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Activation of the Water Molecule. 5. Rhodium(I) Hydride Catalyzed Water Gas Shift Reaction. Identification of the Elemental Reactions Comprising the Catalytic Cycles

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Abstract: Rhodium(I)–hydrido compounds, e.g., $RhHL_3$ (**1**, L = PEt_3; **2**, L = $P(i\text{-}Pr)_3$), $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ (**3**), *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ (**4**), and $RhH[P(t\text{-}Bu)_3]_2$ (**5**), serve as catalyst precursors for the water gas shift (wgs) reaction active under relatively mild conditions (>50 °C). Types of Rh compounds isolated from the wgs reaction were [*trans*-$Rh(CO)(py)L_2]BPh_4$ (**6b**, L = $P(i\text{-}Pr)_3$; **7b**, L = $P(c\text{-}C_6H_{11})_3$; **8b**, L = PEt_3; py = pyridine), *trans*-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$ (**9**), *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (**11**), and $Rh_2(CO)_4[P(t\text{-}Bu)_3]_2$ (**22**). The key intermediates appear to be *trans*-$RhH(CO)L_2$ (**9**; **10**, L = $P(i\text{-}Pr)_3$) and *trans*-$Rh(OH)(CO)L_2$ (**11**; **12**, L = $P(c\text{-}C_6H_{11})_3$) which in pyridine is in equilibrium with the solvated form [*trans*-$Rh(CO)(py)L_2]OH$ (**6a**, L = $P(i\text{-}Pr)_3$; **7a**, L = $P(c\text{-}C_6H_{11})_3$). The formation of **6a** and **7a** from **2** and **3**, respectively, was shown to proceed through oxidative addition of H_2O to give $[RhH_2(py)_2L_2]OH$ (**14a**, L = $P(i\text{-}Pr)_3$; **15a**, L = $P(c\text{-}C_6H_{11})_3$) (step 1) and subsequent reaction of the adduct with CO releasing H_2 (step 2). H_2 evolution from the water adduct $[RhH_2(PEt_3)_3]OH$ (**16a**) of **1** with CO requires more drastic conditions (80 °C) and takes place through an intermediate $[RhH_2(CO)(PEt_3)_3]^+$ (**18**). The water adducts **14a** and **16a** are bases stronger than NaOH in aqueous pyridine. Alternatively, the catalyst precursors may react first with CO to give a Rh(0) compound such as $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (**21**) and $Rh_2(CO)_4L_2$ (**22**; **23**, L = $PPh(t\text{-}Bu)_2$; **24**, L = $P(c\text{-}C_6H_{11})_3$) via *trans*-$RhH(CO)L_2$ (**9**, **10**) (step 3). Then, these carbonyl compounds **21**, **9**, and **10** react with H_2O to give **6a** or **7a** with concomitant evolution of H_2 (step 4). Under a CO atmosphere **11** and **12** yield *trans*-$RhH(CO)L_2$ (**9**, **10**) through a nucleophilic attack of OH^- to the coordinated CO to give $Rh(CO_2H)(CO)L_2$ as a transient species (step 5), followed by decarboxylation (step 6). The intermediacy of $Rh(CO_2H)(CO)L_2$ was suggested by isolating the closely *related trans*-$Rh(CO_2CH_3)(CO)[P(i\text{-}Pr)_3]_2$ (**25**) from the reaction of *trans*-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$ (**13**) with CO. Accordingly, we infer that one cycle starts from **11** or **12** and involves a sequence of steps 5 → 6 → 4 to regenerate **11** or **12**. As the wgs reaction proceeds, another cycle becomes important. This is shown for the $P(i\text{-}Pr)_3$ compound **10**. The cycle is comprised of the reaction with CO_2–H_2O to give $Rh(OCO_2H)(CO)[P(i\text{-}Pr)_3]_2$ (**27**) and H_2 (step 7), transformation of **27** into $Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (**26**) (step 8), and hydrolysis of **26** regenerating **11** or its solvated ion-pair compound **6a** (step 9). In support of the proposed reaction scheme, all the isolated Rh compounds, i.e., *trans*-$Rh(OH)(CO)L_2$, *trans*-$RhH(CO)L_2$, $Rh_2(\mu\text{-}OCO_2)(CO)_2L_4$, and $RhH_2(OCO_2H)L_2$ (precursor of **27**) (L = $P(i\text{-}Pr)_3$ and/or $P(c\text{-}C_6H_{11})_3$), as well as **21** were found to exhibit catalytic activity comparable to that of the catalyst precursor carrying the corresponding phosphine ligand.

