Hydration and Reduction of Carbon Dioxide by Rhodium Hydride Compounds. Preparation and Reactions of Rhodium Bicarbonate and Formate Complexes, and the Molecular Structure of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$

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Abstract: Reaction of Rh(I)-hydride complexes $RhH(P(i\text{-}Pr)_3)_3$, $RhH(N_2)(PPh(t\text{-}Bu)_2)_2$, and $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ with CO_2 in the presence of H_2O has been found to afford novel dihydrido bicarbonato complexes $RhH_2(O_2COH)L_2$ (**1**, L = $P(i\text{-}Pr)_3$; **2**, L = $PPh(t\text{-}Bu)_2$; **3**, L = $P(c\text{-}C_6H_{11})_3$). The crystal and molecular structure of **1** has been determined at −160 °C. The complex $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**) crystallizes in the monoclinic space group C_{2h}^5-$P2_1/c$, with four formula units in a cell of dimensions a = 15.82 (1) Å, b = 10.88 (1) Å, c = 15.49 (1) Å, β = 114.5 (1)°, V = 2428 Å^3. In the solid state **1** consists of distorted octahedral Rh(III) centers coupled by intermolecular hydrogen bonding between bicarbonato ligands. These dihydrido bicarbonato complexes, and analogous dihydrido formato complexes, reduce CO_2 to form Rh(I) carbonyl bicarbonato and formato complexes and H_2O.

Introduction

The use of transition-metal compounds for the fixation of CO_2 is of considerable interest in view of the promising utility of CO_2 as a carbon resource.[2,3] Reactions of CO_2 with transition-metal complexes have sometimes resulted in the formation of CO_2 complexes,[2-8] while reactions with metal complexes containing M–H,[2-4,9-11] M–C,[2-4,7,12,13] M–O,[3,4,14,15] or M–N[2-4,16,17] bonds often afford the corresponding insertion products. Generally these reactions are carried out under anhydrous conditions; thus little is known about the reactions of CO_2 with transition-metal compounds in aqueous media.

Motivated by efficient catalytic activity of Rh(I)hydride complexes, e.g., $RhH(P(i\text{-}Pr)_3)_3$ and $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$,[18] for the water-gas shift reaction,[19] we have carried out detailed studies of the reaction of these Rh(I) hydrides with CO_2 in aqueous organic media. Hitherto unknown dihydrido bicarbonato compounds $RhH_2(O_2COH)L_2$ (**1**, L = $P(i\text{-}Pr)_3$; **2**, L = $PPh(t\text{-}Bu)_2$; **3**, L = $P(c\text{-}C_6H_{11})_3$) were obtained. During the course of our studies we found a surprisingly facile reduction of CO_2 by these dihydrido Rh(III) compounds. This reduction, a reversal of the water-gas shift reaction, has received very little attention,[20] and here we have examined it in detail.

Since the usual product of the reaction of CO_2 with a transition metal hydride complex is a formate complex,[2-4,9-11] these dihydrido bicarbonato complexes were originally believed to be carbon dioxide–formato complexes. It was in the hope of confirming the presence of a weakly bound CO_2 molecule that the present X-ray structure determination of **1** was undertaken, and the true nature of the complexes was revealed. These dihydrido bicarbonato complexes **1–3** are the first η^2-bicarbonato compounds reported from the reaction of CO_2, H_2O, and low-valent transition-metal complexes. A similar reaction of $PdMe_2(PMe_3)_2$ with CO_2 and H_2O affords the η^1-bicarbonato compound *trans*-$PdMe(O_2COH)(PMe_3)_2$.[21] Participation of H_2O has been suggested in the formation of $Rh_2(O_2CO)(PPh_3)_5$ from the reaction of $RhH(PPh_3)_n$ (n = 3, 4) with CO_2.[22] Other carbonato complexes have been reported from the reaction of CO_2 with $Pt(PPh_3)_3$ in the presence of O_2,[23] and from the disproportionation of CO_2 into CO_3^{2-} and CO in a Mo–CO_2 complex.[24]

Although formato complexes were never observed in the direct reaction of these Rh(I) hydride complexes with CO_2, even in the absence of water, formato complexes were easily obtained when the Rh(I)-hydride complexes were treated with formic acid. These formato complexes are exact analogues of the bicarbonato complexes and show very similar reactivities.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dinitrogen or carbon dioxide. ^1H NMR spectra were recorded on JEOL JNM-4H-100 or JNM-C-60 HL spectrometers, ^{31}P spectra on a Varian CFT-20 spectrometer at 32.199 MHz, and IR spectra on a Hitachi Model 295 spectrometer. All reported IR frequencies are from Nujol mull spectra. Literature methods were used for the preparation of *trans*-$RhH(N_2)(PPh(t\text{-}Bu)_2)_2$,[25] $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$,[18] $RhH(P(i\text{-}Pr)_3)_3$,[18] and *trans*-$Rh(OH)(CO)L_2$ (L = PPh_3, $P(i\text{-}Pr)_3$).[26] The compound $Rh(OH)(CO)(P(c\text{-}C_6H_{11})_3)_2$ was prepared by a method similar to that employed for $Rh(OH)(CO)(PPh_3)_2$. Carbon dioxide was obtained from Fuji Midori, Ltd. and was used without purification. Infrared spectral data for the bicarbonato complexes and NMR spectral data are contained in Tables I and II. Satisfactory elemental analyses for C, H have been obtained for all compounds described herein except **7** and **10** (vide infra).

Bis(triisopropylphosphine)dihydridobicarbonatorhodium(III), $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (1). Method A. Carbon dioxide, not predried, was bubbled into a yellow solution of $RhH(P(i\text{-}Pr)_3)_3$ (130 mg, 0.2 mmol) in dry n-hexane (10 mL) at room temperature for 1 h. The resulting colorless solution was stirred for an additional 20 h. The solution was then evaporated and dried in vacuo and the solid residue was recrystallized from toluene-n-hexane to give colorless crystals of **1** (55 mg, 48%), mp 100 °C dec.

Method B. The compound **1** was also prepared by stirring a solution of $RhH(P(i\text{-}Pr)_3)_3$ (585 mg, 1 mmol) in 10 mL of wet THF (10% water by volume) under 1 atm of CO_2 for 2 h. After the reaction mixture was dried in vacuo, **1** was obtained from the residue by recrystallization in ca. 85% yield.

Bis(di-*tert*-butylphenylphosphine)dihydridobicarbonatorhodium(III), $RhH_2(O_2COH)(PPh(t\text{-}Bu)_2)_2$ (2). A toluene solution of $RhH(N_2)(PPh(t\text{-}Bu)_2)_2$ was treated with CO_2 as in method A above. Recrystallization of the dried residue from toluene–n-hexane gave colorless crystals of **2**, mp 120 °C dec, yield 17%.

Bis(tricyclohexylphosphine)dihydridobicarbonatorhodium(III), $RhH_2(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (3). CO_2 (12 mL, 0.5 mmol) was syringed

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Table I. Infrared Data[a] of Bicarbonato Complexes

	$\nu_{Rh\text{-}H}$ or $\nu_{C\equiv O}$	ν_{OH} or ν_{OO}	$\nu_{C=O}$	δ_{OHO}	$\nu_{C\text{-}O} + \nu_{C=O} + \delta_{OHO}$	π_{CO_3}
$RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (**1**)	2120 m, 2140 m	2650 m	1587 s	*b*	1338 s	792 m
$RhH_2(O_2COH)[PPh(t\text{-}Bu)_2]_2$ (**2**)	2145 m, 2220 m	2660 m	1583 s	*b*	1340 s	802 m
$RhH_2(O_2COH)[P(c\text{-}C_6H_{11})_3]_2$ (**3**)	2138 m, 2158 m[c] (2110, 2160)	2640 m	1585 s	1410 w	1340 s	790 m
$Rh(CO)(O_2COH)[P(c\text{-}C_6H_{11})_3]_2$ (**6**)	1942 s	2650 w	1608 s	1420 s	1355 s	821 m
$Rh(CO)(O_2COD)[P(c\text{-}C_6H_{11})_3]_2$	1942 s	2087 w	1590 s	1062 s	1405 s	821 m
$Rh(^{13}CO)(O_2{}^{13}COH)[P(c\text{-}C_6H_{11})_3]_2$	1900 s	2657 w	1575 s	1402 w	1345 s	822 m
$Rh(CO)(O_2COH)[P(i\text{-}Pr)_3]_2$ (**7**)	1952 s	2600 w	1615 s	1413 s	1350 s	823 m
$Rh(CO)(O_2COH)(PPh_3)_2$	1968 s	2650 w	1600 s	1430 s[d]	1350 s	819 m
$(O_2COH)_2{}^{2-}$ [e]		2620 w	1618 s	1405 s	1367 s	830 m
$(O_2COD)_2{}^{2-}$ [e]		2055 w	1615 s	1050 s	1392 s	830 m

[a] ν, stretching; δ, in-plane bending; π, out-of-plane bending. [b] The band probably overlaps with that of Nujol. [c] Sample recrystallized from toluene. The value in parentheses is for the sample recrystallized from THF. [d] The band is a composite of δ_{OHO} and $\nu_{P\text{-}Ph}$. [e] Reference 46.

