Reduction of Carbon Dioxide by {2,6-Bis[(di-*tert*-butylphosphino)methyl]phenyl}dihydridorhodium(III)

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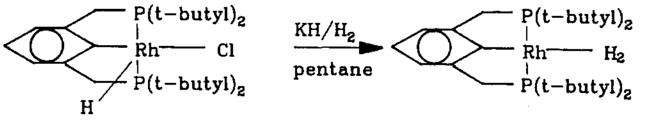
The complex $[H_2Rh\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ interacts with CO_2 to produce a rhodium hydroxide complex, $[HORhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$. Water is eliminated from the hydride hydroxide complex with carbon monoxide to form the corresponding rhodium carbonyl complex. An intermediate formato complex can be detected.

Introduction

Transition-metal complexes and their interaction with carbon dioxide are potential sources of C_1 compounds for the cyclic renewal of carbon chemistry.[1] A specific aspect of this chemistry is the interaction of transition-metal hydrides with CO_2 to produce metalloformates.[2] Many known metalloformates decompose to generate metal carbonyl complexes.[3a,b,9] In this paper we describe a homogeneous metal hydride system that produces a hydrido–hydroxide intermediate that subsequently forms a metal carbonyl complex and water.

Results and Discussion

Interaction of $[H_2Rh\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ with CO_2. We previously showed that a cluster of *tert*-butyl groups around **1** did not hinder the replacement of the HCl fragment with various small molecules including hydrogen to give **2**.[4] The ease by which H_2 could be removed from **2** as hydrogen gas suggested to us that CO_2 might likewise form a η^2-complex with the rhodium atom by displacement of hydrogen. This idea was not entirely confirmed because the rhodium hydride complex reduced CO_2 to water and CO in what amounted to a reversal of the water-gas shift reaction. A summary of our findings is shown in Scheme I.



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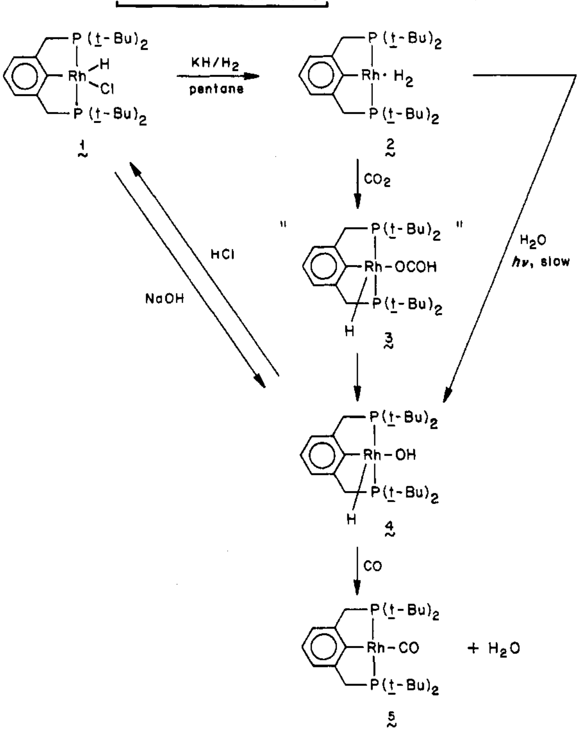
Scheme I. Reaction Pathways for $[ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$



Formation of $[HORhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ (4) and $[OCRh\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ (5). A quantitative yield of **4** was obtained by treating a yellow solution of **2** in pentane with CO_2 at atmospheric pressure for 6–8 h. At higher pressures of 2–3 atm of CO_2 for 10 h in pentane a mixture of **4** and **5** was isolated. After long reaction times in alkane solvents (1 week or more) only **5** was observed. In benzene at 3 atm for 10 h only **4** was isolated.

We characterized **4** by treating it with gaseous HCl to isolate complex **1**[5] and by carefully treating **1** with carbonate-free NaOH in THF/H_2O. The isolated product was identical in melting point, ^1H NMR, and $^{31}P\{^1H\}$ NMR

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(1) Some general references are as follows: (a) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *291*, 6 and references therein. (b) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (c) Walther, D.; Dinjus, E. *Z. Chem.* **1983**, *23*, 237. (d) Hoberg, H.; Jenni, K.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 810, (e) Behr, H.; Herdtweck, E.; Hermann, W. A.; Keim, W.; Kipshager, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1262.