The water gas shift (wgs) reaction has been of great industrial importance in increasing the ratio of H_2/CO of synthetic gas. Current methods for effecting the wgs reaction employ heterogeneous catalysts mainly on the basis of either Fe_2O_3 and related oxides or copper and copper–zinc oxide mixtures all of which are active only at high temperature.[1] Homogeneous catalysts active at lower temperature are attracting considerable interest because of the favorable thermodynamic equilibrium ($K = 1.45 \times 10^3$ at 127 °C and 26.9 at 327 °C).[2] Following the pioneering work by Hieber[3] on iron carbonyl and carbonyl hydrides, various metal carbonyls and carbonyl cluster compounds have been proposed as catalyst components which were coupled with acids or bases.[4] Platinum(II) chloride–tin chloride,[5] PtL_n–H_2O (L = PR_3),[6] and $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$–LiCl (dpm = bis(diphenylphosphino)methane)[7] are active without added acids or bases.

Although the reaction pathways vary depending on the catalyst system and reaction conditions, one could gather from reported mechanistic studies[4j,5,6] that there are a few important elemental reactions common to the wgs catalysis. The first one is a nucleophilic attack by H_2O or OH^- on coordinated CO to give a hydroxycarbonyl complex followed by subsequent β-hydrogen elimination therefrom affording the metal hydride and CO_2 (eq 1 and 2). The second may be the reduction of protons represented by eq 3.

$$M^+\text{–}CO + H_2O \rightarrow M\text{–}COOH + H^+ \qquad (1)$$

$$M\text{–}COOH \rightarrow MH + CO_2 \qquad (2)$$

$$MH + H^+ \rightarrow M^+ + H_2 \qquad (3)$$

Precedents for these types of reactions are known in literature. For example, a stoichiometric formation of $IrHCl_2(CO)L_2$ and CO_2 from $[IrCl_2(CO)_2L_2]Cl$ was confirmed to occur via a stable intermediate, $IrCl_2(CO)(COOH)L_2$ (L = PMe_2Ph).[8] In the wgs reaction catalyzed by PtL_3 (L = $P(i\text{-}Pr)_3$), we were able to confirm involvement of the two processes, (1) and (2), by isolating $[PtH(CO)L_2]^+$ and *trans*-PtH_2L_2 and further by detecting spectroscopically the species $PtH(COOK)L_2$ formed from $[PtH(CO)L_2]^+$ and KOH.[6] Recently *trans*-$PtCl(CO_2H)L_2$ (L = PEt_3) was isolated by Halpern et al.,[9] which has been proposed as an intermediate for the formation of $PtH(Cl)L_2$ from $[PtCl(CO)L_2]^+$

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Table I. Numbering Scheme of Compounds

$RhH(PEt_3)_3$	**1**	$\{RhH_2(py)_2[P(c\text{-}C_6H_{11})_3]_2\}BPh_4$	**15b**
$RhH[P(i\text{-}Pr)_3]_3$	**2**	$[RhH_2(PEt_3)_3]OH$	**16a**
$Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$	**3**	$[RhH_2(PEt_3)_3]BPh_4$	**16b**
trans-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$	**4**	$[RhH_2(PEt_3)_4]OH$	**17a**
$RhH[P(t\text{-}Bu)_3]_2$	**5**	$[RhH_2(PEt_3)_4]BPh_4$	**17b**
$\{$*trans*-$Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}OH$	**6a**	$[RhH_2(CO)(PEt_3)_3]BPh_4$	**18**
$\{$*trans*-$Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4$	**6b**	$\{$*trans*-$Rh(t\text{-}BuNC)_2[P(i\text{-}Pr)_3]_2\}BPh_4$	**19**
$\{$*trans*-$Rh(CO)(acetone)[P(i\text{-}Pr)_3]_2\}BPh_4$	**6c**	$[Rh(CO)_3P(i\text{-}Pr)_3]_2$	**20**
$\{$*trans*-$Rh(CO)(py)[P(c\text{-}C_6H_{11})_3]_2\}OH$	**7a**	$Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$	**21**
$\{$*trans*-$Rh(CO)(py)[P(c\text{-}C_6H_{11})_3]_2\}BPh_4$	**7b**	$Rh_2(CO)_4[P(t\text{-}Bu)_3]_2$	**22**
$[$*trans*-$Rh(CO)(py)(PEt_3)_2]BPh_4$	**8b**	$Rh_2(CO)_4[PPh(t\text{-}Bu)_2]_2$	**23**
trans-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$	**9**	$Rh_2(CO)_4[P(c\text{-}C_6H_{11})_3]_2$	**24**
trans-$RhH(CO)[P(i\text{-}Pr)_3]_2$	**10**	*trans*-$Rh(CO_2CH_3)(CO)[P(i\text{-}Pr)_3]_2$	**25**
trans-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$	**11**	$Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$	**26**
trans-$Rh(OH)(CO)[P(c\text{-}C_6H_{11})_3]_2$	**12**	$Rh(OCO_2H)(CO)[P(i\text{-}Pr)_3]_2$	**27**
trans-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$	**13**	$Rh(OCO_2H)(CO)[P(c\text{-}C_6H_{11})_3]_2$	**28**
$\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}OH$	**14a**	$RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$	**29**
$\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}BPh_4$	**14b**	$RhH_2(O_2COH)[P(c\text{-}C_6H_{11})_3]_2$	**30**
$\{RhH_2(bpy)[P(i\text{-}Pr)_3]_2\}BPh_4$	**14c**	$Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$	**31**
$\{Rh_2H_2(py)_2[P(c\text{-}C_6H_{11})_3]_2\}OH$	**15a**		