Table II. ^1H NMR Spectral Data of Bicarbonato and Formato Compounds[a]

	Rh-H			O_2COH or O_2CH	other
	δ, ppm	$J_{H\text{-}P}$, Hz	$J_{H\text{-}Rh}$, Hz	δ, ppm	
$RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (**1**)	−22.6 (dt)	13.1	26.3	12.3 (br)	CH_3, δ 1.22 (q), $^3J_{H\text{-}P} + {}^5J_{H\text{-}P} = 13.5$ Hz $J_{H\text{-}H} = 6.7$ Hz CH, δ 2.0 (m)
$RhH_2(O_2COH)[PPh(t\text{-}Bu)_2]_2$ (**2**)	−23.4 (dt)	15.3	21.7	11.5 (br)	CH_3, δ 1.36 (t), $^3J_{H\text{-}P} + {}^5J_{H\text{-}P} = 13.2$ Hz Ph, δ 7.1 (m), 8.0 (m)
$RhH_2(O_2CH)[P(i\text{-}Pr)_3]_2$ (**4**)	−23.8[b]	18.0	28.8	8.55 (m)[c]	CH_3, δ 1.20 (q), $^3J_{H\text{-}P} + {}^5J_{H\text{-}P} = 13.2$ Hz $J_{H\text{-}H} = 6.6$ Hz CH, δ ~2.0 (m)
$RhH_2(O_2CH)[P(c\text{-}C_6H_{11})_3]_2$ (**5**)	−23.8[d]	17.2	28.8	8.63 (m)[e]	$c\text{-}C_6H_{11}$, δ 0.89–2.2 (bm)
$Rh(CO)(O_2COH)[P(i\text{-}Pr)_3]_2$ (**7**)				12.1 (br)	CH_3, δ 1.27 (q), $^3J_{H\text{-}P} + {}^5J_{H\text{-}P} = 13.0$ Hz $J_{H\text{-}H} = 6.5$ Hz CH, δ ~2.2 (m)
$Rh(CO)(O_2CH)[P(i\text{-}Pr)_3]_2$ (**9**)				8.78 (br)	CH_3, δ 1.25 (q), $^3J_{H\text{-}P} + {}^5J_{H\text{-}P} = 13.5$ Hz $J_{H\text{-}H} = 6.75$ Hz CH, δ ~2.2 (m)
$Rh(CO)(O_2CH)[P(c\text{-}C_6H_{11})_3]_2$ (**10**)				8.77 (br)	$c\text{-}C_6H_{11}$, δ 0.80–2.2 (br)

[a] Measured in benzene-d_6 at 35 °C. [b] Two double triplets, $^4J_{H\text{-}H} = 1.1$ Hz. [c] $^4J_{H\text{-}H} = 1.1$, $J_{Rh\text{-}H} = 2.0$, $J_{H\text{-}P} = 1.0$ Hz. [d] Two double triplets, $^4J_{H\text{-}H} = 1.0$ Hz. [e] $^4J_{H\text{-}H} = 1.0$, $J_{Rh\text{-}H} = 2$, $J_{H\text{-}P} = 1$ Hz.

into a flask containing a suspension of $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ (380 mg, 0.27 mmol) in wet THF (10 mL, 15% water by volume). After stirring for 20 h at room temperature the suspension was filtered, and the solid was dried and recrystallized from warm THF to give **3** as a colorless, crystalline solid (0.050 g, 12%). The filtered solution was allowed to stand without stirring under 1 atm of CO_2, and additional crystals (ca. 0.2 g) of **3** slowly precipitated.

Bis(triisopropylphosphine)dihydridoformatorhodium(III), $RhH_2(O_2CH)(P(i\text{-}Pr)_3)_2$ (4). Formic acid (39.7 mg, 0.86 mmol) was added to a solution of $RhH(P(i\text{-}Pr)_3)_3$ (440 mg, 0.75 mmol) in THF (15 mL) at −40 °C. The mixture was stirred and allowed to warm to room temperature, and after 30 min was concentrated in vacuo. The residue was recrystallized from pentane to give colorless crystals (90 mg, 26%): mp 80 °C dec; IR $\nu_{Rh\text{-}H}$ 2130, 2145 cm^{-1}, ν_{OCO} 1560, 1310 cm^{-1}.

Bis(tricyclohexylphosphine)dihydridoformatorhodium(III), $RhH_2(O_2CH)(P(c\text{-}C_6H_{11})_3)_2$ (5). A mixture of $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ (368 mg, 0.27 mmol), formic acid (27.6 mg, 0.6 mmol), and toluene (10 mL) was stirred for 2 h at room temperature. The concentrated reaction mixture was recrystallized from *n*-hexane to give colorless crystals (150 mg, 40%): mp 125–127 °C dec; IR $\nu_{Rh\text{-}H}$ 2114, 2140 cm^{-1}, ν_{OCO} 1555, 1310 cm^{-1}.

Bis(tricyclohexylphosphine)carbonylbicarbonatorhodium(I), $Rh(CO)(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (6). Method A. A suspension of $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ (200 mg, 0.14 mmol) in aqueous THF (10 mL, 15% water by volume) was stirred under 1 atm of CO_2 at room temperature for 20 h. The vacuum-dried reaction mixture was recrystallized from toluene-THF to give pale yellow crystals in high yield, mp 169–172 °C dec.

Method B. A solution of $RhH_2(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (**3**, 145 mg) in pyridine (10 mL) was stirred under 1 atm of CO_2 at room temperature for 20 h. The IR spectrum of the concentrated reaction mixture showed the formation of **6** in quantitative yield.

Method C. $Rh(OH)(CO)(P(c\text{-}C_6H_{11})_3)_2$ (84 mg, 0.12 mmol) was dissolved in THF (15 mL) and stirred for 5 min under 1 atm of CO_2 at room temperature. Compound **6** slowly precipitated from the solution, yield 40 mg (44%).

Bis(triisopropylphosphine)carbonylbicarbonatorhodium(I), $Rh(CO)(O_2COH)(P(i\text{-}Pr)_3)_2$ (7), and Tetrakis(triisopropylphosphine)dicarbonylcarbonatodirhodium(I), $Rh_2(CO)_2(O_2CO)(P(i\text{-}Pr)_3)_4$ (8). Method A. A solution of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**, 490 mg, 1.0 mmol) in toluene (30 mL) was stirred under CO (30 mL, 1.3 mmol) for 5 h at room temperature. VPC analysis (activated charcoal) of the gaseous phase proved the formation of H_2 (0.8 mmol, 80%) and CO_2 (0.2 mmol, 20%). IR analysis of the concentrated mixture showed the presence of both $Rh(CO)(O_2COH)(P(i\text{-}Pr)_3)_2$ (**7**) (1952, 1615 cm^{-1}, both strong) and $Rh_2(CO)_2(O_2CO)(P(i\text{-}Pr)_3)_4$ (**8**) (1934, 1533, 1300, 1275 cm^{-1}, all strong; 829 cm^{-1}, weak). Recrystallizing the solid residue from ether gave **8** as yellow crystals (270 mg, 63%), mp 145 °C dec. The molecular weight of **8**, determined cryoscopically in benzene, is 919 (required 963) amu. When the reaction of CO with **1** was permitted to continue for 20 h, **8** was the only product detected and the release of CO_2 (45% based on **1**) was confirmed by VPC analysis of the gaseous phase of the reaction vessel.

Method B. A solution of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (245 mg, 0.5 mmol) in pyridine (10 mL) was stirred under 1 atm of CO_2 for 20 h at room temperature. Recrystallization of the dried residue from ether gave **8** in 75% yield.

Method C. A solution of $Rh(OH)(CO)(P(i\text{-}Pr)_3)_2$ (200 mg, 0.43 mmol) in THF (5 mL) was stirred under 1 atm of CO_2 for 10 h at room temperature. IR analysis of the vacuum-dried residue showed **7** to be the only detectable product. Attempted recrystallization of this material resulted in its complete conversion to **8** (160 mg, 81%).

Bis(triisopropylphosphine)carbonylformatorhodium(I), $Rh(CO)(O_2CH)(P(i\text{-}Pr)_3)_2$ (9). Method A. A pyridine solution of $RhH_2(O_2CH)(P(i\text{-}Pr)_3)_2$ (**4**, 330 mg, 0.7 mmol) containing 20 μL

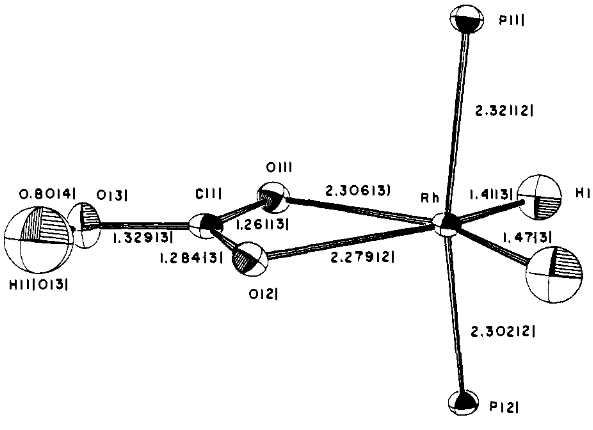


Figure 1. A drawing of the coordination about the rhodium atom of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$. Selected distances (Å) are shown. Thermal ellipsoids are drawn at the 50% probability level.

of THF as an internal reference was stirred under 1 atm of CO_2 for 20 h at room temperature. VPC analysis (Porapak Q, 2.5 m, 140 °C) of the reaction solution showed the quantitative formation of water. H_2 was not detected in the vapor phase. The IR spectrum of the concentrated reaction mixture showed the carbonyl formato complex **9** (1954 vs, 1633 s, 1310 s) as the major product together with a small amount of $Rh_2(CO)_2(O_2CO)(P(i\text{-}Pr)_3)_4$ (**8**) (1934, 1533 cm^{-1}). Upon recrystallization of the dried residue from ether analytically pure $Rh(CO)(O_2CH)(P(i\text{-}Pr)_3)_2$ (**9**) was obtained as pale yellow crystals (180 mg, 52%), mp 106 °C dec.

Method B. $RhH(P(i\text{-}Pr)_3)_3$ (162 mg, 0.28 mmol) and formic acid (27 mg, 0.6 mmol) were added to acetone (10 mL) and the mixture was stirred for 15 min at room temperature. Treating the concentrated reaction mixture as in A above gave **9** (71 mg, 51%).