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(4) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.

(5) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

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with 4 that had been prepared by using CO_2.

The presence of 5 was detected by an infrared spectrum of the reaction mixture that showed a Rh ν(CO)absorption band at 1930 cm^{-1}.[5] When 5 was isolated from the reaction mixture, it had the same $^{31}P\{^1H\}$ NMR and ^1H NMR spectra as those of authentic material.[5]

This was further confirmed by treating 2 with $^{13}CO_2$ under 3-atm pressure in a sealed NMR tube in cyclohexane-d_{12}. After 1 week, the presence of 5 was detected as a doublet of triplets at δ 201.0 ($J_{Rh^{13}CO}$ = 19 Hz). This demonstrates that the presence of 5 must originate from $^{13}CO_2$ as the source of ^{13}CO and not from any CO in the $^{13}CO_2$. In addition it means that the rhodium hydride hydroxide 4 must originate from the $^{13}CO_2$ because ^{13}CO is found in the reaction and coordinates to the rhodium atom.

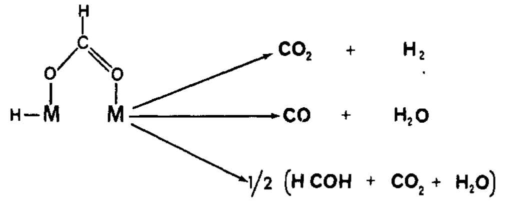
Control experiments without CO_2 showed no evidence for the formation of 4 that could come from adventitous moisture in the equipment or vacuum line (cf. Experimental Section). A control experiment with 2 and water showed that under photolytic conditions formation of 4 is very slow.

When 4 was isolated from the reaction mixture or synthesized independently from 1 and NaOH and treated with CO, 5 was isolated as a yellow solid. It compared identically with the material that was prepared directly from 1 and CO.[5]

Detection of Formate Species.[6] The most logical precursor to 4 would be a metalloformate. Evidence for such a species was obtained by treating 2 with $^{13}CO_2$ and following the course of the reaction. After 12 h, a doublet at δ 172.7 (J_{CH} = 193.3 Hz) was obtained for the formate carbon atom single ^1H coupling that is characteristic of formate.[7] The decoupled spectrum showed a singlet. The formate doublet at δ 172.7 slowly diminished in intensity, and the doublet of triplets at δ 201.0, which indicated the formation of 5, was observed after 1 week. No further evidence for rhodium-coupled ^{13}C atoms were observed in the spectra. An infrared spectrum of the reaction mixture after solvent removal and before complete formation of 5 showed an absorption peak at 1610 cm^{-1}, which we assigned to the formate species. Similar peaks occur for the following formates: (triphos)CuOCOH (ν 1620, 1320 cm^{-1})[8a] and $Rh(PPh_3)_3OCHO$ (1615 cm^{-1}).[8b]

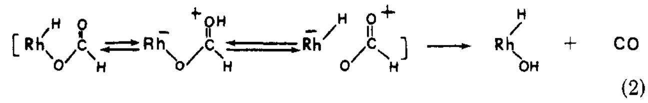
The $^{31}P\{^1H\}$ and ^1H NMR spectra of the initial reaction mixture showed that 2 disappeared immediately. The only species that could be identified were the formate and the hydride–hydroxide. The most likely complex that gives 4 is the formate moiety 3, but the exact mechanism and the importance of other species are not yet clear. The end products 4 and 5 remain the same and can be isolated quantitatively.