Table II. The Water Gas Shift Reaction[a]

	products[b]			products[b]		
catalyst precursor	solvent	H_2	CO_2	solvent	H_2	CO_2
$RhH(PEt_3)_3$ (**1**)	pyridine	10.0	10.0	acetone	4.4	4.3
$RhH[P(i\text{-}Pr)_3]_3$ (**2**)	pyridine	32.2	33.9	acetone	27.2	29.4
$Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ (**3**)	pyridine	17.8	17.2	acetone	9.4	10.0
$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ (**4**)				acetone		0.5
$RhH[P(t\text{-}Bu)_3]_2$ (**5**)				acetone		0.2
$RhCl(PPh_3)_3$				acetone		0.06
$RhCl(CO)(PPh_3)_2$				acetone		0.9[c]

[a] The reaction was carried out by using catalyst precursor (0.1 mmol), H_2O (2 mL), and CO (20 kg/cm^2) in the solvent specified (5 mL) at 100 °C for 18 h; for details see Experimental Section. [b] Mol/mol of Rh per h. [c] The reaction temperature was 150 °C.

and H_2O.[10] The oxygen-exchange reaction of $[Mn(CO)_4(diphos)]^+$ with $H_2{}^{18}O$ as well as the side reaction responsible for the formation of $MnH(CO)_3(diphos)$, both being assumed to occur via intermediacy of Mn–COOH species, can be greatly accelerated by addition of amines, a result explicable in terms of the nucleophilic reaction (eq 1).[11]

The reaction (eq 1) should be facilitated by an increase in the electrophilicity of CO ligand either by increasing the oxidation state of the metal center or by the presence of electron-withdrawing auxiliary ligands. It is known that $Fe(CO)_5$ readily reacts with OH^-, giving $FeH(CO)_4{}^-$ and CO_2 (or H_2CO_3), but does not react with H_2O.[12] This implies that the CO ligands of $Fe(CO)_5$ are not electrophilic enough to undergo the reaction (eq 1). Thus, the requirement of strong bases for the iron carbonyl catalyzed wgs reaction is understandable.

In the case of catalytic systems involving protonic acids, the metal center tends to be stabilized in higher oxidation states. For example, a rhodium(III)–carbonyl species was thought to be important in the wgs reaction catalyzed by $[Rh(CO)_2Cl]_2$–HI–acetic acid.[4k] The high oxidation state should lower the activation energy of the reaction (eq 1). However, it can be an unfavorable factor for the wgs catalysis, as a facile reduction of the metal center by CO and water would be required for reduction of protons. Presumably the reduction of a metal center (eq 4) proceeds via

$$M^{n+} + CO + H_2O \rightarrow M^{(n-2)+} + CO_2 + 2H^+ \qquad (4)$$

a hydroxycarbonyl species. Coordination of CO to a metal, a requisite for (eq 4), would become difficult if the metal is assuming a high oxidation state. The requirement of a soft anion like I^- for Eisenberg's[4k] or Monsanto's[13] systems is understandable in terms of the effective charge transfer of I^- to the Rh(III) center.

