Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164

Cocatalyzed Oxidation of Carbon Monoxide and Triphenylphosphine Using Complexes Derived from Hexarhodium Hexadecacarbonyl as Homogeneous Catalyst. Characterization of Rhodium Carbonyl Intermediates, Oxygen-18 Labeling To Identify Oxygen Atom Sources, and Observation of Catalyzed Oxygen Atom Exchange between Carbon Dioxide and Water

MARK K. DICKSON, NAGARAJ S. DIXIT, and D. MAX ROUNDHILL*[1]

Hexarhodium hexadecacarbonyl, $Rh_6(CO)_{16}$, will cocatalyze a reaction with molecular oxygen involving the conversion both of carbon monoxide to carbon dioxide and of triphenylphosphine to triphenylphosphine oxide. Solution infrared spectroscopy in the carbonyl region in benzene solvent shows that the catalytic cycle passes through the red $Rh_2(CO)_2(PPh_3)_4(C_6H_6)_2$, the yellow $Rh_2(CO)_6(PPh_3)_2$, and the red $Rh_4(CO)_{10}(PPh_3)_2$. Final return to $Rh_6(CO)_{16}$ does not occur under the ambient temperature and pressure conditions used but can be achieved by elevating these conditions. The $^{31}P\{^1H\}$ NMR spectra of the solutions have been collected but provide little structural information because of facile solution intramolecular and intermolecular exchange. As confirmation of declusterification, the compound $Rh_4(CO)_{12}$ will also catalyze the cooxidation of CO and PPh_3, and solution infrared measurements show the same intermediates to be present as found when $Rh_6(CO)_{16}$ is used. Simultaneous measurement of CO_2 and $OPPh_3$ formed under conditions where both the pressure of CO and the concentration of PPh_3 are kept constant shows that the ratio of CO_2:$OPPh_3$ is greater than unity. Monitoring this ratio as the catalytic cooxidation proceeds shows that the value is at a minimum at the earlier stages of the reaction. Addition of water to the anhydrous reaction mixture causes an increase in the yield of CO_2, which is indicative of a contributive pathway from water or hydroxide ion attack at the coordinated carbonyl. The source of oxygen atom nucleophile or oxidant has been investigated with use of labeled $^{18}OH_2$ and $^{18}O_2$. Oxygen-18 from $^{18}OH_2$ is incorporated into carbon dioxide both under conditions where it remains in contact with the catalyst and under experimental conditions where the carbon dioxide is rapidly swept from the reactant solution. Addition of carbon dioxide to a mixture of $Rh_6(CO)_{16}$, CO, and PPh_3 in the presence of added $^{18}OH_2$ shows that the rhodium compounds will catalyze oxygen exchange between carbon dioxide and the oxygen atom of water. Using $^{18}O_2$ as reagent with added $^{16}OH_2$ in the reaction verifies that the product triphenylphosphine oxide is largely $^{18}OPPh_3$ but that the oxygen-18 label in the formed CO_2 is mainly equilibrated by $^{16}OH_2$. Under anhydrous conditions the use of $^{18}O_2$ as oxidant leads to the formation of isotopically labeled carbon dioxide. In all of these cases there is some equilibration of the oxygen-18 label in the carbon dioxide. Under the static 6-h reaction time the distribution ratios between isotopomers m/e 44, 46 and 48 are close to the calculated equilibration values with the added $^{18}OH_2$. A pathway for equilibration of oxygen isotope in the catalyzed conversion of coordinated carbonyl to carbon dioxide via metallocarboxylate intermediates is proposed. The equilibration of oxygen isotope from water into carbon dioxide catalyzed by rhodium carbonyl clusters is suggested to proceed via hydroxyrhodium intermediates.

Introduction

An area of homogeneous catalysis that has produced much recent interest revolves around the concept of cluster catalysis.[2] The focus of such work is the formation of cluster compounds or solution intermediates where multisite chemistry can occur leading to different reaction pathways than arise at a single site. One difficulty in interpreting the chemistry with such systems is that of determining the state of aggregation of the species in solution. In particular, this problem becomes vital when one tries to deduce the molecular size of any interme-diates involved and decide whether more than one metal center is responsible for reactivity.

A second field of active research interest is the search for homogeneous oxidation catalysts. A major goal of these projects is the development of complexes that will act as oxygen-transfer catalysts to carbon by selective nonradical mechanisms. In particular, it is believed likely that such a system with molecular oxygen as oxidant will necessarily either require two or more substrates to be oxidized or proceed in a stepwise fashion via an intermediate oxo transition-metal compound. The purpose of this article is to present our results on the function of the cluster compound $Rh_6(CO)_{16}$ as a homogeneous catalyst for the cooxidation, with molecular oxygen, of carbon monoxide to carbon dioxide and of triphenylphosphine to triphenylphosphine oxide. Although many transition-metal compounds will function as homogeneous catalysts for triphenylphosphine oxidation, the occurrence of this reaction with $Rh_6(CO)_{16}$ has some significance because of the use of phenylphosphinated polymers for attachment of rhodium clusters to immobilized supports.[3] The primary goals of this project are to identify the solution species present during the catalytic cycle and to investigate any mechanistic relationship between the cooxidation of triphenylphosphine and carbon monoxide. The current literature on catalyzed cooxidations with molecular oxygen which have been studied in any mechanistic detail is rather sparse.[4] Hence, such reactions

(1) Present address: Department of Chemistry, Tulane University, New Orleans, LA 70118.
(2) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91–137. Muetterties, E. L. *Science (Washington, D.C.)* **1977**, *196*, 838–848. Muetterties, E. L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 545–558. Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207–273. Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145–222. Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148. Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855–6857. Pittman, C. U., Jr.; Wilemon, G. M.; Wilson, W. D.; Ryan, R. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 478–479. Moskovits, M. *Acc. Chem. Res.* **1979**, *12*, 229–236. Ford, P. C.; Rinker, R. G.; Ungermann, C.; Laine, R. V.; Landis, V.; Moya, S. A. *J. Am. Chem. Soc.* **1978**, *100*, 4595–4597. Vidal, J. L.; Fiato, R. A.; Cosby, L. A.; Pruett, R. L. *Inorg. Chem.* **1978**, *17*, 2574–2582. Bianchi, M.; Matteoli, U.; Menchi, G.; Frediani, P.; Pratesi, S. Piacenti, F.; *J. Organomet. Chem.* **1980**, *198*, 73–80. Otero-Schipper, Z.; Lieto, J.; Gates, B. C. *J. Catal.* **1980**, *63*, 175–181. Balavoine, G.; Dang, T.; Eskenazi, C.; Kagan, H. B. *J. Mol. Catal.* **1980**, *7*, 531–534. Graff, J. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 2123–2125. Whitmire, K.; Shriver, D. F. *Ibid.* **1980**, *102*, 1456–1457. Bradley, J. S.; Ansell, G. B.; Hill, E. W. *Ibid.* **1979**, *101*, 7417–7419. Bradley, J. S. *Ibid.* **1979**, *101*, 7419–7421. Roundhill, D. M.; Dickson, M. K.; Dixit, N. S.; Sudha-Dixit, B. P. *Ibid.* **1980**, *102*, 5538–5542.
(3) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 6.6. Jarrell, M. S.; Gates, B. C.; Nicholson, E. D. *J. Am. Chem. Soc.* **1978**, *100*, 5727–5732.

are important both because of the need to find selective catalytic oxidations with molecular oxygen and because of their possible relation to biological oxidation processes.