Homogeneous synthesis of metal carbonyls with formic acid and formates are well-known, although the precise mechanisms of carbonyl formation are not clear (eq 1).[2c,9]



(1)

The dehydration pathway normally would form the most thermodynamically stable metal carbonyl complex. This product should be observed immediately.[9] The treatment of highly hindered 2 with CO_2 gives the kinetic product 3. After this the isolation of 4 and then 5 can be observed. One possible pathway for the formation of 4 is based on heterogenous catalytic studies shown in eq 2.[3a,10] Another possibility, of course, is that hydroxy carbonyls formed by possible formate isomerization would readily generate 4.[3c]



(2)

Perhaps most carbonylations with formic acid and metal formate decompositions that produce CO actually proceed via metal hydrido–hydroxide intermediates, but they are too unstable for isolation in the presence of carbon monoxide and the metal carbonyl is isolated instead.[10] The steric role of the bulky *tert*-butyl groups is not clear, but in this case they may facilitate the isolation of the hydride–hydroxide complex. Independent treatment of the hydride–hydroxide complex with CO does give 5.

Conclusions

1. The rhodium dihydride complex in benzene with excess CO_2 gives exclusively the product 4 and CO.
2. In alkane solvents, the initial product is a metalloformate.
3. The rhodium dihydride in alkane solvents produces 4 and CO which eventually gives 5 and water.
4. The reaction is not catalytic but does produce CO and water; a reverse of the water-gas shift reaction.[2b]

Experimental Section

General Procedures, Instrumentation, and Chemicals. All manipulations were performed under pure argon which had been passed through molecular sieves (13X), alumina, and two columns of Phillips Catalyst[11] to further remove oxygen and water. The reactions were performed in 25- or 50-mL heavy-wall glass bottles to which were attached Teflon stopcocks[12] with Teflon O-ring seals. No silicone lubricants were used. Brass tees with butyl rubber, Teflon, or silicone stoppers were used on top of the bottles to introduce gases.[13] Gases were transferred via flexible metal tubing, or heavy-wall butyl rubber tubing. The products were

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[6] We were not able to isolate a stable formate by treating 1 with thallium or silver formate. Moreover, treatment of 1 with $H^{13}CO_2H$ in cyclohexane-d_{12} and recording the ^{13}C NMR spectra showed that no reaction occurred.

[7] The coupling constant for the formate carbon atom varies from 170–230 Hz; the chemical shifts for the carbonyl carbon in ethyl formate and formic acid are δ 160.7 and 166.7, respectively, but for formate ion it depends upon the pH; it is generally δ 170; most formates have a ^1H chemical shift that varies from δ 9 to δ-10; the formate ion hydrogen atom chemical shift observed in this work is δ 12 (b, J_{CH} = 194.8 Hz). See also: Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223 (for ^{13}C of the formate ion). Roberts, D. R.; Geoffroy, G. L.; Bradley, M. C. *J. Organomet. Chem.* **1980**, *198*, C75–C78. Staldor, C. J.; Chao, S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 6318. Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley: New York, 1972. Strothers, J. B. *Nuclear Magnetic Resonance*; Academic: New York, 1972; p 304. There was no evidence for rhodium coupling to the formate carbon atom. There have been no conclusive reports of rhodium–carbon coupling in carbonato or formato complexes with strong metal–oxygen bonds; hence it is difficult to conclude if rapid dissociation of the formate ion from the rhodium atom is the reason for the lack of observable Rh–^{13}C coupling. See $(Cy_3P)_2Rh(CO)O_2CH$). Willis, W.; Nicholas, K. M. *Inorg. Chim. Acta* **1984**, *90*, L51. See also: Yoshida. T.; Youngs, W. J.; Sakaeda, Ueda, T.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *105*, 6273. Dahlenberg, L.; Prengel, C.; Hock, N. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 718.

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[9] Sapienza, R.; Slegeir, W.; Mahajan, D. *Polyhedron* **1986**, *5*, 249.

[10] Cleare, M. J.; Griffith, W. P. *J. Chem. Soc.* **1969**, 372. Douglas, P. G.; Shaw, B. L. *J. Chem. Soc.* **1969**, 1491.

[11] Krauss, H. L.; Stach, H. *Z. Anorg. Allg. Chem.* **1969**, *366*, 34.

[12] Young, J., Scientific Glassware, Brunfeldt, R. J., Box 2066, Bartlesville, OK 74005.

[13] Barefield, E. K. *J. Chem. Educ.* **1973**, *198*, 50.

the same regardless of the precautions taken to reduce contamination by water.