Bis(tricyclohexylphosphine)carbonylformatorhodium(I), $Rh(CO)(O_2CH)(P(c\text{-}C_6H_{11})_3)_2$ (10). This compound was obtained as pale yellow crystals in 60% yield from the reaction of $RhH_2(O_2CH)(P(c\text{-}C_6H_{11})_3)_2$ (**5**, 210 mg, 0.33 mmol) with CO_2 as in method A for **9**, mp 160–167 °C dec. The compound **10** was also obtained in poor yield from the direct reaction of $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ with a large excess of formic acid, the major product being the dihydrido formato complex **5**. IR of **10**: 1945, 1630, 1292 cm^{-1}. Anal. ($C_{38}H_{67}O_3P_2Rh$) C, H; C: calcd, 61.95; found, 62.98.

Reaction of $^{13}CO_2$ with $RhH_2(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (3). A pyridine solution of **3** (20 mg, 0.03 mmol) was stirred with $^{13}CO_2$ (23 mL at 1 atm, 1.0 mmol; generated from the reaction of $Ba^{13}CO_3$ (90% ^{13}C) with aqueous HCl) for 0.7 h at room temperature. The IR spectrum of the concentrated residue showed the near-quantitative formation of $Rh(CO)(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (**6**), with incorporation of ^{13}C into both the carbonyl and bicarbonato ligands. The ratio $[^{12}CO]/[^{13}CO]$ assessed from the IR band intensities of the terminal carbonyl stretching modes ($\nu_{^{12}CO}$ 1942, $\nu_{^{13}CO}$ 1900 cm^{-1}) was 0.17, with a similar $^{12}C/^{13}C$ ratio found from the bicarbonato stretching frequencies ($\nu_{^{12}CO_3}$ 1608, $\nu_{^{13}CO_3}$ 1575 cm^{-1}). Assuming full scrambling of the bicarbonato ligand of **3** with $^{13}CO_2$ prior to reduction, the calculated ratio is 0.14.

Reaction of $^{12}CO_2$ with $Rh(^{13}CO)(O_2{}^{13}COH)(P(c\text{-}C_6H_{11})_3)_2$ (6). The ^{13}C-labeled complex **6** prepared above was dissolved in pyridine (5 mL) and stirred under 1 atm of $^{12}CO_2$ for 0.7 h at room temperature. The IR spectrum of the concentrated residue showed essentially complete conversion of the ^{13}C-bicarbonato ligand into ^{12}C-bicarbonate. The $[^{12}CO]/[^{13}CO]$ ratio of the carbonyl ligand remained unchanged.

X-ray Data Collection. Diffraction studies were performed on single crystals of **1**, $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$, prepared as above and recrystallized from toluene-hexane. Preliminary room-temperature X-ray photographic data showed the crystals to be monoclinic, with systematic absences ($h0l$, l odd; $0k0$, k odd) which are consistent with the space group C_{2h}^5-$P2_1/c$. The initial unit cell parameters from the photographic data led to a density of 1.30 g/cm^3 calculated for four $RhP_2(C_{19}H_{45}O_3)$ units in the cell; the measured density is 1.28 (2) g/cm^3 (flotation in aqueous $ZnCl_2$). The crystals are colorless plates with major faces of the form {100} and with irregular edges. Although the compound is stable in air for at least several days, the crystals used for diffraction studies were carefully handled in inert atmospheres (Ar or N_2).

Table III. Summary of Crystal Data and Intensity Collection

compd	$RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$
formula	$C_{19}H_{45}O_3P_2Rh$
formula weight	486.42 amu
temp	≈−160 °C
a	15.82 (1)Å
b	10.88 (1)Å
c	15.49 (1)Å
β	114.5 (1)°
V	2428 $Å^3$
Z	4
density (calcd)	1.33 g cm^{-3}
density (obsd)	1.28 g cm^{-3} (25 °C)
space group	$C_{2h}^5 - P2_1/c$
crystal dimensions	0.21 × 0.44 × 0.39 mm
crystal shape	prismatic plate, faces of forms {100}, {10$\bar{2}$}, {11$\bar{1}$}
crystal volume	0.0472 mm^3
radiation	Mo Kα (λ(Mo $K\alpha_1$) = 0.709 30 Å) from monochromator
linear absorption coefficient	8.35 cm^{-1}
transmission factors	0.738–0.851
takeoff angle	2.8°
scan speed	2° in 2θ/min
scan range	0.9° below $K\alpha_1$ peak to 0.9° above $K\alpha_2$ peak
background counts	10 s with rescan option
2θ limits	4.0–59.2°
final no. of variables	238
unique data used, $F_0^2 > 3\sigma(F_0^2)$	5844
R	0.028
R_w	0.035
error in observation of unit weight	1.41 electrons

The data set was collected on a computer-controlled Picker diffractometer with the crystal at ≃−160 °C in a stream of cold nitrogen.[27] Cell constants obtained from 18 hand-centered reflections[28] at this temperature are a = 15.82 (1) Å, b = 10.88 (1) Å, c = 15.49 (1) Å, β = 114.5 (1)°, V = 2428 $Å^3$ (λ(Mo $K\alpha_1$) = 0.709 30 Å). A total of 7462 reflections in the range 4.0 ≤ 2θ(MoKα) ≤ 59.2° was collected. From these the 5844 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. A set of seven standards, remeasured every 100 reflections during the data collection, showed no significant intensity fluctuations. Further information regarding the data collection is given in Table III.

Solution and Refinement of the Structure. For all nonhydrogen atoms the usual scattering factors were used;[29] anomalous dispersion terms[29] were included in F_c for rhodium and phosphorus atoms. The hydrogen scattering factors of Stewart, Davidson, and Simpson were used for all hydrogen atoms.[30] The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$

The rhodium and phosphorus atoms were easily found from a Patterson map,[31] and all remaining nonhydrogen atoms were located by Fourier methods. After several cycles of isotropic refinement and one cycle of anisotropic refinement, the positions of most of the isopropyl hydrogen atoms, the hydroxy hydrogen atom, and the two hydrido ligands were clear on a difference Fourier map. The isopropyl hydrogen atoms were placed in idealized locations (C–H = 0.95 Å, tetrahedral angles), each given an isotropic thermal parameter B 1.0 $Å^2$ greater than the equivalent B of the carbon atom to which it is attached, and held fixed during all subsequent refinement. Two further cycles of anisotropic refinement, in which both hydrido and the hydroxy hydrogen atoms were refined isotropically, resulted in convergence with R = 0.028, R_w = 0.035. A final difference Fourier synthesis revealed no peaks above 0.5 e/$Å^3$ but there were holes of ca. −1.0 e/$Å^3$ approximately 0.6 Å from the metal along the Rh–P bond vectors. The atomic positional and thermal parameters are listed in Table IV and interatomic distances and angles in Table V. A list of $10|F_o|$ vs. $10|F_c|$ and a table of hydrogen atom positions are available.[32]

Table IV. Positional and Thermal Parameters for the Atoms of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$

ATOM	X[A]	Y	Z	B11[B] OR B,A^2	B22	B33	B12	B13	B23
RH	0.239811(10)	0.077886(14)	0.197990(10)	11.20(7)	11.74(12)	11.12(7)	0.79(7)	4.66(5)	-0.68(7)
P(1)	0.188070(35)	0.272392(47)	0.214311(35)	12.51(22)	13.07(37)	12.19(22)	0.24(23)	5.33(18)	-0.07(23)
P(2)	0.308718(36)	-0.111265(48)	0.209398(36)	14.49(23)	14.20(37)	12.33(22)	2.60(23)	5.85(18)	0.61(23)
C(11)	0.23574(14)	0.34027(19)	0.33659(14)	16.28(91)	18.7(15)	13.16(89)	-0.34(95)	6.22(75)	-1.84(94)
C(14)	0.32967(17)	0.28560(25)	0.40388(16)	25.6(12)	52.1(24)	16.5(10)	11.0(13)	-1.20(90)	-11.6(13)
C(15)	0.24186(17)	0.48006(21)	0.34192(16)	31.1(12)	20.8(17)	19.9(10)	-3.7(12)	10.64(92)	-6.5(11)
C(12)	0.06076(14)	0.26915(19)	0.17992(14)	12.38(84)	19.2(15)	17.61(91)	0.49(94)	6.05(72)	-2.62(98)
C(16)	0.01585(16)	0.39334(21)	0.18267(17)	17.82(97)	26.3(17)	26.3(11)	5.9(10)	9.52(86)	-1.1(11)
C(17)	0.03704(15)	0.17398(21)	0.23905(16)	18.23(97)	30.0(18)	26.0(11)	-2.7(11)	13.72(88)	-1.8(11)
C(13)	0.20309(15)	0.39227(19)	0.13652(15)	20.26(96)	15.0(15)	17.03(93)	-0.58(95)	10.08(79)	2.41(95)
C(18)	0.30484(16)	0.39598(22)	0.15036(17)	22.1(11)	37.8(20)	29.0(12)	-6.7(11)	15.51(95)	2.5(12)
C(19)	0.13942(17)	0.37379(21)	0.03119(16)	29.2(11)	24.8(17)	16.47(98)	0.9(12)	8.93(88)	4.0(11)
C(21)	0.38667(17)	-0.16316(21)	0.33105(15)	27.5(11)	32.1(18)	14.48(96)	14.5(12)	5.80(85)	5.2(11)
C(24)	0.46871(18)	-0.07510(27)	0.37913(17)	25.2(12)	68.9(26)	16.5(10)	12.4(15)	-2.71(88)	-1.5(14)
C(25)	0.33621(22)	-0.18245(27)	0.39530(18)	54.5(18)	51.5(25)	21.9(12)	15.9(17)	19.5(12)	11.4(14)
C(22)	0.38145(14)	-0.11967(20)	0.14090(14)	13.05(85)	26.0(16)	16.30(92)	1.02(98)	7.13(74)	-0.9(10)
C(26)	0.44356(15)	-0.23397(22)	0.16293(16)	17.33(97)	34.0(18)	23.7(11)	7.1(11)	8.76(84)	-3.5(12)
C(27)	0.43638(16)	-0.00166(22)	0.14519(18)	18.5(10)	34.8(19)	30.7(12)	-1.5(11)	12.83(93)	2.7(12)
C(23)	0.23006(15)	-0.24748(19)	0.16308(16)	19.21(96)	16.8(16)	24.8(10)	-0.93(98)	12.43(83)	-1.3(11)
C(28)	0.19569(16)	-0.26638(22)	0.05567(17)	22.7(11)	23.9(17)	28.0(11)	-5.7(11)	6.65(91)	-7.0(12)
C(29)	0.14552(17)	-0.23750(23)	0.18758(19)	26.5(12)	28.5(19)	48.4(15)	3.0(12)	24.8(11)	8.7(14)
C(1)	0.12573(14)	0.05146(18)	0.01864(14)	15.58(88)	12.6(15)	14.21(88)	0.97(87)	5.48(73)	-0.34(88)
O(1)	0.20764(10)	0.08649(13)	0.03865(10)	15.21(65)	22.7(12)	15.46(66)	-1.33(73)	6.72(54)	-0.52(74)
O(2)	0.097505(96)	0.02826(13)	0.083597(98)	13.40(63)	20.6(11)	13.24(64)	-2.05(70)	6.02(53)	-1.39(70)
O(3)	0.06777(11)	0.03883(16)	-0.07206(11)	14.71(71)	42.9(14)	13.24(68)	-4.12(81)	4.43(57)	-1.24(80)
H(1)RH	0.3317(19)	0.1162(26)	0.2537(19)	2.20(57)					
H(2)RH	0.2457(20)	0.0419(28)	0.2920(20)	2.81(67)					
H(1)O(3)	0.0170(28)	0.0235(39)	-0.0759(27)	3.9(10)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B11h^2 + B22k^2 + B33l^2 + 2B12hk + 2B13hl + 2B23kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