Results and Discussion

Hexarhodium hexadecacarbonyl catalyzes the oxidation, with molecular oxygen, of triphenylphosphine, methyldiphenylphosphine, and triphenylarsine to their respective oxides under ambient conditions.[5] In addition there is a concomitant conversion of added carbon monoxide into carbon dioxide. The compound $Rh_6(CO)_{16}$ exhibits negligible solubility in dry benzene at room temperature, and the heterogeneous mixture will *not* catalyze the oxidation of carbon monoxide to any measurable extent. Upon addition of excess tertiary phosphine or arsine, complexation occurs and a stirred mixture gradually becomes *homogeneous*. Introduction of oxygen and carbon monoxide to this solution results in the cooxidation of both carbon monoxide and the phosphine or arsine. This reaction is only moderately fast at room temperature under a 1-atm total pressure of CO and O_2; a stirred mixture containing $Rh_6(CO)_{16}$ (23 mg, 0.02 mmol) and PPh₃ (310 mg, 1.2 mmol) in benzene (30 mL) results in complete conversion to OPPh₃ after approximately 2 h.[6]

Initial solubilization of $Rh_6(CO)_{16}$ in the presence of PPh₃ and benzene leads to the formation of a yellow solution, but as the solution finally becomes homogeneous under vacuum or inert-atmosphere conditions, the color changes to red. During the course of reaction with CO and O_2 the solution color changes from red through yellow, and then back to red, as triphenylphosphine is completely converted to triphenylphosphine oxide. The solution remains homogeneous throughout. The concurrent oxidation of CO to CO_2 is catalytic in the presence of excess CO. This oxidation of carbon monoxide does not occur prior to PPh₃ addition and *ceases* after complete conversion to OPPh₃. It is apparent from these observations that $Rh_6(CO)_{16}$ is not the discrete catalytically active species responsible for these oxidation reactions but that a series of substitution complexes are formed under the experimental conditions. Furthermore, any one or more of these phosphine-substituted rhodium carbonyls could be the precursor compound yielding the catalytically active species. During all reactions a low carbon monoxide pressure is maintained over the mixture throughout. This carbon monoxide serves both as a cooxidant and as a ligand, the latter function preventing the irreversible formation of metallic rhodium or rhodium oxide precipitates.

(i) Carbonyl Infrared Data. As a method to try and identify the solution species formed during the catalytic cycle, we have monitored the carbonyl region (~ 2000 cm⁻¹) of the infrared spectrum as the catalysis proceeds. Samples have been transferred by syringe between sealed systems (vacuum line and infrared cell) in order that the experimental conditions in the solution infrared cell closely match those prevailing in the catalytic cycle. A reliable infrared spectrum of the initial

yellow solution in benzene could not be obtained because of the inhomogeneity caused by the presence of still unreacted $Rh_6(CO)_{16}$. When homogeneity is achieved, the benzene solution is deep red and the infrared spectrum in the carbonyl region shows bands at 1992 s, 1975 s, 1960 sh, 1812 m, 1775 w, and 1752 s cm⁻¹. This spectrum closely resembles the one published by Wilkinson for the red compound $Rh_2(CO)_2$-$(PPh_3)_4(solvent)_2$ if it is mixed with some $Rh_2(CO)_4(PPh_3)_4$.[7] This formulation as a solvated complex is the one suggested for the product obtained in the decarbonylation reaction of $Rh_2(CO)_4(PPh_3)_4$. In that work Wilkinson used dichloromethane as solvent, so we expect there to be slight differences from our spectrum measured in benzene solvent. In order to obtain additional information about our benzene-soluble compound, we have separately synthesized the compound $Rh_2(CO)_4(PPh_3)_4$ under a CO atmosphere by the published method of Haszeldine.[8] Subsequent exposure of a benzene solution of this compound to an argon atmosphere or vacuum conditions gives conversion of the yellow benzene solution to a deep red compound having infrared spectral bands at 1994 s, 1976 s, 1962 s, 1814 s, and 1752 s cm⁻¹. These bands correspond very closely with those found for the compound in the catalytic cycle where the rhodium is introduced as $Rh_6(CO)_{16}$. We therefore propose that the compounds are the same and that the solution contains $Rh_2(CO)_2(PPh_3)_4(C_6H_6)_2$ insofar that previous structure assignments as a binuclear complex are correct.[9] Attempts to isolate the compound from solution give mixtures of rhodium complexes, but from all these solutions the compound $Rh_2(CO)_4(PPh_3)_4$ can be easily regenerated by the passage of CO through the solution. Our assignment of stoichiometry and structure to $Rh_2(CO)_2$-$(PPh_3)_4(C_6H_6)_2$ must however reamin tentative. It is possible that the compound is a cluster of higher nuclearity which has not yet been structurally assigned, but we have not yet found any definitive technique for the unambiguous structural characterization of these labile clusters in solution.

Upon addition of O_2 and CO to the deep red benzene solution the color rapidly turns yellow, and the former infrared spectrum is replaced by one having bands due to $\nu(CO)$ at 1970 vs and 1820 w cm⁻¹. This spectrum resembles that recorded for the complex $Rh_2(CO)_6(PPh_3)_2$,[8,10] and we have separately isolated this compound from the solution ($\nu(CO)$ 1960 s, 1955 s, 1910 w cm⁻¹ (Nujol mull)). As complete conversion of PPh₃ to OPPh₃ occurs during the catalytic cycle, the solution gradually returns to a red color. This red solution shows values of $\nu(CO)$ at 2065 s, 2035 s, 1995 s, 1970 s, 1850 m, 1820 s, and 1788 w cm⁻¹. After 5–6 h the solution spectrum of the reaction mixture shows no further changes in band intensities, and the final infrared spectrum shows carbonyl bands at 2067 s, 2041 s, 2012 s, 1840 ms, and 1818 m cm⁻¹. The presence of the small residual band at 1970 cm⁻¹ indicates a low concentration of remaining $Rh_2(CO)_6(PPh_3)_2$. This final infrared spectrum, however, corresponds with that published for the compound $Rh_4(CO)_{10}(PPh_3)_2$.[8,10]

As further confirmation that changes in cluster nuclearity are occurring with the hexarhodium hexadecacarbonyl intro-

(4) Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161–166. Dudley, C.; Read, G. *Tetrahedron Lett.* **1972**, *52*, 5273–5276. Dudley, C.; Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883–888. Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1–29. Arzoumanian, H.; Lai, R.; Lopez Alvarez, R.; Metzger, J.; Petrignani, J. F. *J. Mol. Catal.* **1980**, *7*, 43–49. Uhlrich, V. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 701–712. Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169–177. James, B. R. *Adv. Chem. Ser.* **1980**, *No. 191*, 253–276. Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981. Roundhill, D. M. "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, in press; Chapter 12.

(5) Roundhill, D. M.; Dickson, M. K.; Dixit, N. S.; Sudha-Dixit, B. P. *Adv. Chem. Ser.* **1981**, *No. 196*, 291–301.

(6) These data translate to a turnover number in the region of 1.7/min. The GLC analysis shows complete conversion of free PPh₃ to OPPh₃ in the solution. Nevertheless, infrared spectroscopy shows that the final rhodium compounds in solution are carbonyl triphenylphosphine complexes.

(7) Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660–2665.

(8) Booth, B. L.; Else, M. J.; Fields, R.; Haszeldine, R. N. *J. Organomet. Chem.* **1971**, *27*, 119–131.

(9) From the deep red color and the preparative route using ligand dissociation, we would suppose the compound to be a higher nuclearity cluster compound. We seriously considered this option, and two likely possibilities are the compounds $Rh_4(CO)_8(PPh_3)_4$ and $Rh_6(CO)_{10}(PPh_3)_6$. These compounds, however, have strong infrared stretching bands both at 1790 cm⁻¹ and in the range 1800–1900 cm⁻¹, a region which is transparent in our spectrum. Reimann, W.; Abboud, W.; Basset, J. M.; Mutin, R.; Rempel, G. L.; Smith, A. K. *J. Mol. Catal.* **1980**, *9*, 349–353.

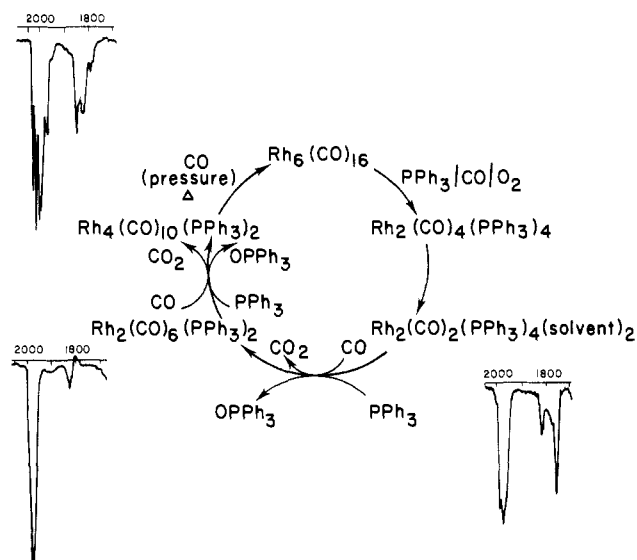(10) Whyman, R. *J. Chem. Soc., Dalton Trans.* **1972**, 1375–1381.