The rhodium dihydride was prepared in one bottle and filtered into a second bottle under hydrogen gas without detaching any of the glassware. This was necessary because the slightest trace of oxygen caused the dihydride to turn green. Pentane, Aldrich chromatographic quality, was treated with fuming sulfuric acid to remove traces of olefins, dried, and distilled from benzophenone ketyl which had been generated with a small amount of diphenyl ether. Potassium hydride was washed free of oil with pentane and stored under argon. It was further treated with trimethylchlorosilane to remove any basic impurities.[14] Deuterated cyclohexane (Aldrich) was distilled under argon from $LiAlH_4$. Dichloromethane was treated with concentrated sulfuric acid, washed with water, dried over CaH_2, and distilled under argon from $LiAlH_4$. Silver hexafluorophosphate (Strem) was used as received. The dihydride was transferred in cyclohexane-d_{12} to heavy-wall 5-mm NMR tubes to which was attached a brass tee to allow introduction of CO_2 via metal hoses. The CO_2 was Matheson Research Grade 99.999%; the $^{13}CO_2$ was from ICON Services 19 OX Bow Lane, Summit, NJ 07901, and was allowed to stand over Phillips Catalyst (SiO_2 chromia). The Matheson Grade CO_2 was allowed to stand over Phillips catalyst to remove any traces of oxygen and water. GC mass spectroscopic analysis of the gas after such a treatment showed no oxygen or water in the sample. Some of the reactions were performed in glassware that was treated with "Glass Clad", i.e., flasks, glass frits, and NMR tubes,[15] to minimize surface water contamination. The products obtained were not changed when less stringent conditions were used although the total elimination of trace water was not possible.

Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian CFT-20 for ^1H (80 MHz) and ^{13}C (20 MHz), a Bruker 500 MHz for ^1H (500 MHz), ^{31}P (202.47 MHz), and ^{13}C (125.76 MHz), or a NT-300 MHz spectrometer for ^1H (300 MHz), ^{31}P (121.4 MHz), and ^{13}C (75.4 MHz). The ^{31}P NMR chemical shifts are reported in parts per million referenced to a capillary of 85% H_3PO_4 set at 0 ppm in a 5-mm tube that contained benzene-d_6 at 25 °C. Downfield resonances are positive. The ^1H and ^{13}C chemical shifts are reported relative to Me_4Si as an external standard or the internal standard of hydrogen atoms in cyclohexane-d_{12} (1.38 ppm relative to Me_4Si). Elemental analyses were performed by Analytische Laboratorien, Postfach 1249, 5250 Engelskirchen, West Germany, and Oneida Research Services, 1 Halsey Road, Whitesboror, NY 13492.

Preparation of $[HORhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$. A solution of NaOH (7.5 mg, 0.188 mmol) (made from NaH and H_2O under argon to eliminate CO_2 in 0.1 mL of degassed water) was slowly added by syringe to a yellow THF solution of 1 (100 mg, 0.188 mmol) at room temperature. The reaction solution was allowed to stir for 2 h whereupon all the THF was removed and benzene was added. The yellow-orange benzene solution was filtered from NaCl and freeze-dried to give a yellow solid: 0.1 g, 97%; mp 270–290 °C dec; ^1H NMR (C_6D_6) δ 1.2 (t, 36, J_{PH} = 68 Hz, $C(CH_3)_3$), 3.26 (t, 4, J_{PH} = 3.7 Hz, CH_2), 7.1–7.25 (m, 3, C_6H_3), −27.4 (dt, 1, RhH, J_{RhH} = 51.0 Hz, J_{PH} = 12.0 Hz), 16.4 (b, OH); $^{31}P\{^1H\}$ NMR δ 74.9 (d, J_{RhP} = 114.8 Hz); IR (Nujol) ν(OH) 3430 cm^{-1}. The mass spectrum showed a peak at *m/e* 496.18 which is the title compound minus H_2O. Anal. Calcd for $C_{24}H_{45}P_2ORh$: C, 56.03; H, 8.81; P, 12.04. Found: C, 55.75; H, 8.57; P, 12.38.

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Registry No. 1, 60399-58-8; 2, 111112-39-1; 3, 111112-40-4; 4, 111112-41-5; 5, 60399-59-9; CO_2, 124-38-9.

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