Results and Discussion

Description of the Structure. As can be seen from a drawing of the inner coordination sphere, Figure 1, the molecular structure of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ consists of a distorted octahedral Rh(III) center, with no imposed symmetry but a local point-group symmetry close to $C_{2v}(mm)$. Modest hydrogen bonding between bicarbonato groups (O-H···O = 2.65 Å) couples molecules in the crystal, as illustrated in the packing diagram (Figure 2). Each hydrogen-bonded dimer possesses a crystallographic inversion center, with overall symmetry of the dimer approaching $C_{2h}(2/m)$. Rhodium-phosphorus bond lengths of 2.321 (2) and 2.302 (2) Å are slightly shorter than other Rh-P distances recently reported for triisopropylphosphine rhodium complexes $RhCl(L)(P(i\text{-}Pr)_3)_2$ (L = O_2, N_2, $CH_2{=}CH_2$) (2.348-2.363 Å).[33] The rhodium-oxygen distances (2.279 (2), 2.306 (2) Å) are very long compared with other Rh-O distances, for instance, in acetonylacetate complexes (1.97-2.08 Å)[34-36] and the related carbonato complex $Rh_2(CO_3)(PPh_3)_5$[22] (2.12 Å). This lengthening may result from the influence of the two trans hydride ligands. Rhodium-oxygen distances of 2.23 Å have been found trans to ortho-metalated phenyl rings.[37] Distances within the η^2-coordinated bicarbonato ligand are similar to those in *trans*-$PdMe(\eta^1\text{-}O_2COH)(PMe_3)_2$,[21] $M(OCO_2H)$ (M = Na,[39] K[40]), and related transition-metal carbonate compounds.[22,24,38]

The rhodium-hydride distances found in this complex (av 1.44 (5) Å) are shorter than typical metal-hydride bond distances of 1.5-1.7 Å[41] and are close to the Rh-H distance (1.48 Å) reported in an earlier structure.[42] While metal-hydride distances are determined with limited accuracy by X-ray methods,[43,44] the trends in the published data are for Rh(III)-hydride distances to be short (1.48 Å;[42] 1.37 (8) Å;[45] 1.41 (3), 1.47 (3) Å in the present study) and for Rh(I)-hydride distances to be more nearly normal (1.6 (1),[44] 1.66 (5) Å[25]). This may reflect a shift in electron density from the "hydride" nucleus toward a Rh(III) center, relative to a Rh(I) center.

Table V. Selected Bond Distances (Å) and Angles (deg) in $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$

Rh-P(1)	2.321 (2)	C(21)-C(24)	1.535 (4)
Rh-P(2)	2.302 (2)	C(21)-C(25)	1.527 (4)
Rh-O(1)	2.306 (3)	C(22)-C(26)	1.534 (4)
Rh-O(2)	2.279 (2)	C(22)-C(27)	1.537 (3)
Rh-H(1)	1.41 (3)	C(23)-C(28)	1.535 (4)
Rh-H(2)	1.47 (3)	C(23)-C(29)	1.538 (3)
Rh-H(av)	1.44 (4)	C-C (av)	1.533 (5)
C(1)-O(1)	1.261 (3)[a]	P(1)-Rh-P(2)	169.93 (2)
C(1)-O(2)	1.284 (3)	O(1)-Rh-O(2)	57.91 (7)
C(1)-O(3)	1.329 (3)	H(1)-Rh-H(2)	81 (2)
O(3)-H(1)O(3)	0.80 (4)	O(1)-Rh-H(1)	111 (1)
O(3)···O(2)′	2.649 (4)	O(2)-Rh-H(2)	110 (1)
P(1)-C(11)	1.876 (3)	O(1)-Rh-P(1)	98.52 (4)
P(1)-C(12)	1.859 (3)	O(2)-Rh-P(1)	91.22 (6)
P(1)-C(13)	1.857 (2)	O(1)-Rh-P(2)	90.34 (4)
P(2)-C(21)	1.861 (3)	O(2)-Rh-P(2)	97.57 (6)
P(2)-C(22)	1.863 (2)	O(1)-C(1)-O(2)	121.5 (2)
P(2)-C(23)	1.877 (3)	O(1)-C(1)-O(3)	118.7 (2)
P-C av	1.865 (9)	O(2)-C(1)-O(3)	119.8 (2)
C(11)-C(14)	1.538 (3)	H(1)O(3)-O(3)-C(1)	109 (3)
C(11)-C(15)	1.525 (3)		
C(12)-C(16)	1.536 (3)		
C(12)-C(17)	1.529 (3)		
C(13)-C(18)	1.534 (3)		
C(13)-C(19)	1.535 (3)		

[a] The value in parentheses is the standard deviation of a single observation and is the larger of that estimated from the average standard deviation of the individual observations or on the assumption that the values averaged are from the same population.

Synthesis and Spectra of $RhH_2(O_2COH)L_2$ (1, L = $P(i\text{-}Pr)_3$; 2, L = $PPh(t\text{-}Bu)_2$; 3, L = $P(c\text{-}C_6H_{11})_3$). Reaction of $RhH(P(i\text{-}Pr)_3)_3$ with CO_2 in dry *n*-hexane under ambient conditions of temperature and pressure affords a dihydrido bicarbonato compound $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**) in 48%

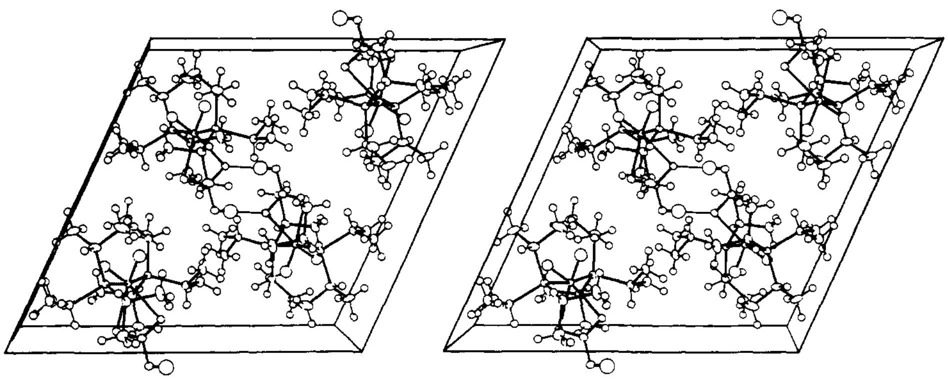


Figure 2. Stereoscopic view of the unit cell contents of $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$. Alkyl hydrogen atoms are included with an artificial *B* of 1.0 Å². The view is down the *y* axis, with the *x* axis across the page. At the center of each drawing is the inversion center which serves as the coordinate origin for Table IV.

yield. A $PPh(t\text{-}Bu)_2$ analogue **2** was obtained in 17% yield from a similar reaction of CO_2 with $RhH(N_2)(PPh(t\text{-}Bu)_2)_2$. The formation of these dihydrido bicarbonato compounds was totally unexpected; in fact, we originally formulated them as formato carbon dioxide complexes, and their correct formulation was the result of the X-ray analysis of **1**. Traces of water, present as an impurity in the CO_2 gas, are most probably responsible for their formation. When water was deliberately added to the reaction mixture the yield of the dihydrido bicarbonato complexes was dramatically improved to 85% for **1** (see Experimental Section).

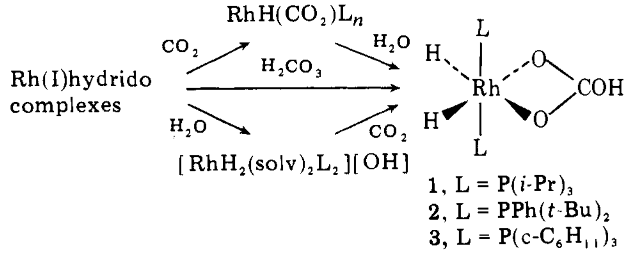
The dihydrido bicarbonato compounds **1–3** are obtained as colorless crystals which are stable in air for several days. ¹H NMR spectra of **1** and **2** show a hydride signal as a doublet of triplets resulting from coupling with two equivalent phosphorus nuclei and the rhodium nucleus, and a broad bicarbonato proton signal (Table II). The methyl proton signal of the phosphine ligands in **1** and **2** is split into a quartet and triplet, respectively, owing to virtual coupling. Thus the ¹H NMR data are consistent with a stereochemical assignment of cis hydrido ligands and trans phosphine ligands as found in the X-ray analysis of **1** (Figure 1). Poor solubility of the $P(c\text{-}C_6H_{11})_3$ analogue **3** prevented observation of either the hydrido or the bicarbonato proton signals, but the compound was unequivocally characterized by its infrared spectrum (Table I).