Figure 1. Catalytic cycle for the cooxidation of carbon monoxide and triphenylphosphine. Interconversion between multimetallic rhodium(0) compounds were observed by solution infrared spectroscopy.

Table I. Effect of Variation of Oxygen Pressure on the Molar Yield of Carbon Dioxide[a]

$p(CO)$, torr	amt of CO, mmol	$p(O_2)$, torr	amt of CO_2, mmol	amt of $OPPh_3$, mmol	$p(O_2)/p(CO)$	mole ratio CO_2 : $OPPh_3$
101	1.63	155	0.65	0.36	1.53	1.84
101	1.63	109	0.53	0.39	1.08	1.35
184	2.97	83	0.54	0.40	0.45	1.35
101	1.63	158	0.81	0.38	1.52	2.09[b]

[a] Conditions: $Rh_6(CO)_{16}$ 11 mg (11 μmol), PPh_3 100 mg (381 μmol), hexamethylbenzene 50 mg, benzene 10 mL, time 6 h, temperature 25 °C, volume 300 mL. Values are accurate to within 10% over a series of experiments. [b] Water (0.2 mL) added to the reaction.

duced into the reaction, we have prepared a stirred solution of the tetrameric cluster $Rh_4(CO)_{12}$ with excess triphenylphosphine in dry benzene under vacuum or argon-atmosphere conditions. This mixture we find to be also catalytically active for the cooxidation of triphenylphosphine and carbon monoxide. The red solution formed has an infrared spectrum in the carbonyl region that is identical with that of the initial red solution formed by using $Rh_6(CO)_{16}$. Addition of CO and O_2 produces the same yellow solution of rhodium dimer, and the final solution species is again $Rh_4(CO)_{10}(PPh_3)_2$.

In Figure 1 we outline these transformations that are believed to occur in catalyzed cooxidation of CO and PPh_3. The final solution species at ambient or lower pressure of CO is $Rh_4(CO)_{10}(PPh_3)_2$, but the initial compound $Rh_6(CO)_{16}$ is recoverable to complete the whole cycle if the final reaction mixture is treated with CO at elevated temperature and pressure. It appears, therefore, that $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ undergo substitution with triphenylphosphine leading to lower nuclearity rhodium(0) compounds and that one or more of these compounds is catalytically active for the oxidation reaction. We presume that oxygen coordination occurs and that subsequent steps lead to the cooxidation reaction. In addition to monitoring the metal carbonyl region of the infrared spectrum, we have also looked for changes in the 750–900-cm^{-1} range. No new bands appear in this region throughout the catalytic cycle, indicating that any formed oxygen adducts do not reach sufficient concentration to be observable by this technique.

It has previously been shown that the compound Rh_2-$(CO)_4(PPh_3)_4$ reacts with molecular oxygen to form the carbon dioxide complex $Rh_2(CO)_2(\mu\text{-}CO_2)(PPh_3)_2$.[11] Other such compounds have been reported to be formed on treatment of osmium carbonyl clusters with oxygen.[12] Our failure to observe any infrared bands due to complexed dioxygen of carbon dioxide is not unanticipated since a coordinated carbon dioxide molecule will likely be displaced by the excess carbon monoxide or triphenylphosphine present in the reaction mixture.[13] Indeed, the occurrence of this facile substitution is a necessary requisite for observation of *catalytic* conversion of carbon monoxide to carbon dioxide with molecular oxygen. We

cannot therefore make any definitive statement about oxygen binding to rhodium(0) or its "activation" to reactivity. Also the solution composition is constantly changing during the course of the catalytic reaction and we cannot identify which specific intermediate reacts with oxygen. We presume the identity of the rhodium compounds present depends on the relative concentrations of CO and PPh_3. Therefore, if CO and PPh_3 are being removed from the solution at different rates by oxidation, these concentrations, and hence the relative amounts of the different rhodium compounds, are not time independent.

(ii) ^{31}P NMR Spectral Data. The $^{31}P\{^1H\}$ NMR spectrum of the initial red solution from the catalytic reaction gives only a single broad peak (δ 0.75) indicative of fast exchange between free and coordinated triphenylphosphine. The data imply that both intermolecular and intramolecular phosphine exchange occur, in agreement with the observed intramolecular exchange in the compound $Rh_4(CO)_8[P(OPh)_3]_4$.[14] Under experimental conditions where the yellow complex Rh_2-$(CO)_6(PPh_3)_2$ is proposed to be present in solution, the $^{31}P\{^1H\}$ NMR spectrum still shows significant quantities of triphenylphosphine oxide in the solution. Thus although the use of $^{31}P\{^1H\}$ NMR techniques appears to be conceptually useful for determining the nuclearity and structures of these rhodium clusters, we, like others, find this optimism to remain unfulfilled.[15]

(iii) Effect of Oxygen Pressure. In order to obtain information relevant to the mechanism of the cooxidation of carbon monoxide and triphenylphosphine, we have made simultaneous quantitative measurements on the CO_2 and $OPPh_3$ produced under changing oxygen pressure conditions at a temperature of 25 °C.[16] The series of three experiments shown in Table I have been obtained with use of vacuum line conditions with a constant pressure of CO (101 torr). Reactions are run to completion, which we define as being total conversion of triphenylphosphine to oxide. A contact time of 6 h is used both to complete the reaction and to ensure complete mixing of the formed gases to give reliable carbon dioxide analytical values. These reactions are carried out with a constant ratio of carbon monoxide to triphenylphosphine for a fixed molarity of $Rh_6(CO)_{16}$. This condition ensures that changes in product $CO_2:OPPh_3$ ratio are not simply a consequence of the changed initial $CO:PPh_3$ ratio causing differences in the initial relative amounts of the different carbonyl triphenylphosphine rhodium(0) complexes in the solution. This precaution is a necessary one since we do not know which of these solution intermediates are on the reaction pathway for catalytic oxidation, nor do we know their relative kinetic reactivities if more than

(11) Iwashita, Y.; Hayata, A. *J. Am. Chem. Soc.* **1969**, *91*, 2525–2528.
(12) John, G. R.; Johnson, B. F. G.; Lewis, J.; Wong, K. C. *J. Organomet. Chem.* **1979**, *169*, C23–C26.
(13) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172.

(14) Heaton, B. T.; Longhetti, L.; Garleschelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1980**, *192*, 431–435.
(15) Jamerson, J. D.; Pruett, R. L.; Billig, E.; Fiato, F. A. *J. Organomet. Chem.* **1980**, *193*, C43–C45.
(16) Kiji, J.; Furukawa, J. *J. Chem. Soc., Chem. Commun.* **1970**, 977–978.