Recently we found that transfer of two electrons to a water molecule can be achieved by such a low-valent metal compound as PtL_n[14] and $RhHL_n$ (n = 2 and 3) or $(RhHL_2)_2(\mu\text{-}N_2)$[15] resulting in coordinated H^- and OH^-. The oxidative addition of water to the (hydrido)rhodium compound is of particular interest because of the cis alignment of the hydrido ligands in the adduct $[RhH_2(S)_2L_2]OH$ (S = solvent). Further, we observed facile H_2 evolution upon treatment of the *cis*-dihydride compound with CO or RNC.[16] As expected, $RhHL_n$ and related (hydrido)rhodium compounds turned out to be highly active homogeneous catalysts for the wgs reaction. Certainly they were more active than PtL_n with corresponding L.[6] One of the greatest advantages of the catalyst systems, $RhHL_n/H_2O$, was that they were active under relatively mild conditions (>50 °C) and isolation of various active species was thus possible. In order to elucidate the mechanism, our efforts were mainly devoted to identifying a series of component reactions. This was achieved by isolating various metal species by varying either the solvent or the ligands. Sometime we synthesized the possible intermediate compounds through different routes and examined the elemental reactions with these species. Unprecedented attention was also paid to reactions of various active species with CO_2 or H_2CO_3. It was during this phase of our studies on the wgs reaction that we found an astonishingly facile reduction of CO_2 with water effected by such (hydrido)rhodium species as $RhHL_3$ and $Rh_2H_2(\mu\text{-}N_2)L_4$ (L = PR_3), the reverse wgs reaction.[17] The numbered compounds

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Table III. The Water Gas Shift Reaction[a]

compd	products[b] H_2	products[b] CO_2	compd	products[b] H_2	products[b] CO_2
trans-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$ (9)	18.3	18.9	$Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (21) + $3P(i\text{-}Pr)_3$	28.3	31.7
trans-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (11)	26.7	21.7	$Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (26)	27.2	29.4
trans-$Rh(OH)(CO)[P(c\text{-}C_6H_{11})_3]_2$ (12)	19.7	19.4	$RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (29)	35.6	34.4
trans-$Rh(OH)(CO)(PPh_3)_2$	8.3	7.2	$RhH_2(O_2COH)[P(c\text{-}C_6H_{11})_3]_2$ (30)	18.3	17.8
$Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (21)	16.1	14.4	$Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$ (31)	32.2	32.8

[a] The reaction was carried out by using catalyst (0.1 mmol)–H_2O (2.0 mL)–CO(20 Kg/cm^2) in pyridine (5.0 mL) at 100 °C for 18 h.
[b] Mol/mol of Rh per h.

described herein are given in Table I.

Results and Discussion

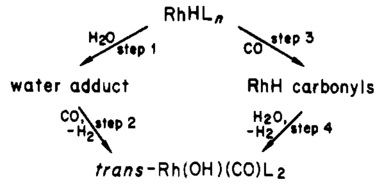
General Aspects of the Rhodium(I) Hydride Catalyzed wgs Reaction. The wgs reaction was carried out at 100 °C under CO pressure (20 Kg/cm^2) for 18 h with rhodium(I)–hydrido compounds as catalyst precursors; no attempt was made to optimize the reaction conditions for the rate. Rhodium(I)–hydrido complexes examined were $RhH(PEt_3)_3$ (**1**), $RhH[P(i\text{-}Pr)_3]_3$ (**2**), $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ (**3**), $RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ (**4**), and $RhH[P(t\text{-}Bu)_3]_2$ (**5**). The catalytic activity of the rhodium(I)–hydrido complexes depends on the nature of the auxiliary phosphine ligand and decreases in the order **2** > **3** > **1** ≫ **4** > **5** (Table II). The complex $RhCl(PPh_3)_3$ is virtually inactive as catalyst under similar conditions, and *trans*-$RhCl(CO)(PPh_3)_2$ could be isolated from the reaction mixture. *trans*-$RhCl(CO)(PPh_3)_2$ was also found to be inactive as the catalyst even at higher temperatures (150 °C).

The reaction rate is greatly influenced by the reaction medium. The rate was faster in strongly coordinating pyridine than in acetone. The trend is opposite to that observed for the wgs reaction catalyzed by $Pt[P(i\text{-}Pr)_3]_3$.[6] With **2**, the conversion of CO into CO_2 reaches 90% after 18 h in pyridine at 150 °C. Remarkably **2** in pyridine is active at a temperature as low as 50 °C (turnover value for H_2 3.6 and for CO_2 3.4 mol/mol of **2** per h). In acetone above 125 °C using **2** as a catalyst precursor, catalytic reduction of acetone takes place affording *i*-PrOH (turnover value 1.2 at 125 °C, and 11.1 mol/mol of **2** per h at 150 °C). This is not unexpected as **2** actively hydrogenates ketones even at ambient conditions.[18]

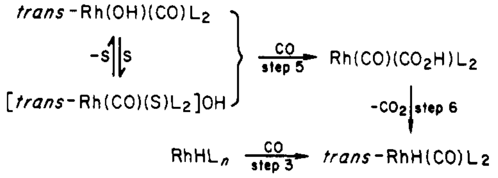
The wgs reaction catalyzed by **2** in acetone under the conditions described in Table II was terminated after 18 h. The degassed contents of the autoclave were evaporated to remove the water and solvent. The concentrate, maintaning the original amount of rhodium, also shows a catalytic activity comparable with that of **2**, the turnover value for CO_2 being 20 (mol/mol of **2** per h). The substantial retention of the activity is consistent with the fact that essentially comparable rates of the wgs catalysis were observed with isolated rhodium compounds (vide infra).