Infrared spectra of **1–3** show two vibrations assignable to ν_{Rh-H} in the region 2120–2220 cm⁻¹. Interestingly, when **3** is recrystallized from toluene the Rh–H IR stretching frequencies (2138, 2158 cm⁻¹) are different from those observed (2110, 2160 cm⁻¹) when **3** is precipitated from THF. The O_2COH vibrations (Table I) resemble those of the known bicarbonato dimer dianion $(HCO_3)_2{}^{2-}$ of point-group symmetry C_{2h}.[46] In the bicarbonato complexes **1–3** $\nu_{C=O}$ is at lower frequency than $\nu_{C=O}$ of *trans*-$PdMe(\eta^1\text{-}O_2COH)(PMe_3)_2$ and of $(HCO_3)_2{}^{2-}$, and this shift is consistent with η^2-bicarbonato coordination in **1–3**. The low value of ν_{O-H} (2649–2660 cm⁻¹) of **1–3** is a manifestation of hydrogen bonding between bicarbonato ligands. From the correlation between ν_{OH} and O–H- - -O distances in several hydrogen-bonded dimers,[47] an O–H- - -O distance of 2.65 Å for the dimeric complexes **1–3** is calculated. This value agrees remarkably well with the distance found in **1** (2.649 (4) Å). That the hydrogen bonding persists in benzene solution is shown by a cryoscopic molecular weight determination of **1** (observed 793, required for dimer 973 amu).

Formation of $RhH_2(O_2COH)L_2$ Complexes. Three possible pathways for the formation of the dihydrido bicarbonato complexes from the Rh(I) hydride complexes are depicted in Scheme I.

(1) A Rh–CO_2 complex may be formed which subsequently undergoes nucleophilic attack by H_2O at the coordinated CO_2 group. Several attempts were made to detect or isolate a CO_2 complex by treating $RhH(P(i\text{-}Pr)_3)_3$ with CO_2, carefully dried with molecular sieves, in dry *n*-hexane. All attempts failed, and the only compound observed (except for unreacted starting material) was **1** in trace amounts. (2) The Rh(I) hydride complexes may oxidatively add H_2CO_3, formed by the reaction of CO_2 with H_2O. (3) Water may be oxidatively added by the Rh(I) hydride complexes. The compound $RhH(P(i\text{-}Pr)_3)_3$ readily adds water at room temperature in aqueous pyridine to give an ion pair dihydrido hydroxy complex $[RhH_2(py)_2(P(i\text{-}Pr)_3)_2][OH]$; the cation may be isolated as the BPh_4^- salt.[48] The apparent pH of $[RhH_2(py)_2(P(i\text{-}Pr)_3)_2][OH]$ indicates that the system is more basic than NaOH in aqueous pyridine. Therefore, a facile formation of the bicarbonate anion from OH^- and CO_2 would be expected. Routes 2 and 3 appear to be more likely than 1; which route dominates may depend on the pH and Rh:H_2O:CO_2 ratio.

Scheme I



1, L = $P(i\text{-}Pr)_3$
2, L = $PPh(t\text{-}Bu)_2$
3, L = $P(c\text{-}C_6H_{11})_3$

Formation of $RhH_2(O_2CH)L_2$ (4, L = $P(i\text{-}Pr)_3$; 5, L = $P(c\text{-}C_6H_{11})_3$). Since facile insertion of CO_2 into transition metal-hydride bonds has been amply documented,[2-4,9-11] it is rather surprising that these Rh(I) hydride complexes react with CO_2 to form instead the dihydrido bicarbonato complexes **1** and **3**, even under ostensibly anhydrous conditions. Despite careful searching we have been unable to detect the expected insertion product, a formato complex, in the reaction of $RhHL_3$ with CO_2. Therefore formato complexes were prepared separately to examine their chemical behavior.

Formato complexes $RhH_2(O_2CH)L_2$ (**4**, L = $P(i\text{-}Pr)_3$; **5**, L = $P(c\text{-}C_6H_{11})_3$) could be obtained as stable, colorless crystals by treating the Rh(I) hydride complexes with formic acid. The compounds **4** and **5** are stable in air in the solid state, and in solution they do not evolve H_2 at room temperature. The ¹H NMR spectra (Table II) of **4** and **5** suggest that the two hydrido and the two phosphine ligands are mutually cis and trans, respectively, and these compounds are probably structurally very similar to **1**.

Interestingly, the two hydrido hydrogen nuclei couple with the formato proton across the four intervening bonds. The hydrido resonance of **4** is observed as two sets of double triplets ($^{4}J_{\mathrm{H-H}}$ = 1.1, $J_{\mathrm{H-Rh}}$ = 28.8, $J_{\mathrm{H-P}}$ = 18.0 Hz), and the formato proton signal consists of seven slightly broadened lines ($^{4}J_{\mathrm{H-H}}$ = 1.1, $^{3}J_{\mathrm{H-Rh}}$ = 2.0, $^{4}J_{\mathrm{H-P}}$ = 1 Hz). The $P(c\text{-}C_6H_{11})_3$ analogue **5** shows a similar long-range coupling between the hydrido and formato hydrogen nuclei ($^{4}J_{\mathrm{H-H}}$ = 1.0 Hz). A related dithioformato Ir complex $IrH_2(S_2CH)(PPh_3)_2$ also has a long-range coupling $^{4}J_{\mathrm{H-H}}$ = 1.5 Hz.[49] Observation of W-type long-range coupling suggests that the $RhH_2(O_2CH)$ moiety in **4** and **5** is planar.[51]

Two Rh–H stretching bands are observed in the IR spectra of **4** (2130, 2145 cm^{-1}) and **5** (2114, 2140 cm^{-1}) and indicate that the hydrido ligands are cis, again as in the dihydrido bicarbonato complexes **1** and **3**. The formato ligands of **4** and **5** give rise to vibrational bands at 1560 and 1310, and 1555 and 1310 cm^{-1}, respectively. These values are comparable with those reported for $RuH(O_2CH)(PPh_3)_3$ (1553, 1310 cm^{-1})[51] and *trans*-$PtH(O_2CH)(P(i\text{-}Pr)_3)_2$ (1530, 1310 cm^{-1}).[11]

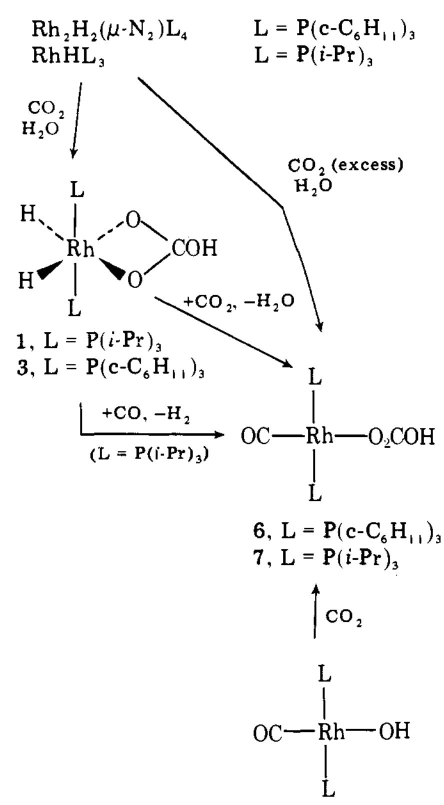
Formation of $Rh(O_2COH)(CO)L_2$ (6, L = $P(c\text{-}C_6H_{11})_3$; 7, L = $P(i\text{-}Pr)_3$) and $Rh_2(O_2CO)(CO)_2(P(i\text{-}Pr)_3)_4$ (8). Carbonyl bicarbonato (**6, 7**) and carbonyl formato (**9, 10**) complexes were obtained, at first totally unexpectedly, from the reaction of the corresponding dihydrido complexes with carbon dioxide. The bicarbonato compounds are also involved in the mechanism of the catalysis of the water-gas shift reaction by the Rh(I) hydride complexes.[19] Here we report details of their preparation, their spectral data, and their subsequent reactions.

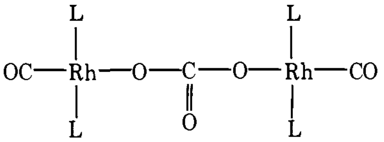
The carbonyl bicarbonato complexes may be prepared by three separate routes, summarized in Scheme II. The dihydrido bicarbonato complexes **1** and **3** reduce CO_2 to give the carbonyl bicarbonato complexes and H_2O (discussed below). Alternatively, the dihydrido bicarbonato complexes may be treated with CO to form the carbonyl bicarbonato complexes and H_2. A third, totally independent method of synthesizing the carbonyl bicarbonato complexes is from the reaction of the corresponding carbonyl hydroxy compounds with CO_2. Spectral data and melting point determinations prove that these diverse preparative methods give identical products.