one complex is involved. The reactions are carried out under vacuum line conditions with use of dry benzene that is further purified by freeze–thaw–pump techniques after introduction into the vacuum line. From Table I it is apparent that the ratio between the relative quantities of CO_2 and $OPPh_3$ produced in the catalytic cycle is not 1:1. Under the conditions used the quantity of CO_2 formed is greater than that of $OPPh_3$. Thus, different amounts of CO_2 and $OPPh_3$ are formed when the moles of oxygen introduced is varied. Decreasing the oxygen pressure from 155 to 109 torr causes a change in the ratio of CO_2:$OPPh_3$ from 1.84 to 1.35. It is also apparent from Table I that this ratio decrease is a consequence of the lower amount of CO_2 formed since within experimental error the quantity of $OPPh_3$ formed remains unchanged. It should be noted though that this constant yield of triphenylphosphine oxide is a necessary prerequisite since all catalytic reactions are continued until complete triphenylphosphine oxidation has occurred. Interestingly it is apparent from Table I that an increase in CO pressure from 101 to 184 torr does not cause any increase in the quantity of CO_2 produced. This fact that the yields of CO_2 and $OPPh_3$ are not in a 1:1 ratio shows that these two products are not being formed from a single intermediate which can simultaneously or sequentially transfer each separate oxygen atom from the oxygen molecule to CO and PPh_3 in a selective manner. This situation differs from that found for the $RhCl(PPh_3)_3$ catalyzed cooxidation of 1-alkenes and triphenylphosphine with molecular oxygen. In this process Read[4] proposes that the first oxygen atom is transferred to the alkene carbon by metallocycle formation and that the oxygen to form triphenylphosphine oxide comes from reaction of the oxetane with triphenylphosphine. Also the observation with $Rh_6(CO)_{16}$ of more CO_2 being produced than $OPPh_3$ is significant in understanding mechanistic details of the reaction. The ratio of CO_2:$OPPh_3$ does vary as the oxygen pressure is changed, but the value is always above unity after complete oxidation of triphenylphosphine to oxide has occurred. The magnitude of this ratio thus makes it infeasible that the only route leading to CO oxidation is one induced by the triphenylphosphine cooxidation.
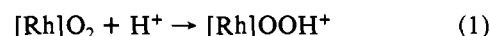
The literature on the oxidation of carbon monoxide to carbon dioxide with molecular oxygen has many high-temperature studies with metal or metal oxide catalysts.[17] Mechanistically these studies propose the involvement of oxygen atoms, an implausible pathway under our experimental conditions. Other compounds have been found which apparently catalyze the conversion of CO to CO_2 with molecular oxygen, but no definitive studies have yet been made that identify whether the oxygen molecule is the reactive oxygen atom species that directly forms the bond to the carbon of CO.[11,18] The catalyzed oxidation of triphenylphosphine has

Table II. Effect on CO_2 and $OPPh_3$ Yield of Variation in Time and Change in the Initial Mole Fraction Ratio of Oxygen and Carbon Monoxide[a]
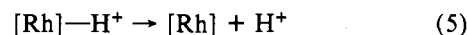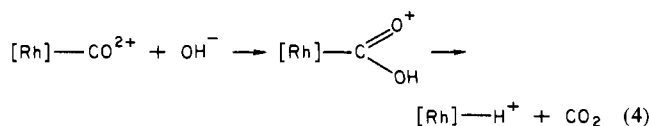
$p(O_2)/$ $p(CO)$	amt of water, mL	time, h	amt of CO_2, mmol	amt of $OPPh_3$, mmol	mole ratio CO_2: $OPPh_3$
0.45	0	6.0	0.54	0.40	1.35
1.08	0	0.67	0.13	0.20	0.65
1.08	0	1.16	0.27	0.22	1.21
1.08	0	6.0	0.53	0.39	1.30
1.53	0	1.16	0.21	0.17	1.24
1.53	0	1.58	0.32	0.21	1.56
1.53	0	6.0	0.60	0.32	1.88
1.52	0.2	1.33	0.33	0.14	2.35
1.52	0.2	6.0	0.86	0.39	2.20

[a] Conditions as in Table I except for the variation in reaction time.

been observed for a wide range of transition-metal phosphine complexes. A system that has been studied in some detail is the one catalyzed by $Pt(PPh_3)_3$.[19] The proposed mechanism involves protonation and displacement of coordinated oxygen by triphenylphosphine to yield the free hydroperoxide ion. This hydroperoxide ion then oxidizes a free triphenylphosphine molecule. Extrapolation of this pathway to our rhodium(0) compounds leads to a sequence of steps shown in eq 1–3, in the presence of an adventitious proton source. In these equations rhodium carbonyl cluster compounds are designated [Rh].

$$[Rh]O_2 + H^+ \rightarrow [Rh]OOH^+ \qquad (1)$$

$$[Rh]OOH^+ + PPh_3 \rightarrow [Rh]PPh_3^{2+} + HOO^- \qquad (2)$$

$$HOO^- + PPh_3 \rightarrow OPPh_3 + HO^- \qquad (3)$$

Previous studies on metal carbonyls have shown that the coordinated carbon atom is susceptible to nucleophilic attack by hydroxide ion leading to conversion of the carbonyl group into carbon dioxide.[20] The proposed pathway via a metallocarboxylate intermediate is shown in eq 4. Since our ratio

$$[Rh]-CO^{2+} + OH^- \rightarrow [Rh]-C\overset{\displaystyle O^+}{\underset{\displaystyle OH}{\big\langle}} \rightarrow$$

$$[Rh]-H^+ + CO_2 \quad (4)$$

$$[Rh]-H^+ \rightarrow [Rh] + H^+ \qquad (5)$$

of CO_2:$OPPh_3$ can reach the value of 2, we may need to interpret our data on the basis that the oxidation of *both* triphenylphosphine and coordinated CO may not solely arise by a sequence of reactions outlined in eq 1–5.

A further indication that the oxidation of CO and PPh_3 does not occur by transfer of separate oxygen atoms from a single intermediate is shown by the change in the ratio of CO_2:$OPPh_3$ as the catalytic cycle proceeds. In Table II it can be seen that the CO_2:$OPPh_3$ ratio increases as the reaction proceeds. Thus for an initial ratio of 1.53 for O_2:CO, the ratio of CO_2:$OPPh_3$ formed increases from 1.24 to 1.56 and then to 1.88, as the catalytic cycle is sample monitored after 70, 105, and 360 min, respectively.[21] This time-dependent change in relative yield

(17) Engel, T.; Ertl, G. *Adv. Catal.* **1979**, *28*, 1–78. Lee, H.-I.; White, J. M. *J. Catal.* **1980**, *63*, 261–264. Watters, K. L.; Howe, R. F.; Chojnacki, T. P.; Fu, C.-M.; Schneider, R. L.; Wong, N.-B. *Ibid.* **1980**, *66*, 424–440. Taylor, J. L.; Ibbotson, D. E.; Weinberg, W. H. *Ibid.* **1980**, *62*, 1–12. Engel, T.; Ertl, G. *J. Chem. Phys.* **1978**, *69*, 1267–1281. Matsushima, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1956–1960. Matsushima, T. *Surf. Sci.* **1979**, *79*, 63–75. Strozier, J. A.; Cosgrove, G. J.; Fischer, D. A. *Ibid.* **1979**, *82*, 481–499. Golchet, A.; White, J. M. *J. Catal.* **1978**, *53*, 266–279. Matsushima, T. *Ibid.* **1978**, *55*, 337–347.
(18) Mercer, G. D.; Shu, J. S.; Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1967–1968. Roundhill, D. M.; Allen, G. H.; Bechtold, R. A.; Beaulieu, W. B. *Inorg. Chim. Acta* **1981**, *54*, L99–L100. Chin, C. S.; Sennett, M. S.; Vaska, L. *J. Mol. Catal.* **1978**, *4*, 375–378. Chin, C. S.; Sennett, M. S.; Wier, P. J.; Vaska, L. *Inorg. Chim. Acta* **1978**, *31*, L443–L444. Elizarova, G. L.; Matvienko, L. G.; Yurchenko, E. N.; Tretyakov, V. P.; Mastikhin, V. M.; Varnek, V. M. *React. Kinet. Catal. Lett.* **1975**, *2*, 349–353; *Chem. Abstr.* **1976**, *84*, 50319r. Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F. *Inorg. Chem.* **1979**, *18*, 3104–3112. Jarrell, M. S.; Gates, B. C. *Ibid.* **1978**, *54*, 81–93. Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 1789–1790.

(19) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337–8339.
(20) Halpern, J.; Harkness, A. C. *J. Am. Chem. Soc.* **1961**, *83*, 1258–1259. Halpern, J.; Nakamura, S. *Ibid.* **1961**, *83*, 4102–4103. James, B. R.; Rempel, G. L. *J. Chem. Soc. A* **1969**, 78–84. Bercaw, J. E.; Goh, L.-Y.; Halpern, J. *J. Am. Chem. Soc.* **1972**, *94*, 6534–6536.