Isolation of Rhodium Species. In order to obtain information on the fate of the catalyst precursors employed, we made an effort to isolate as many rhodium species as possible. The reaction carried out with **2** in pyridine under the conditions specified in Table II was terminated by cooling the mixture to room temperature and degassing. On addition of $NaBPh_4$ to the homogeneous yellow solution remaining in the autoclave and subsequent evaporation of pyridine and H_2O in vacuo, *trans*-$\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4$ (**6b**) solidifed as yellow crystals in 70% yield. A similar treatment of the reaction mixture effected by **3** or **1** in pyridine gave analogous yellow compounds, *trans*-$[Rh(CO)(py)L_2]BPh_4$ (**7b**, L = $P(c\text{-}C_6H_{11})_3$, 50%; **8b**, L = PEt_3, 85%). The isolation of **6b**, **7b**, and **8b** provides definite proof for the formation of ionic hydroxo complexes of general formula *trans*-$[Rh(CO)(py)L_2]OH$ (the characterization will be described later). The isolation of these BPh_4^- salts, however, does not necessarily imply these cationic carbonyl species to be the most predominant species in the reaction mixture. Their parent compounds, $[Rh(CO)(py)L_2]OH$, are reactive and susceptible to further transformation under the wgs reaction conditions as described later.

Scheme I



Scheme II



The rhodium compounds which can be isolated from the wgs reaction mixture varies depending on the catalyst precursor and reaction medium. Thus, *trans*-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$ (**9**) was obtained in 58% yield by simply concentrating the yellow solution obtained from the shift reaction catalyzed by **3** in acetone. Note that a bulky phosphine stabilizes the (hydrido)carbonylrhodium species $RhH(CO)L_2$. The concentrated yellow residue from the catalytic reaction of **2** in acetone was found to contain *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (**11**) by IR spectroscopy (ν(OH) = 3645 and ν(CO) = 1925 cm^{-1}). This is rather expected since we already know that the wgs reaction in pyridine gives **6b** which must be formed from the ionic compound *trans*-$\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}OH$ (**6a**) (vide infra).

From the reaction catalyzed by **5** in acetone, a binuclear rhodium(0)–carbonyl compound $Rh_2(CO)_4[P(t\text{-}Bu)_3]_2$ (**22**) was isolated as red crystals in 60% yield. Thus the types of rhodium compounds which could be isolated from the wgs reaction mixture or detected spectroscopically in situ are *trans*-$RhH(CO)L_2$, *trans*-$Rh(OH)(CO)L_2$, *trans*-$[Rh(CO)(py)L_2]^+$, and $Rh_2(CO)_4L_2$.

The compounds **9** and **11** proved to be efficient catalysts for the wgs reaction (Table III), a result suggestive of involvement of **9** and **11** in the catalytic cycle. The ionic complex *trans*-$[Rh(CO)(py)L_2]BPh_4$ (**6b** and **7b**) was again isolated upon treatment with BPh_4^- of the shift reaction mixture effected by **9** and **11** in pyridine. Table III also contains the results of the wgs reaction catalyzed by other types of Rh(I), Rh(III), and Rh(0) compounds bearing in the catalytic reactions.

Elemental Reactions Leading to Main Catalytic Chain Carriers. From the results described above we could infer that *trans*-$Rh(OH)(CO)L_2$ and *trans*-$RhH(CO)L_2$ are important active species, acting as the carriers of the catalytic cycle. In this section, possible routes leading to these key intermediates will be discussed.

In the case of the PtL_3-catalyzed (L = e.g., $P(i\text{-}Pr)_3$) wgs reaction, CO coordination occurs on the water adduct, *trans*-$[PtH(S)L_2]OH$ (S = solvent), giving *trans*-$[PtH(CO)L_2]OH$, one of the key intermediates. This step is then followed by a nucleophilic attack of OH^- on the CO ligand, resulting in PtH_2L_2 presumably via a transient species, $PtH(COOH)L_2$.[6] Similar reaction patterns are expected for $RhHL_n$, as they are strong nucleophiles similar to PtL_n (see the following section). Two

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(18) Yoshida, T.; Otsuka, S., unpublished results.