Because of very limited solubility and a reversible decarboxylation (vide infra) our attempts to detect the bicarbonato hydrogen NMR signal of $Rh(CO)(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (**6**) have failed. However, the $P(i\text{-}Pr)_3$ analogue **7** is readily soluble in organic solvents and can be characterized by ^{1}H NMR spectroscopy (Table II). The IR spectrum of **6** shows a strong absorption from the coordinated CO molecule at 1942 cm^{-1} and several bands from the bicarbonato ligand (Table I). Upon deuteration, the bands from $\nu_{\mathrm{O-H}}$ and δ_{OHO} are shifted from 2650 to 2087 and from 1420 to 1062 cm^{-1}, respectively, while the coupled vibration $\nu_{\mathrm{C-O}} + \nu_{\mathrm{C=O}} + \delta_{\mathrm{OHO}}$ is shifted from 1355 up to 1405 cm^{-1}. The trends are consistent with those observed for the bicarbonato dimer dianion[46] (Table I). The $\nu_{\mathrm{C=O}}$ band also shifts markedly upon deuteration (1608 to 1590 cm^{-1}). These data indicate strong O—H hydrogen bonding in **6**, and it is likely that both **6** and **7** form hydrogen-bonded dimers similar to **1**.[21]

While the $P(c\text{-}C_6H_{11})_3$ complex **6** is stable at room temperature, the $P(i\text{-}Pr)_3$ analogue **7** readily forms the binuclear carbonato complex **8** with the evolution of CO_2. The formation of **7** has been confirmed by ^{1}H NMR and IR spectra (Tables I and II) but its instability has prevented the isolation of an analytically pure sample. Attempts to recrystallize **7** result in the formation of **8**. Compound **8** is also obtained from the reaction of CO_2 with **1** in pyridine, although **7** is probably a transient intermediate. The ^{1}H NMR spectrum of **8** measured at room temperature shows two broad signals centered at δ 1.24 and 2.27, which are assignable to the CH_3 and CH protons of $P(i\text{-}Pr)_3$. On cooling the sample to −10 °C the methyl proton signal was observed at δ 1.26 as a quartet ($^{3}J_{\mathrm{H-P}} + {}^{5}J_{\mathrm{H-P}}$ = 13.4, $J_{\mathrm{H-H}}$ = 6.7 Hz) owing to virtual coupling. The low-temperature ^{1}H NMR spectrum indicates equivalence of all four $P(i\text{-}Pr)_3$ ligands. Equivalence of all four phosphorus nuclei is also seen in the low-temperature ^{31}P NMR spectrum ($J_{\mathrm{P-Rh}}$ = 129.6 Hz, δ 53.8 ppm downfield from H_3PO_4; −55 °C in toluene). The room-temperature and high-temperature ^{31}P NMR spectra are complicated, with broad lines and the appearance of free phosphine. One interpretation of the NMR data is that the bridging carbonato ligand is η^1-η^1 at low temperature but rapidly loses phosphine and equilibrates with a η^1-η^2 structure at higher temperatures, eq 1. The IR spectrum of **8** has bands arising from the carbonato ligand at 1533 s, 1300 s, 1275 s, and 829 w cm^{-1}, which differ significantly from those of known η^1-η^2 bridging carbonato complexes $Rh_2(O_2CO)(PPh_3)_5$ (1485, 1460, 1350, 820 cm^{-1})[22] and $Mo_2(CO)_2(O_2CO)_2(PMe_2Ph)_6$ (1835 cm^{-1}),[24] and from those of a mononuclear η^2 carbonate $Pt(O_2CO)(PPh_3)_2$ (1680, 1180, 815 cm^{-1}).[23] The strong $\nu_{\mathrm{C\equiv O}}$ band of **8** (1934 cm^{-1}) with a shoulder (1950 cm^{-1}) is consistent with η^1-η^1 coordination, as two strong $\nu_{\mathrm{C\equiv O}}$ bonds would be expected for η^1-η^2 coordination. Formation of the binuclear carbonato complex **8** from two molecules of the bicarbonato complex **7** most likely proceeds via intermolecular oxidative addition of the bicarbonato O-H group, followed by reductive elimination of H_2CO_3 (eq

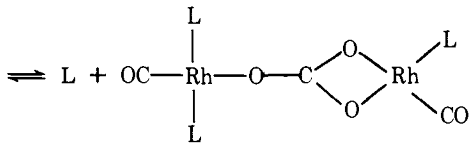
Scheme II



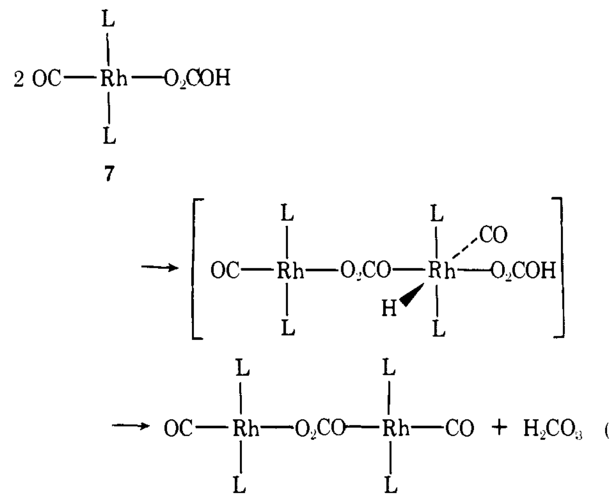


$$(OC)L_2Rh-O-C(=O)-O-RhL_2(CO)$$

8



(1)



7

8

(2)

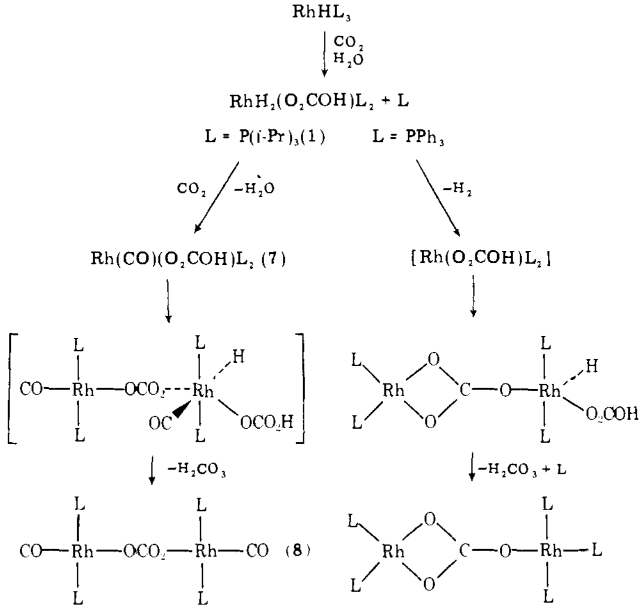
2). We confirmed the evolution of 0.45 mol of CO_2 per mol of **7**.

The relative stability of **6** we explain by the steric bulk of $P(c\text{-}C_6H_{11})_3$ (cone angle[52] 170°; compare $P(i\text{-}Pr)_3$, cone angle 160°) which prevents the bimolecular reaction of **6**. When heated in THF, however, **6** undergoes decarboxylation to give $Rh(OH)(CO)(P(c\text{-}C_6H_{11})_3)_2$ ($\nu_{C\equiv O}$ 1927, ν_{OH} 3600 cm^{-1}) together with an uncharacterized carbonyl-containing compound (ν_{CO} 1945 cm^{-1}). The reverse reaction, insertion of CO_2 into the Rh-OH bond of $Rh(OH)(CO)(P(c\text{-}C_6H_{11})_3)_2$, occurs readily at room temperature to regenerate **6**. Reversible decarboxylation is also suggested by the exchange of ^{12}C-bicarbonate for ^{13}C-bicarbonate under $^{12}CO_2$ (see Experimental Section). Similar decarboxylation reactions are known for a cobalt bicarbonato complex[53] and for alkylcarbonato,[15,54] carbamato,[16] and formato[4,55] complexes.

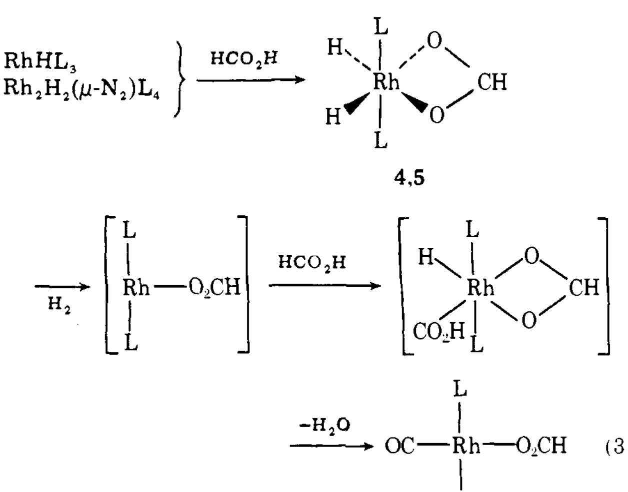
Formation of the analogous bicarbonato complex with triphenylphosphine, $Rh(CO)(O_2COH)(PPh_3)_2$, from the reaction of $Rh(OH)(CO)(PPh_3)_2$ with CO_2 has been reported.[56] Interestingly, the reported IR spectrum of this complex (1977 s, 1655 s, 1368 s, 1290 s, 1083 m cm^{-1}) differs significantly from the spectra of **6** and **7** (Table I). A supposed carbon dioxide complex, $Rh(OH)(CO)(CO_2)(PPh_3)_2$,[57] has a spectrum (1966 vs, 1620 s, 1351 s, 821 s cm^{-1}) much more closely resembling those of **6** and **7** (Table I). We have reexamined these complexes and believe that the "carbon dioxide" complex is actually the bicarbonato complex, and the reported "bicarbonato" complex is actually an alcoholate, possibly the ethyl carbonato complex $Rh(CO)(O_2COC_2H_5)(PPh_3)_2$, formed from the reaction of the genuine bicarbonato complex with alcohol (the solvent). In support of this postulate, treating $Rh(CO)(O_2COH)(PPh_3)_2$ with different alcohols (methanol, ethanol, 2-propanol) gives complexes with noticeably different IR spectra. The IR spectrum of the product obtained from the reaction with ethanol is identical with that reported[56] for the "bicarbonato" complex. In nonalcoholic solvents or at elevated temperatures these complexes are unstable and tend to decompose, resulting in what is believed to be a dimeric complex,[56] and we have not been able to obtain analytically pure samples nor reliable ^1H NMR data for any of these hypothetical alcoholates.