Table III. Relative Isotopomer Distribution of Oxygen-18 in Product Carbon Dioxide and Triphenylphosphine Oxide[a]

soln components[b]	conditions	mole fraction isotopomer distribn
$Rh_6(CO)_{16}/CO/O_2/^{18}OH_2$	flow	CO_2 (m/e 44, 46, 48) 0.69, 0.27, 0.04
$Rh_6(CO)_{16}/CO_2/^{18}OH_2$	flow	CO_2 (m/e 44, 46, 48) 0.97, 0.03, 0.00
$Rh_6(CO)_{16}/CO/O_2/^{18}OH_2$	static (6 h)	CO_2 (m/e 44, 46, 48) 0.42, 0.44, 0.14; Ph_3PO 0.94; $^{18}OPPh_3$ 0.06
$Rh_6(CO)_{16}/CO_2/CO/^{18}OH_2$	static (6 h)	CO_2 (m/e 44, 46, 48) 0.43, 0.42, 0.15
$CO_2/^{18}OH_2/PPh_3$	static (6 h)	CO_2 (m/e 44, 46) 1.00, 0.00
$Rh_6(CO)_{16}/CO/^{18}O_2/PPh_3$	static (6 h)	CO_2 (m/e 44, 46, 48) 0.35, 0.48, 0.17
$Rh_6(CO)_{16}/CO/^{18}O_2/PPh_3/H_2O$	static (6 h)	CO_2 (m/e 44, 46, 48) 0.97, 0.03, 0.00; Ph_3PO 0.13; $^{18}OPPh_3$ 0.87

[a] Conditions as in Table I. In two cases the reactant and product gases were in contact with the solution for only a short time. The added $^{18}OH_2$ (0.2 mL) has 32.99 atom % oxygen-18. The oxygen gas has 94 atom % oxygen-18. [b] Triphenylphosphine is present in all reactions.

of CO_2 and $OPPh_3$ is not possible if a simple mechanism is operative with a single intermediate leading to cooxidation being proposed. This increasing proportion of CO_2 to $OPPh_3$ with time of the catalytic reaction could be a consequence of eq 3. This second mole of hydroxide ion which becomes available for attack at the coordinated carbonyl is produced as a result of triphenylphosphine oxidation and is an oxygen atom derived from oxygen gas. This means that the available hydroxide ion for attack at the coordinated carbonyl increases with time, and this change could be responsible for this increasing CO_2:$OPPh_3$ ratio. In addition we cannot eliminate the possibility that more CO_2 is formed by hydroperoxyl attack at coordinated carbonyl as the concentration of PPh_3 decreases[22] or that a rhodium species produced in the later stages of the reaction is a more active catalyst for CO oxidation. Nevertheless the data in Table II show that the mole ratio of CO_2:$OPPh_3$ does not increase with time in the presence of added excess water, supportive of the concept that the increase in CO_2:$OPPh_3$ ratio under dry conditions may result from the increasing hydroxyl ion concentration with time.

The scheme outlined in eq 1–4 requires a proton source. Under the anhydrous conditions used in our catalysis we expect the concentration of any protolytic source to be extremely low.[23] Nevertheless, we can never completely exclude the possibility that a small amount of water or other protolytic source is present. It should be noted, however, that if this concentration of water or hydroxide ion is very small the respective rate constants for the catalytic reactions must become proportionately large for the reactions to proceed at an appreciable rate. Also from the reaction stoichiometry it is apparent that almost 1 equiv of water must be present in the dry benzene for a ratio of 1.84 to be achieved, if one assumes that water is the only oxygen atom source to give carbon dioxide. As a means to test the effect of any other protolytic

and oxygen nucleophile source on the reaction product, we have added water (0.2 mL) to the reaction mixture. From Table I it is apparent that the proportion of CO_2:$OPPh_3$ rises from 1.84 to 2.09 upon addition of water because of the increased yield of CO_2 to 0.81 mmol.[24] This increase in CO_2 formed lends credence to the concept that a Wacker mechanism involving attack of water or hydroxide ion at the coordinated carbonyl can be at least *partially* responsible for CO_2 formation. Nevertheless, if hydroxide ion were the only oxygen source reacting with the carbonyl, an increase in molar amount from 0.65 to 0.81 for CO_2 formed does not seem sufficiently large to account for an increase in water from a trace concentration to that of a saturated water–benzene two-phase system. Also assuming that phase transfer of water into benzene is not rate limiting, we have a total available water concentration of 1.1 M under these conditions.[25]

(iv) Oxygen-18 Labeling Studies. Certain mechanistic features of this cocatalyzed oxidation cannot be addressed without using isotopically labeled oxygen sources. We have therefore carried out two sets of experiments using oxygen-18 labeled dioxygen or water to identify the source of oxygen atom transferred into the product carbon dioxide and triphenylphosphine oxide. The first set of labeling experiments (A) have been carried out under the vacuum line conditions used throughout this study. Mass spectral analysis of $OPPh_3$ shows 6.0 atom % oxygen-18 incorporation at $^{18}OPPh_3$ from the $^{18}OH_2$ in solution.[26] This quantity of $^{18}OPPh_3$ in the reaction mixture is small but must come from $^{18}OH_2$ during the catalytic oxidation of triphenylphosphine since triphenylphosphine oxide itself does not undergo oxygen-18 exchange with labeled water.[27] Accordingly the atom percent of oxygen-16 in $OPPh_3$ is 93.6, and hence the predominant oxygen atom source for incorporation into $OPPh_3$ is oxygen gas, O_2.

Analysis of the oxygen-18 content in the formed carbon dioxide sample shows complete equilibration of the label with water; thus, the relative respective fractions for m/e 44, 46, and 48 are found experimentally to be 0.42, 0.44, and 0.14.[28]

(21) This unbalanced changing ratio for CO and PPh_3 oxidation does mean that the relative concentrations of these species are changing with time. As discussed in the section on infrared spectroscopy, we cannot exclude the possibility that this changing ratio will cause changes in the relative concentrations of the different rhodium complexes and, hence, in the catalytic activity of the solution. Our only evidence that these changes may not cause significant variation in catalytic activity is shown in Table I. We find that the CO_2:$OPPh_3$ ratio remains constant at 1.35 (with no molar change in either component) when there is an approximate halving of the O_2 pressure and a doubling of the CO pressure, for a constant concentration of rhodium and triphenylphosphine.

(22) The formed hydroperoxyl ion may react at a coordinated carbonyl to produce a rhodium-substituted peracid complex which can subsequently decarboxylate:
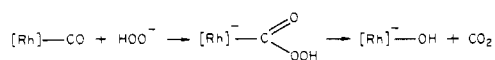
Such a reaction between a peroxide ion and a metal carbonyl complex has been previously observed. Thus the discrimination for hydroperoxide attack at triphenylphosphine or a coordinated carbonyl will depend on the relative rates of these reactions, with the former, however, being the likely predominant reductive pathway. Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1976**, 369–370. Likholobov, V.; Zudin, V.; Eremenko, N.; Ermakov, Y. *Kinet. Catal. (Engl. Transl.)* **1974**, *15*, 1433.

(23) Since the benzene solvent is dried continuously over $LiAlH_4$, we expect protolytic sources other than water to be also removed.

(24) Since the maximum yield of obtainable carbon dioxide under our experimental conditions is 1.63 mmol, this small observed increase is not simply a consequence of carbon monoxide having been completely depleted after 0.81 mmol of carbon dioxide has been formed.

(25) This concentration is based on the assumption that the rate of dissolution of water in benzene in the two-phase system is fast compared to the rate of catalytic oxidation, and hence the total volume of added water is available for reaction.

(26) The atom percent of $^{18}OPPh_3$ formed is actually slightly less than 6.0% because no correction has been made to subtract the statistical quantity of $OPPh_3$ present at m/e 264, which is an isotopomer with two carbon-13 atoms in the molecule.

(27) Samuel, S.; Silver, B. L. *Adv. Phys. Org. Chem.* **1965**, *3*, 123–186.