Table IV. Spectral Data of H_2O Adducts of Rhodium(I)-Hydrido Compounds

		^{1}H NMR			
compd	IR ν(Rh-H),[a] cm^{-1}	δ(Rh-H)	J_{Rh-H}, Hz	J_{P-H}, Hz	$\delta(PR_3)$
$\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}OH$ (**14a**)		−20.3 (q)[b]	16.8	16.8 (cis)	1.08 (q, CH_3, $^3J_{H-P} + {}^5J_{H-P}$ = 12.8 Hz, J_{H-H} = 6.4 Hz), ~2.0 (m, CH)
$\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}BPh_4$ (**14b**)	2112, 2076	−19.9 (q)[c]	16.4	16.4 (cis)	0.98 (q, CH_3, $^3J_{H-P} + {}^5J_{H-P}$ = 13.2 Hz, J_{H-H} = 6.6 Hz), ~2.0 (m, CH)
$\{RhH_2(bpy)[P(i\text{-}Pr)_3]_2\}BPh_4$ (**14c**)	2135, 2080	−17.2 (q)[d]	15.6	15.6 (cis)	1.02 (q, CH_3, $^3J_{H-P} + {}^5J_{H-P}$ = 12.0 Hz), ~2.0 (m, CH)
$\{RhH_2(py)_2[P(c\text{-}C_6H_{11})_3]_2\}BPh_4$ (**15b**)[e]	2020, 2005				
$[RhH_2(PEt_3)_3]OH$ (**16a**)		−11.7 (b d)[b]		~125 (equatorial)	
$[RhH_2(PEt_3)_3]BPh_4$ (**16b**)	2038, 1982	−12.0 (two d)[c,f]	11.0	124.5 (equatorial) 16.5 (axial)	~1.0 (m, CH_3), ~1.6 (m, CH)
$[RhH_2(PEt_3)_4]BPh_4$ (**17b**)	2020, 2005	−11.7 (two d)[g]	11.0	124.5 (equatorial) 16.0 (axial)	

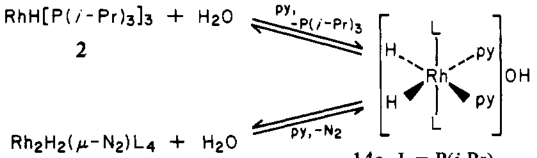
[a] Measured in Nujol mull. [b] Measured in pyridine–H_2O (4:1 volume ratio) at room temperature. [c] Measured in pyridine. [d] Measured in acetone-d_6. [e] The hydrido signal was not detected due to low solubility in organic solvents. [f] The hydrido signal in THF was observed at δ −11.9(two d, J_{Rh-H} = 11.2 Hz, $J_{P-H(equatorial)}$ = 124.0 Hz, $J_{P-H(axial)}$ = 16.4 Hz). [g] Measured in THF.

pathways are possible leading to *trans*-Rh(OH)(CO)L_2 (Scheme I). Each step has been studied independently as will be described later.

With respect to the formation of the hydrido carbonyl species *trans*-RhH(CO)L_2, again two pathways are conceivable (Scheme II). The route, steps 5 and 6, is essentially analogous to the formation of PtH_2L_2 from *trans*-[PtH(CO)L_2]OH.[6]

These active rhodium species could react with the CO_2 or H_2CO_3 that is produced. We also studied, therefore, these reactions (steps 7–9), as will be described in a later section.

Oxidative Addition of Water (Step 1). Oxidative addition of H_2O to **2** in pyridine (eq 5) occurs readily at room temperature,



(5)

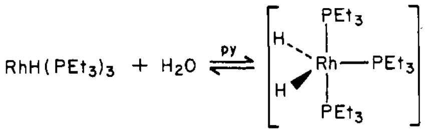
3, L = P(c-C_6H_{11})$_3$

14a, L = P(*i*-Pr)$_3$
15a, L = P(c-C_6H_{11})$_3$

dissociating 1 mol of P(*i*-Pr)$_3$ to give $\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}OH$ (**14a**), as can be monitored by ^{1}H NMR spectroscopy. Thus, the ^{1}H NMR spectrum of **2** measured in H_2O–pyridine (volume ratio 1:4) at room temperature shows a hydrido signal at δ −20.3 as a quartet (J_{H-Rh} = 17.0 Hz, J_{H-P} = 17.0 Hz) and a CH_3 proton signal at δ 1.08 as a 1:3:3:1 quartet ($^3J_{H-P} + {}^5J_{H-P}$ = 12.8 Hz, J_{H-H} = 6.4 Hz), suggesting that the two hydrido ligands are cis and two phosphine ligands are mutually trans. Although **14a** is stable in aqueous pyridine, a facile reductive elimination of H_2O takes place in dry solvents and attempts to isolate **14a** were unsuccessful. Thus, **2** was regenerated on concentration of an aqueous pyridine solution of **14a** to dryness.