A reaction closely related to the present ones is the formation of a carbonato complex $Rh_2(O_2CO)(PPh_3)_5$ from $RhH(PPh_3)_n$ ($n = 3, 4$) and free CO_2. Both H_2O and CO_2 have been suggested as possible sources of the carbonato ligand, but no mechanistic aspects were reported.[22] The formation of $Rh_2(O_2CO)(PPh_3)_5$ may involve a sequence of steps similar to those in the formation of $Rh_2(CO)_2(O_2CO)(P(i\text{-}Pr)_3)_4$ (**8**) (see Scheme III). In both cases the first step, in the presence of water, is the formation of $RhH_2(O_2COH)L_2$. The difference in steric bulk of the phosphine ligands determines the stability of the dihydride coordination in $RhH_2(O_2COH)L_2$ and thereby the course of the subsequent reactions. The Rh-H stretching frequencies and, presumably, the strength of the Rh-H bond decrease with a decrease in the cone angle of the phosphine, $PPh(t\text{-}Bu)_2$ (cone angle ~170° [58]) ≥ $P(c\text{-}C_6H_{11})_3$ (170° [52]) > $P(i\text{-}Pr)_3$ (160° [52]) (see Table I). A similar trend was found for the Rh-H stretching frequencies of RhH_2ClL_2, L = $P(t\text{-}Bu)_3$[45] (cone angle 182° [52]), $P(c\text{-}C_6H_{11})_3$,[59] PPh_3[60] (145°), where the dihydride coordination of the $P(t\text{-}Bu)_3$ complex is stable but that of the PPh_3 analogue is reversible. A facile reductive elimination of H_2 from $RhH_2(O_2COH)(PPh_3)_2$ can therefore be postulated, resulting in $Rh(O_2COH)(PPh_3)_2$ which subsequently forms the carbonato complex through a bimolecular oxidative addition of the bicarbonato OH bond. In contrast, the dihydride coordination in $RhH_2(O_2COH)L_2$ (**1**, L = $P(i\text{-}Pr)_3$; **2**, L = $PPh(t\text{-}Bu)_2$; **3**, L = $P(c\text{-}C_6H_{11})_3$) is stable toward reductive elimination and instead reduces CO_2 to give $Rh(CO)(O_2COH)L_2$. For L = $P(i\text{-}Pr)_3$ dimerization occurs to give the carbonato complex **8**.

Scheme III



Formation of $Rh(CO)(O_2CH)L_2$ (9, L = $P(i\text{-}Pr)_3$; 10, L = $P(c\text{-}C_6H_{11})_3$). Both **9** and **10** may be obtained in high yield from the reaction of CO_2 with the corresponding dihydrido formato



4,5

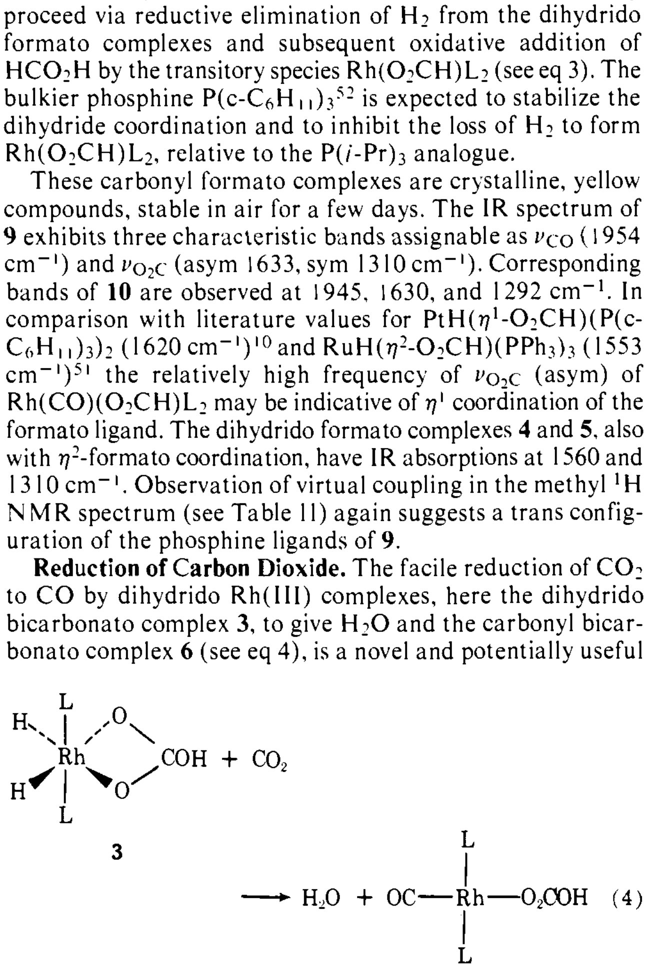
(3)

9,10

complexes **4** and **5**. Compound **9** may also be obtained from the direct reaction of $RhH(P(i\text{-}Pr)_3)_3$ with 2 equiv of formic acid at room temperature, with evolution of H_2. This direct method is less effective for the preparation of **10.** Treating $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ with a large excess of formic acid gives **10** as a minor product, the major product being the dihydrido formato complex **5**. This result suggests the dihydrido formato complexes **4** and **5** are intermediates in the formation of $Rh(CO)(O_2CH)L_2$ (**9** and **10**) from $RhHL_3$ or $Rh_2H_2(\mu\text{-}N_2)L_4$ and excess formic acid. The reaction may proceed via reductive elimination of H_2 from the dihydrido formato complexes and subsequent oxidative addition of HCO_2H by the transitory species $Rh(O_2CH)L_2$ (see eq 3). The bulkier phosphine $P(c\text{-}C_6H_{11})_3$[52] is expected to stabilize the dihydride coordination and to inhibit the loss of H_2 to form $Rh(O_2CH)L_2$, relative to the $P(i\text{-}Pr)_3$ analogue.

These carbonyl formato complexes are crystalline, yellow compounds, stable in air for a few days. The IR spectrum of **9** exhibits three characteristic bands assignable as ν_{CO} (1954 cm^{-1}) and ν_{O_2C} (asym 1633, sym 1310 cm^{-1}). Corresponding bands of **10** are observed at 1945, 1630, and 1292 cm^{-1}. In comparison with literature values for $PtH(\eta^1\text{-}O_2CH)(P(c\text{-}C_6H_{11})_3)_2$ (1620 cm^{-1})[10] and $RuH(\eta^2\text{-}O_2CH)(PPh_3)_3$ (1553 cm^{-1})[51] the relatively high frequency of ν_{O_2C} (asym) of $Rh(CO)(O_2CH)L_2$ may be indicative of η^1 coordination of the formato ligand. The dihydrido formato complexes **4** and **5**, also with η^2-formato coordination, have IR absorptions at 1560 and 1310 cm^{-1}. Observation of virtual coupling in the methyl ^1H NMR spectrum (see Table II) again suggests a trans configuration of the phosphine ligands of **9**.

Reduction of Carbon Dioxide. The facile reduction of CO_2 to CO by dihydrido Rh(III) complexes, here the dihydrido bicarbonato complex **3**, to give H_2O and the carbonyl bicarbonato complex **6** (see eq 4), is a novel and potentially useful reaction that has received very little attention. To the best of our knowledge the only previous reports of similar reactions are the reaction of $RhCl(PPh_3)_3$ with H_2 and CO_2 at high pressure and 100 °C to give $RhCl(CO)(PPh_3)_2$[20] and the formation of $RhCl(CO)(PPh_3)_2$ from $RhClH(Si(OEt)_3)(PPh_3)_2$ and CO_2.[61] The reverse reaction, the formation of H_2 and CO_2 from H_2O and CO, is the well-known water-gas shift reaction. Since the water-gas shift reaction is thermodynamically favorable and is readily catalyzed by Rh(I)-hydride complexes,[19] it is very surprising that the formation of a Rh(I)-carbonyl complex from CO_2 and a Rh(III)-dihydride complex is also thermodynamically favorable. We therefore examined the reaction carefully to prove that it does indeed proceed as in eq 4.



$$+\ CO_2 \longrightarrow H_2O + OC\text{—}\overset{L}{\underset{L}{Rh}}\text{—}O_2COH \quad (4)$$

3

6

1. The metal complexes involved have been well characterized. The starting complex $RhH_2(O_2COH)(P(c\text{-}C_6H_{11})_3)_2$ (**3**), both by its IR spectrum and by its method of preparation, is analogous to $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**), which has in turn been characterized by diffraction methods. In fact, **1** itself reacts with CO_2 in a similar fashion but the initial bicarbonato complex **7** is unstable and subsequently dimerizes to form **8**. The metal-containing product, the carbonyl bicarbonato Rh(I) complex, has been characterized spectroscopically and synthesized by independent methods.

2. The water formed in the reaction has been detected by VPC analysis of the reaction mixture.

3. Reaction of $^{13}CO_2$ with the dihydrido bicarbonato complex **3** gives the ^{13}C-labeled carbonyl bicarbonato complex (see Experimental Section). This rules out the possibility that the rhodium carbonyl product might have been formed from traces of CO in the "CO_2" or alcohols in the solvent.

4. The IR spectrum of the reaction residue shows no absorption bands ascribable to free or coordinated phosphine oxide.[62] Combined with the observation of near-quantitative yields[20] this eliminates the possibility of an oxygen atom transfer from CO_2 to PR_3.[8,63]

5. The dihydrido formato complexes **4** and **5** react with CO_2 in an exactly analogous manner. Reacting **4** with CO_2 in pyridine affords $Rh(CO)(O_2CH)(P(i\text{-}Pr)_3)_2$ (**9**) together with a small amount of **8**. VPC analysis of the reaction mixture shows the quantitative formation of water, and H_2 was not detected in the vapor phase.