(28) Solution of the simultaneous equilibria

$$CO_2 + H_2O^* \rightleftharpoons OCO^* + H_2O \ (K_1)$$

$$OCO^* + H_2O^* \rightleftharpoons {}^*OCO^* + H_2O \ (K_2)$$
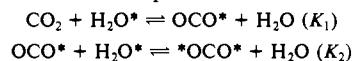
leads to a respective mole fraction statistical distribution between CO_2 (m/e 44), OCO^* (m/e 46), and $^*OCO^*$ (m/e 48) of 0.44, 0.44, and 0.11. The calculation has ignored isotope effects by setting the ratio of K_1/K_2 to the value 4. The mole fraction of $^{18}OH_2$ in the supplied sample is 0.33. The fraction of $^{17}OH_2$ in the sample is 0.0022, and thus the negligible percentage of oxygen-17 in the CO_2 produced has not been included in the calculation.
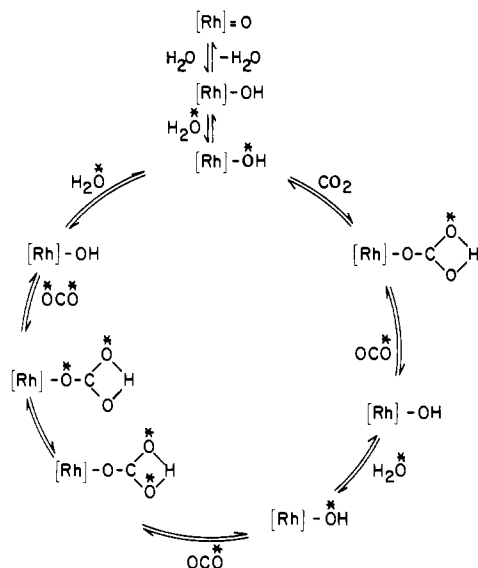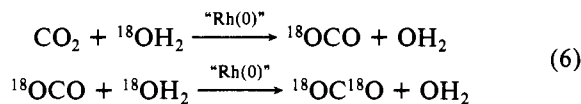
Figure 2. Proposed pathway for incorporation of isotopic label from water into carbon dioxide. The symbol [Rh] designates a rhodium cluster species, and the double-bond unsaturation has been omitted from the metallocarboxylate intermediates for clarity.

A control experiment has been carried out with use of conditions identical with those for the catalyzed oxidation to form CO_2, except that now CO_2 is introduced into the reaction mixture instead of oxygen. Oxygen must be absent from this control experiment in order to eliminate any oxygen-18 label becoming incorporated into CO_2 by the oxidation of CO. After 6 h reaction time under stirred conditions with 0.2 mL of $^{18}OH_2$ added to the benzene solvent, mass spectroscopic analysis of the CO_2 again shows equilibration of the oxygen-18 from $^{18}OH_2$ into CO_2. The respective mole fractions found for m/e 44, 46, and 48 are 0.43, 0.44, and 0.15. Scrambling of this oxygen-18 label into CO_2 from $^{18}OH_2$ in the presence of triphenylphosphine carbonyl rhodium(0) compound shows that these complexes catalyze the oxygen atom isotopic exchange between CO_2 and H_2O. This exchange is shown in eq 6. Stirring a mixture of benzene (10 mL) and $^{18}OH_2$ (0.2

$$CO_2 + {}^{18}OH_2 \xrightarrow{\text{``Rh(0)''}} {}^{18}OCO + OH_2$$

$$({}^{18}OCO + {}^{18}OH_2 \xrightarrow{\text{``Rh(0)''}} {}^{18}OC^{18}O + OH_2 \qquad (6)$$

mL) with CO, CO_2, and PPh₃ (104 mg, 0.4 mmol) for 6 h in the *absence* of $Rh_6(CO)_{16}$ leads to *no* measurable incorporation of oxygen-18 label into the CO_2 introduced into the mixture. This lack of oxygen-18 incorporation from $^{18}OH_2$ into CO_2 shows that the uncatalyzed oxygen scrambling subsequent to CO_2 formation is negligibly slow under our experimental conditions. These results can be rationalized by a sequence of reactions involving hydroxyrhodium complexes shown in Figure 3. For determination of the origin of oxygen label incorporated into carbon dioxide formed by oxidation of carbon monoxide, this rhodium(0)-catalyzed isotopic exchange between CO_2 and H_2O is an experimental problem that must be circumvented. A method described by Taube,[29] and also used by Eisenberg,[30] minimizes isotopic equilibration of the product CO_2 with the $^{18}OH_2$ present in the reaction medium by sweeping the CO_2 from the solvent medium as rapidly as possible after it is formed. The CO_2 is then collected in a low-temperature trap for mass spectral analysis. We have therefore carried out a second set of labeling experiments (B) with $^{18}OH_2$ using this sweeping technique. Analysis of the CO_2

collected in the final cooled trap, and the OPPh₃ isolated from the reaction solution, shows complete conversion of PPh₃ to OPPh₃ and a respective CO_2 distribution ratio of 0.69, 0.27, and 0.03 for m/e 44, 46, and 48. As a final check that this incorporation of oxygen-18 into CO_2 is not due to a rhodium(0)-catalyzed isotopic exchange subsequent to its formation, we have carried out the control experiment now under these flow system conditions (experiment C). Isotopic analysis of the CO_2 collected shows *no* increased in oxygen-18 label from that present in the supplied CO_2 cylinder.[31] This control experiment verifies that the rhodium(0)-catalyzed isotopic exchange of oxygen atom between CO_2 and H_2O is sufficiently slow to be prevented by this gas purge method. The incorporation of oxygen-18 in the CO_2 produced by the oxidation reaction under these purge conditions must therefore have arisen during the catalyzed oxidation of carbon monoxide. The observed mole fraction of 0.27 for m/e 46 shows that a significant proportion of oxygen atom must be transferred from $^{18}OH_2$ (atom fraction of oxygen-18 is 0.33) rather than O_2.

An oxygen-18 labeling experiment has been conducted to confirm the origin of the oxygen incorporated into OPPh₃. This experiment (D) differs from earlier ones in that the oxygen-18 label is introduced from $^{18}O_2$ (94% enrichment by mass spectroscopy) rather than from $^{18}OH_2$. Analysis of the CO_2 formed shows complete equilibration of label with incorporation of oxygen-16 from OH_2.[32] Isolation and mass spectroscopic analysis of the OPPh₃ produced shows that the mole fraction percent of $^{18}OPPh_3$ is 0.87. This result is in agreement with that using O_2 and $^{18}OH_2$, where it was concluded that the predominant source of oxygen atom in the formed triphenylphosphine oxide is from O_2.

As a final check that an oxygen atom from O_2 can indeed be transferred to a coordinated carbonyl group, we have carried out the oxidation with oxygen-18 labeled O_2 under anhydrous conditions. To a mixture of $Rh_6(CO)_{16}$ (7.3 mg), PPh₃ (183 mg), and dry benzene (5 mL) is added $^{18}O_2$ (94 atom %) to give an approximate pressure of 300 torr. Carbon monoxide was introduced to yield a total pressure of 1 atm, and the reaction mixture was stirred for 6 h. Cooling the sample collector to 77 K condensed the formed carbon dioxide, thereby separating it from the rhodium catalyst. Analysis of this CO_2 sample yields a mass spectrometric mole fraction distribution among m/e 44, 46, and 48 of 0.35, 0.48, and 0.17. The observed excess of singly labeled carbon dioxide (m/e 46) confirms that atom transfer to the coordinated carbonyl occurs primarily from O_2 under these experimental conditions. The observation of significant quantities of unlabeled (m/e 44) and doubly labeled (m/e 48) CO_2 can only be explained by the presence of a small quantity of water in the reaction mixture, which results in the catalyzed equilibration of the oxygen atom label, especially since this particular labeling experiment is not carried out under rigorously anhydrous conditions.

(v) Mechanistic Considerations. The low-temperature catalytic oxidation of triphenylphosphine in the presence of $Rh_6(CO)_{16}$ does not occur with other transition-metal carbonyl compounds. Thus, negligible quantities of triphenylphosphine oxide are obtained when mixtures of triphenylphosphine and oxygen are stirred under ambient conditions with $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, or $Ru_3(CO)_{12}$. From this study of the $Rh_6(CO)_{16}$-catalyzed oxidation it is apparent that initial complexation of triphenylphosphine must occur before the catalyzed reaction with oxygen can proceed.

From our experiments on the $Rh_6(CO)_{16}$-catalyzed cooxidation of CO and PPh₃ we can make a number of comments

(29) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1953**, *75*, 4099–4101.
(30) Hendrickson, D. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1976**, *98*, 4662–4664.

