CH)	bi- ^a	1585, 1330	2a,c
(Ph ₃ P) ₂ RuMe(CO)(O ₂ CH)	bi- ^b	1548, 1360	7
(diphos)Re(O ₂ CH)	bi- ^b	1555, 1356	8
(triphos)Cu(O ₂ CH)	uni- ^a	1620, 1320	2d
(C ₅ H ₅)Fe(CO) ₂ (O ₂ CH)	uni- ^a	1620, 1293	9
(Ph ₃ P) ₂ (CO) ₂ Os(O ₂ CH) ₂	uni- ^b	1630, 1280	10
(Ph ₃ P) ₃ Rh(O ₂ CH)	uni- ^b	1615	11
(Cy ₃ P) ₂ Rh(CO)(O ₂ CH)	uni- ^b	1634, 1300	this work

^aProven by X-ray structure determination. ^bAssigned on the basis of IR data and typical coordination numbers.

34.2–26.9 (C₆H₁₁); ³¹P NMR (CH₂Cl₂) δ 37.5 (d, *J*_{Rh-P} = 121 Hz); *Anal.* Calcd. for C₃₈H₆₇O₃P₂Rh: C, 62.0; H, 9.1; P, 8.4. Found: C, 62.5; H, 9.6; P, 8.4.



The presence of the formate ligand in **2** is most clearly indicated by the IR absorption at 1634 cm⁻¹ (*ν* OCO), the ¹H NMR resonance at δ 8.88 (O₂CH), and the ¹³C NMR resonance of 165.9 ppm (O₂CH). Considering the general preference of Rh(I) for square planar coordination geometry and the high value of Δ*ν*_(asy-sym) OCO (see Table I), we propose a unidentate coordination mode for the formate 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 CO₂ with (Cy₃P)₂RhH₂(O₂CH) [6]. In contrast to the corresponding reactions of (Ph₃P)₂CuBH₄ with CO₂ 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 CO₂ and HCOOH, it appears that they follow a different pathway than the corresponding reactions of the hydride species (R₃P)₂RhH(CO). The latter

complexes react with CO₂ to produce dihydrido-carbonato derivatives, (R₃P)₂RhH₂(CO)O₂COH, and with formic acid to afford dihydridoformate derivatives, (R₃P)₂RhH₂(CO)O₂CH [6].

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

Acknowledgement

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