While facile reduction of CO_2 by **3** occurs in pyridine, the reduction does not occur in toluene or THF. This may simply reflect the very limited solubility of **3** in these solvents at room temperature. The compound $Rh_2H_2(\mu\text{-}N_2)(P(c\text{-}C_6H_{11})_3)_4$ in THF-H_2O reduces CO_2 when treated with excess amounts, probably via the initial formation of **3** which in turn reacts with excess CO_2 before precipitating. The IR spectrum of the solid residue obtained upon evaporating a pyridine solution of **3** shows $\nu_{C=O}$ at 1695 cm^{-1}, a considerable shift from $\nu_{C=O}$ of **3** itself (1585 cm^{-1}), and the ν_{OH} band can no longer be found. This suggests that the η^2-bicarbonato ligand in **3** may be converted to η^1 coordination upon attachment of pyridine. A second explanation is that pyridine disrupts the probable hydrogen-bonded dimeric structure of **3**. A third possibility is that pyridine displaces the bicarbonato ligand entirely to form $[RhH_2(py)_2(P(c\text{-}C_6H_{11})_3)_2][O_2COH]$.

The mechanism of CO_2 reduction by the dihydrido bicarbonato complexes **1** and **3** probably proceeds by CO_2 insertion into the Rh-H bond, leading to either a hydroxycarbonyl species $RhH(CO_2H)(O_2COH)L_2$ or a formate complex $RhH(O_2CH)(O_2COH)L_2$. Elimination of water completes the reaction. Generally, insertion of CO_2 into a transition metal-hydride bond gives a formato complex[2-4,9-11] although formation of a hydroxycarbonyl complex has been reported.[64] We cannot distinguish between the two possible intermediates $RhH(CO_2H)(O_2COH)L_2$ and $RhH(O_2CH)(O_2COH)L_2$ from our present data, but the hydroxycarbonyl complex is the more intuitively appealing.

There are also two possible modes for the oxidative addition of HCO_2H to the hypothetical intermediate species $Rh(O_2CH)L_2$, leading to either $RhH(CO_2H)(O_2CH)L_2$ or $RhH(O_2CH)_2L_2$. Again elimination of water completes the reaction to form $Rh(CO)(O_2CH)L_2$. Here also the literature contains reports of both possible intermediates. The C-H fission of HCO_2H accounts for the formation of a hydroxycarbonyl species Ir-CO_2H in the reaction of $IrCl_3L_3$ with formic acid.[65] Decarbonylation of hydroxycarbonyl species has been observed, for example, in the formation of *trans*-$PtCl(CO)(PEt_3)_2$ from $PtCl(CO_2H)(PEt_3)_2$,[66] and is postulated for oxygen exchange reactions of metal carbonyls with $H_2{}^{18}O$.[67-69] The usual reaction of formate complexes is decarboxylation to give free CO_2 and metal hydride complexes.[10,11,51,70] If such a process were occurring rapidly in the reaction of $Rh(O_2CH)L_2$ with formic acid, the net result would be the catalytic decomposition of HCO_2H into H_2 and CO_2 with restoration of the dihydrido formato complex $RhH_2(O_2CH)L_2$. Since the CO_2 thus formed would rapidly react with $RhH_2(O_2CH)L_2$, we again cannot distinguish between the possible intermediates from our present data.

Summary and Conclusions

Rh(I)-hydride complexes with bulky phosphine ligands have been found to react with CO_2 and H_2O to form dihydrido bicarbonato Rh(III) complexes; no reaction occurs if water is excluded. Similar dihydrido formato complexes are formed when the Rh(I)-hydride complexes react with formic acid. These dihydrido Rh(III) compounds will react further with CO_2, CO, or excess formic acid to form Rh(I) carbonyl complexes. We had hoped that studies of the formato complexes would provide some mechanistic information on the reaction of the rhodium dihydride complexes with CO_2, but the formate complexes studied here behave so similarly to the rhodium-hydride-carbon dioxide systems that obvious mechanistic information was not obtained.

The formation of $Rh(CO)(O_2COH)L_2$ and H_2O from $RhH_2(O_2COH)L_2$ and CO_2

$$CO_2 + RhH_2(O_2COH)L_2 \rightarrow H_2O + Rh(CO)(O_2COH)L_2 \quad (5)$$

is, at first glance, the reverse of the water-gas shift reaction[71]

$$H_2O + CO \rightarrow CO_2 + H_2;\ \Delta H_{298\,°C} = -9.85\ \text{kcal/mol},\ -41.2\ \text{kJ/mol}$$

$$K_p = 40.4 \quad (6)$$

and should therefore be thermodynamically unfavorable. In retrospect, however, the driving force for the reduction of CO_2 is seen to be the formation of the Rh(I)-carbonyl bond.[4] It can easily be shown that the reduction of CO_2 (eq 5) is thermodynamically favorable, even with the knowledge that the water-gas shift reaction (eq 6) is also favored, if the direct reaction with free CO

$$CO + RhH_2(O_2COH)L_2 \rightarrow H_2 + Rh(CO)(O_2COH)L_2 \quad (7)$$

is favorable. This has been demonstrated for **1**, L = P(*i*-Pr)$_3$.

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Supplementary Material Available: A list of $10|F_o|$ vs. $10|F_c|$ and a table of hydrogen atom positions (41 pages). Ordering information is given on any current masthead page.

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Stereoselectivity in Ion-Pair Formation. The Contribution of the Rotamers to the Interaction of Mono- and Disubstituted Succinate Dianions with Tris(ethylenediamine)cobalt(III)[1]

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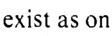
Abstract: The changes in the circular dichroism (CD) spectra of optically active tris(ethylenediamine)cobalt(III) have been measured upon addition of monosubstituted succinate dianions (malate, thiomalate, aspartate, methylsuccinate, phenylsuccinate, chlorosuccinate, bromosuccinate, and succinate ($^-OOCCH_2CH(R)COO^-$; R = OH, SH, NH_2, CH_3, C_6H_5, Cl, Br, and H)), and upon addition of 1,2-disubstituted succinate dianions (dibromosuccinate, dimethylsuccinate, tartrate (dihydroxysuccinate), and 1,2-cyclohexanedicarboxylate ($^-OOCCH(R)CH(R)COO^-$; R = Br, CH_3, and OH, and R–R = $CH_2(CH_2)_4$-CH_2)). It is found that the resultant CD changes, which are due to the outer-sphere association with these dianions, are similar in shape and magnitude for the monosubstituted succinate dianions, while they vary depending upon the kind of two substituents R for the disubstituted succinate dianions. These findings are examined on the basis of the idea that the substituted succinate dianion interacts with the complex ion through the COO^- group as a mixture of their two rotamers, in which the two COO^- groups are gauche and trans to each other. It is, eventually, concluded that the resultant CD changes are dependent on the fractional populations of gauche and trans rotamers, and the populations of these rotamers are controlled only by the electrostatic repulsion between the two COO^- groups for the monosubstituted succinate dianions, while they are controlled by the interaction between the substituents R as well for the disubstituted succinate dianions. Furthermore, it is proposed that the conformation of the dicarboxylate dianion can be determined by the analysis of the CD change. Actually, the fractional populations of rotamers of *trans*-1,2-cyclohexanedicarboxylate are calculated by this analysis (gauche form 60% and trans form 40%).

Introduction

Several interesting studies have been reported on the stereoselectivity in outer-sphere association of metal complexes. One of the familiar examples of this kind is on the stereoselective association of L-(2*R*,3*R*)-tartrate with Λ- and Δ-$[Co(en)_3]^{3+}$ (en: ethylenediamine) in aqueous solution.[3-6] For the purpose of clarifying the origin of this stereoselectivity, we have investigated the ion-pair structure in solution between the dicarboxylate anion and the complex ion. We have already elucidated by measuring CD changes that the dicarboxylate anion interacts with the complex ion through the carboxyl group (COO^-), and that the skeleton I is essential to a favorable association in this system.[7,8] However, most of the dicarboxylate anions do not exist as only one species in solution but as some rotamers. Therefore, the interaction of the dicarboxylate anion with the complex ion cannot be elucidated until the contribution of each rotamer to the interaction becomes clear. It is, at present, not clear in detail how the rotamers contribute to the interaction with the complex ion. Thus we investigated the interaction of the rotamers of monosubstituted and 1,2-disubstituted succinate dianions with the complex ion by utilizing the CD measurement.



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In solution, the rotational isomerism of dicarboxylate dianions can be investigated by means of the NMR technique. In fact, the fractional populations of rotamers of dicarboxylate dianions, e.g., malate[9,10] and aspartate,[11,12] have been already determined from the NMR coupling constants. This method is applicable to the species showing ABX patterns of ^1H NMR spectra. However, it seems that this method is limited to the monosubstituted succinate dianion. As for the disubstituted succinate dianion, the information on the rotational isomerism is obtained from the comparison with the acid dissociation constants.[13] The result from this method is qualitative but applied to the rotational isomerism between meso and *dl* acids of disubstituted succinate dianions. On the basis of the information on the rotational isomerism obtained in these manners, we attempted to make clear the contribution of the rotamers to the interaction of monosubstituted and 1,2-disubstituted succinate dianions with the complex ion.

Experimental Section

Materials. Tris(ethylenediamine)cobalt(III) Bromide. $[Co(en)_3]$-$Br_3 \cdot 3H_3O$ was prepared and resolved into enantiomers, Λ- and Δ-$[Co(en)_3]Br_3 \cdot H_2O$, by using silver L-(+)-tartrate. The purity of these complexes was checked by elemental analysis and spectroscopic methods.

Monochlorosuccinic and Monobromosuccinic Acids.[14] The preparation of these compounds was made by passing a stream of N_2O_3 mixed with N_2 into ice-cooled aqueous solutions of (+)-aspartic acid and hydrochloric or hydrobromic acid. Monochlorosuccinic acid: $[\alpha]_D$ −55° (ethyl acetate). Anal. Calcd for $C_4H_5O_4Cl$: C, 31.48; H, 3.30. Found: C, 31.27; H, 3.30. Monobromosuccinic acid: $[\alpha]_D$ −75° (ethyl acetate). Anal. Calcd for $C_4H_5O_4Br$: C, 24.39; H, 2.56. Found: C, 24.38; H, 2.57.

***dl*-Dibromosuccinic Acid.**[15] This compound was prepared by the

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