The formation of **14a** was unequivocally confirmed by isolation of $\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}BPh_4$ (**14b**) as colorless crystals by metathesis with $NaBPh_4$ in 76% yield. The IR spectrum of **14b** shows two ν(Rh–H) at 2112 and 2076 cm^{-1} while ν(Rh–D) of the corresponding dideuteride, obtained by addition of D_2O to **2**, was observed at 1500 cm^{-1} (cf. ν(Rh–H)/ν(Rh–D) = 1.38). The observation of the ^{1}H NMR hydrido signal due to the ionic compound **14a** in aqueous pyridine at room temperature suggests that the equilibrium favors the addition of H_2O (eq 5). Similarly, the reaction of **3** with H_2O in pyridine at room temperature produces $\{RhH_2(py)_2[P(c\text{-}C_6H_{11})_3]_2\}OH$ (**15a**) which can be isolated as BPh_4^- salt (**15b**). Due to the extremely low solubility in organic solvents, NMR measurements have not been attempted. The cis ligation of two hydrides, however, is confirmed by the observation of two IR ν(Rh–H) bands (Table IV).

The oxidative addition of H_2O to RhH(PEt_3)$_n$ (n = 3, 4) also occurs at room temperature in pyridine. The ^{1}H NMR spectrum of RhH(PEt_3)$_3$ (**1**) dissolved in pyridine–H_2O (4:1 volume ratio) shows two hydrido signals as broad doublets at δ −11.7 (J_{H-P} = 125 Hz) and −19.4 (J_{H-P} = 110 Hz) in an approximately equal intensity, suggesting the formation of two hydrido species, one of which is readily assigned as **16a** as will be described below. Addition of $NaBPh_4$ to the above mixture gave [$RhH_2(PEt_3)_3$]BPh_4 (**16b**) (80%) as a sole isolatable hydride (eq 6).

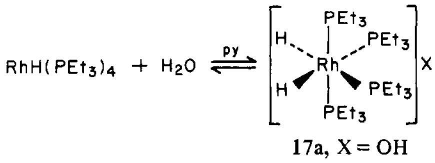


(6)

16a, X = OH

A trigonal-bipyramidal structure with *cis*-dihydrido ligands in the equatorial plane was deduced for **16b** from the hydrido ^{1}H NMR signal observed at δ −12.0 as two double triplets (J_{H-Rh} = 11.0 Hz, $J_{H-P(axial)}$ = 16.5 Hz, $J_{H-P(equatorial)}$ = 124.5 Hz). In view of the close similarity in both chemical shift and magnitude of $J_{H-P(equatorial)}$ between **16b** and the species which shows the lower field hydride signal (δ −11.7), it is reasonable to assume that the hydrido species formed in situ is a dihydrido hydroxo compound [$RhH_2(PEt_3)_3$]OH (**16a**). The other hydrido species associated with the higher hydrido signal (δ −19.4) was not well characterized due to its thermal instability and ill-defined broad ^{1}H NMR signal. The almost quantitative yield of **16b**, however, suggests that the second hydrido species is readily transformed into **16b** during isolation. Hence, we tentatively assign the unstable compound as a hexacoordinate species, $RhH_2(OH)(PEt_3)_3$ or [RhH_2(py)(PEt_3)$_3$]OH.

The addition of H_2O to RhH(PEt_3)$_4$ was then studied. RhH(PEt_3)$_4$ tends to dissociate one PEt_3 (K_d = 1.1 × 10^{-1} M, 20 °C in heptane).[19] When an excess of PEt_3 in pyridine was added to prevent the formation of RhH(PEt_3)$_3$ as much as possible, H_2O was added to the solution at room temperature. The formation of [$RhH_2(PEt_3)_4$]OH (**17a**) (eq 7) was confirmed by isolating the BPh_4^- salt (**17b**) in 47% yield. Recrystallization of **17b** from pyridine–MeOH in the absence of free PEt_3 gave **16b**, indicating a facile dissociation of one of the coordinated PEt_3 ligands. Consistently, the ^{1}H NMR spectrum of **17b** in THF showed only



(7)

17a, X = OH

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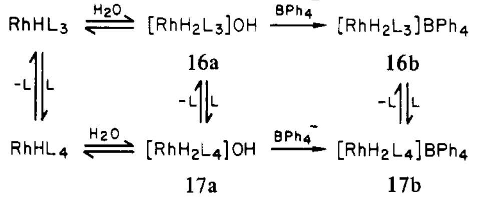
(19) Yoshida, T.; Thorn, D. L.; Okano, T.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 6451–6457.