(31) The actual measured respective mole fractions for m/e 44, 46, and 48 are 0.97, 0.03, and 0.00.
(32) The respective mole fractions for m/e 44 and 46 are 0.97 and 0.03.

pertinent to the mechanism. Retention of label from either oxygen-16 or oxygen-18 gas in the formed OPPh$_3$ confirms that water, or any species in rapid equilibrium with it, does not provide a significant fraction of the oxygen atom source for this product. This observation is particularly pertinent for the pathway sequence in eq 1–3. In the Pt(PPh$_3$)$_3$-catalyzed oxidation of triphenylphosphine it is proposed[19] that the *second* molecule of triphenylphosphine is oxidized by a reaction between the hydroxyl ion in conjunction with the formed platinum(II) cation. We can eliminate any such second step for phosphine oxidation from hydroxyl ion catalyzed by any higher valent rhodium compounds because the extremely fast equilibration between hydroxyl ion and water would transfer label from the original dioxygen source into the water. With $^{16}O_2/^{18}OH_2$ and $^{18}O_2/^{16}OH_2$, the respective mole fractions of $^{18}OPPh_3$ are 0.06 and 0.87, confirming that O$_2$ is the oxygen atom source for triphenylphosphine oxide. From eq 3 we expect the label from oxygen gas to be incorporated into OPPh$_3$ without any scrambling with water since the hydroperoxyl ion does not exchange oxygen atoms with water. If this is the sole pathway for triphenylphosphine oxide formation, we can explain our failure to observe isotopic incorporation from the added water. Since we do not therefore have a significant second-step mechanism where a higher valent rhodium complex catalyzes the conversion of PPh$_3$ into OPPh$_3$ using the oxygen atom of hydroxide ion, any formed hydroxyl ion reacts faster with the coordinated carbonyl to yield metallocarboxylate complexes and finally carbon dioxide. As further support, adding water to a mixture of Rh$_6$(CO)$_{16}$, PPh$_3$, CO, and O$_2$ causes an increase in the yield of CO$_2$ formed over that obtained under anhydrous reaction conditions (Table I).

Our proposal that the reactive species for attack at the coordinated carbonyl ligand is hydroxide ion rather than water is a consequence of work by Darensbourg[33] which has concluded that water will not react as a nucleophile toward a carbonyl on an uncharged metal carbonyl complex. We believe therefore that the reactions shown in eq 1–4 can explain our data obtained for the rhodium-catalyzed conversion of CO to CO$_2$ in the presence of O$_2$ with added H$_2$O or $^{18}O_2$. In Figure 2 we outline in more detail the proposed intermediates we believe to be involved in the oxidation reaction. In a complementary catalytic cycle we show a reaction sequence that will rationalize our observation that oxygen-18 from $^{18}OH_2$ can become incorporated into the CO$_2$ as it is formed from CO (Figure 3). The proposed involvement of hydroxyrhodium complexes as catalytic intermediates results from the known reported insertion chemistry of carbon dioxide. Insertion of carbon dioxide into the Rh–OH bond results in the formation of the bicarbonato complex (eq 7),[34] which is a plausible

$$[Rh]—OH + CO_2 \longrightarrow [Rh]—O—C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}} \qquad (7)$$
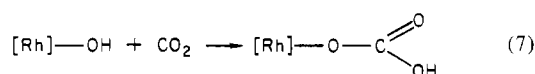
intermediate for oxygen-18 exchange with $^{18}OH_2$. The alternative intermediacy of rhodium hydrides would result in the formation of formato, rather than metallocarboxylato, complexes, and such intermediates do not appear to readily lead to the observed oxygen-18 exchange.

As a probe of hydroperoxyl participation we have measured the quantity of triphenylphosphine oxide formed upon addition of α-naphthol or 2,6-di-*tert*-butyl-*p*-cresol to the Rh$_6$-(CO)$_{16}$-catalyzed oxidation. In the presence of these com-

pounds we observe a decrease in the yield of triphenylphosphine oxide formed, which could be indicative of free-radical hydroperoxyl chemistry in the formation of triphenylphosphine oxide, although since both these added compounds have acidic phenolic protons which could react with a coordinated oxygen, it is possible that the protolysis to form hydroperoxyl rhodium compounds (eq 1) is actually a consequence of the presence of these free-radical probes.

The mechanism may also be different under anhydrous conditions. Under these conditions 0.65 mmol of CO$_2$ is obtained when the yield of OPPh$_3$ (complete oxidation of PPh$_3$ added) is 0.36 mmol. Equations 1–3 account for a stoichiometric yield of 0.35 mmol of hydroxide ion, but this leaves an additional 0.29 mmol of hydroxide ion (presumably from water) to be accounted for which will react with a coordinated carbonyl to form carbon dioxide. Under anhydrous conditions the coordinated oxygen molecule can be the nucleophile to the coordinated carbon atom of the carbonyl ligand.[35] Intermolecular attack from the coordinated oxygen molecule leads to a metallocyclic intermediate (eq 8) which can decarboxylate
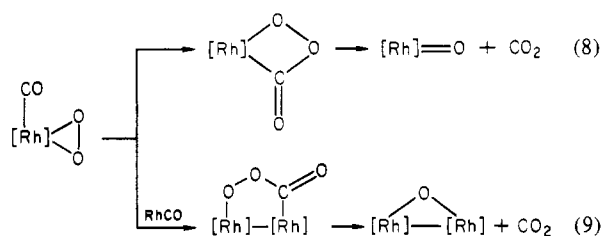
with formation of an oxorhodium intermediate.[14] Such an intermediate could then transfer a second oxygen atom to carbon monoxide either by direct means or following protonation and hydroxide ion dissociation. This mechanism for oxidation of a coordinated carbonyl shows similarities to the photocatalyzed formation of CO$_2$ from oxygen and chromium carbonyl in a low-temperature matrix.[36] These catalytic reactions in the absence of added water have been carried out with all precautions taken to eliminate water from the reaction mixture. Nevertheless, eq 1–5 show the pathway involving adventitious water is *catalytic* in H$_2$O; thus, a very fast reaction operating through such a series of steps could yield CO$_2$ even in the presence of negligible quantities of H$_2$O. The alternative intramolecular route would be a bimolecular one leading to a five-membered ring bimetallic intermediate which could then decarboxylate to a bridged oxorhodium compound (eq 9).[37]

Experimental Section

Reagents. Benzene (J. T. Baker) was continuously dried over LiAlH$_4$ in a recirculating distillation apparatus under a nitrogen atmosphere prior to use. Carbon monoxide (Linde) was passed through a series of three packed columns of Linde 3A molecular sieve (4–8 mesh) and then through calcium chloride to remove traces of water. Oxygen (Liquid Air) was dried by passage through a single column packed with Linde 3A molecular sieve and calcium chloride prior to use. Hexamethylbenzene and triphenylphosphine (Aldrich) were used as supplied, the latter having been shown by GLC to contain negligible quantities of triphenylphosphine oxide. The compounds Rh$_6$(CO)$_{16}$ and Rh$_4$(CO)$_{12}$ were prepared as described previously.[38]

Apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer in 0.05-mm matched NaCl solution cells. Solid-sample spectra were run in a Nujol mull or as a KBr disk. Infrared samples were prepared and all manipulations of the sample

(33) Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300–3302. From this work and inspection of our proposed sequence for oxygen atom incorporation from $^{18}OH_2$, it is apparent that catalyzed incorporation of oxygen-18 into CO can occur. No peak can be observed at *m/e* 30 for labeled CO, indicating that the reaction does not occur or that the concentration of this species is too small to be measurable.

(34) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965–969.

(35) Sheldon, R. A.; Van Doorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115–129. Beaulieu, W. B.; Mercer, G. D.; Roundhill, D. M. *J. Am. Chem. Soc.* **1978**, *100*, 1147–1152. Ugo, R.; Zanderighi, G. M.; Fusi, A.; Carreri, D. *Ibid.* **1980**, *102*, 3745–3751. Tatsuno, Y.; Otsuka, S. *Ibid.* **1981**, *103*, 5832–5839.

(36) Poliakoff, M.; Smith, K. P.; Turner, J. J.; Wilkinson, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 651–657.

(37) Kubota, M. *Abstr. Int. Conf. Homog. Catal.* **1982**, 3.

(38) Chaston, S. H. H.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 500–502. Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 315–318.
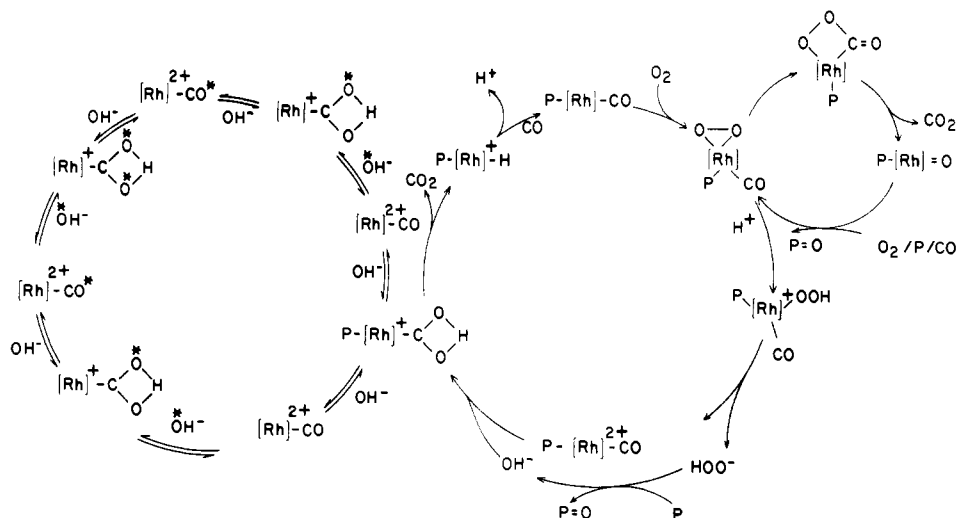
Figure 3. Proposed intermediates for the rhodium(0)-catalyzed oxidation of CO and PPh₃ to CO₂ and OPPh₃ and pathways for oxygen-18 incorporation into the formed CO₂ leading to both singly and doubly labeled product. The symbol [Rh] designates a rhodium cluster species, and the double-bond unsaturation has been omitted from the metallocarboxylate intermediates for clarity.

were carried out under inert-gas Schlenk conditions. Infrared spectra were calibrated against a polyethylene sample. Mass spectral data were obtained with a Hewlett-Packard 5985 GC/MS system. ³¹P NMR spectra were measured on a Bruker WH90/SXP Fourier transform spectrometer, with peaks referenced as positive high-frequency ppm shifts from 85% H₃PO₄. Gas-sample analyses were performed on a Varian Aerograph Model 90P thermal conductivity gas chromatograph. The Carbosive S (100–120 mesh) column (Supelco) was used with helium carrier gas. The helium (Liquid Air) was dried with use of a column of calcium chloride and Linde 3A molecular sieve. Gas samples were taken with Analytical Pressure-Lok gas syringes obtained from Precision Sampling Corp. A calibration curve was prepared with use of CO₂ gas samples ranging from 0.03 to 0.01 mL (STP) of the gas. The calibration curve was linear over this range and the slope calculated by linear regression analysis. The validities of these calibrations were periodically checked by analyzing known gas mixtures prepared on the vacuum system, with reproducibility of ±10% being obtained. Liquid-sample analysis for triphenylphosphine and triphenylphosphine oxide were performed on a Hewlett-Packard Model 5830A gas chromatograph in conjunction with a Model 18850A microprocessor. The column was a 10% UCW 982 (80–100 mesh) with nitrogen carrier gas. Liquid samples were withdrawn with Hamilton Precision Microliter syringes.

The all-glass reactor vessels (250 mL) consisted of a calibrated cylinder with two side arms. One side arm, equipped with a stopcock, served for attachment to the vacuum line, and the other side arm was attached to a round-bottom flask (50 mL). This flask has a side arm sealed with a septum cap to allow for periodic gas and liquid sampling. Typically, Rh₆(CO)₁₆, triphenylphosphine, and hexamethylbenzene were placed in this flask. Benzene (10 mL) was added under nitrogen to the calibrated cylinder, and the reaction vessel was attached to the vacuum line. The design incorporated both a manometer and a gas inlet. The benzene was degassed by freeze pumping using liquid nitrogen, after which it was transferred to the flask. The reaction was magnetically stirred until all solid reactants had dissolved. The gases CO and O₂ were mixed in a ballast bulb attached to the vacuum line, and the mixture was used to charge the reaction vessel to the desired pressure. Gas and liquid samples were removed as required by syringe through the septum. Gas stoichiometries were analyzed by direct comparison to standard calibration and liquids (PPh₃ and OPPh₃ in benzene solvent) by reference to hexamethylbenzene internal calibrant. Reactions were run to completion with triphenylphosphine as the limiting reagent, and 6 h was allowed to elapse for gas mixture equilibration to occur prior to analysis. The amount of CO₂ produced was estimated as the sum total in the gas and liquid phases, the latter being calculated by assuming Henry's law behavior from the known solubility of CO₂ in benzene.[39]

For the isotopic labeling experiments [¹⁸O]water (33 atom %) was purchased from Yeda Research and Development Company Ltd. and [¹⁸O]oxygen (94 atom %) from Stohler Isotope Chemicals. The suppliers assay of the labeled water showed the composition to be oxygen-18, 33.199%; oxygen-17, 0.216%; and deuterium, 34.6%. The oxygen gas was originally purchased as 99 atom % oxygen-18. The sample has been used previously by us, and some atmospheric leakage into the vessel has occurred. The sample has therefore been reanalyzed by mass spectroscopy and found to contain 94 atom % oxygen-18 as m/e 36. The sample contains no measurable quantity of the isotopomer with m/e 34. The amount of unlabeled oxygen gas (m/e 32) from air was estimated from its radio to that of the nitrogen (m/e 28) peak. The experimental techniques used for the catalytic experiments (A–D) with these labeled-oxygen-containing compounds were the same as those described for the gas experiments with unlabeled oxygen compounds. For experiment A, with Rh₆(CO)₁₆ (11 mg) and PPh₃ (100 mg) in a solvent mixture of ¹⁸OH₂ (0.2 mL, 33 atom % oxygen-18) and dry benzene (10 mL), a mixture of oxygen and carbon monoxide $(p(O_2):p(CO) = 1.5)$ is introduced. After 6 h under stirred conditions a CO₂ sample is removed for gas analysis. The benzene solvent is then removed by vacuum evaporation, and the triphenylphosphine oxide formed in the reaction is isolated by sublimation. For the catalytic experiments carried out under flow conditions, experiment B, CO and O₂ are bubbled through a benzene solution of Rh₆(CO)₁₆ (26.4 mg, 24.8 μmol), PPh₃ (795 mg, 303 mmol), and ¹⁸OH₂ (0.2 mL) for 1.5 h. The gases are then passed through two traps cooled at −10 °C and a final trap at −160 °C. After this final trap was warmed to room temperature, a gas sample was removed for mass spectral analysis. In experiment C, a mixture of CO and CO₂, in the controlled absence of O₂, is bubbled slowly into a stirred benzene solution. This solution contains Rh₆(CO)₁₆ (27.3 mg, 25.6 μmol) and PPh₃ (805 mg, 307 mmol) in dry benzene (20 mL) to which ¹⁸OH₂ (0.2 mL, 33 atom % oxygen-18) has been added. The gas flow is again passed for 1.5 h through the two traps maintained at −10 °C and −160 °C. For the experiment (D) using ¹⁸O₂ with added ¹⁶OH₂, Rh₆(CO)₁₆ (4.7 mg, 4.4 μmol) and PPh₃ (24.2 mg, 92 μmol) with benzene (5 mL), water (0.2 mL), ¹⁸O₂ (0.579 mmol), and CO (0.412 mmol) were reacted for 6 h.

(39) Gjaldbeck, J. C. *Acta Chem. Scand.* **1953**, *7*, 537–544. Gerard, W. "Solubility of Gases and Liquids"; Plenum Press: New York, 1976; Chapter 8.