Table V. Apparent pH of the $RhHL_3$-H_2O in Pyridine at 20 °C[a]

compd	pH_{app}	compd	pH_{app}
$RhH(PEt_3)_3$	14.5	$Pt(PEt_3)_3$	14.3
$RhH[P(i\text{-}Pr)_3]_3$	14.2	$Pt[P(i\text{-}Pr)_3]_3$	14.1
		NaOH	13.5

[a] [compound] = 9.8×10^{-3} M. Volume ratio of H_2O vs. pyridine was 2:3.

a hydride signal identical with that observed for **16b**, no other hydride signal being observed. Characterization of **17b** was therefore relied on the IR spectrum which exhibited two ν(Rh–H) (2003 and 2015 cm^{-1}) consistent with cis coordination of two hydrido ligands. The dissociative equilibria involved in system $RhH(PEt_3)_n$–H_2O (n = 3, 4) are summarized in eq 8.



(8)

Isolation of the unstable water adduct *trans*-$PtH(OH)L_2$ could be achieved only when two coordinate compounds, PtL_2, were used. The presence of free phosphines apparently facilitates reductive elimination of water from the adduct.[14] Accordingly attempts were made to isolate a neutral adduct $RhH_2(OH)L_2$ employing $(RhHL_2)_2(\mu\text{-}N_2)$ (L = $P(i\text{-}Pr)_3$) which exists mainly as $RhHL_2$ in solution.[20] Addition of an excess of H_2O to an orange solution of $(RhHL_2)_2(\mu\text{-}N_2)$ in THF at room temperature under a dinitrogen atmosphere resulted in precipitation of the starting material. The failure to isolate the adduct may be ascribed to the small equilibrium constant K_0.

$$RhHL_2 + H_2O \overset{K_0}{\rightleftharpoons} RhH_2(OH)L_2$$

The reductive elimination should be more facile in trigonal-bipyramidal $RhH_2(OH)L_2$ than in square-planar *trans*-$PtH(OH)L_2$.[14]

A variety of cationic dihydridorhodium compounds are known, e.g., $[RhH_2L_4]^+$, $[RhH_2(S)_2L_2]^+$, and $RhH_2(bpy)L_2{}^+$ (L = phosphines, phosphites, and arsines; S = solvent).[21,22] They were prepared from cationic rhodium(I)–olefin complexes employing H_2. The present preparation with H_2O has no precedent to our knowledge.

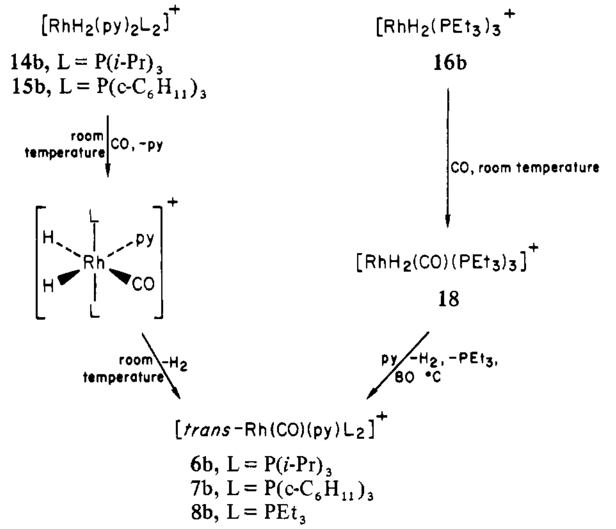
The compounds **14a** and **16a** extensively dissociate into the corresponding rhodium(III)–dihydrido cation and OH^- (eq 9 and 10). This is manifested in the free OH^- concentrations of the

$$\mathbf{14a} \rightleftharpoons [Rh(H)_2(py)_2L_2]^+ + OH^- \qquad (9)$$

$$\mathbf{16a} \rightleftharpoons [Rh(H)_2L_3]^+ + OH^- \qquad (10)$$

$RhHL_3$–H_2O system (L = PEt_3, $P(i\text{-}Pr)_3$) in pyridine–H_2O (Table V). The $RhH(PEt_3)_3$–H_2O system exhibits a slightly stronger basicity than the corresponding $P(i\text{-}Pr)_3$ analogue. The basicities of the $RhHL_3$–H_2O system are comparable to those of the isoelectronic Pt(0) system PtL_3–H_2O (L = PEt_3, $P(i\text{-}Pr)_3$),[14] and their apparent pH values are even greater than the value of NaOH in this mixed solvent (Table V). An addition of H_2O to $[Rh(en)_2]^+$ (en = ethylenediamine) prepared in situ by electrochemical reduction of $[RhCl_2(en)_2]^+$ has been reported to produce $[RhH(OH)(en)_2]^+$ which also exhibits strong basicity due to dissociation into $[RhH(en)_2]^{2+}$ and OH^-.[23]

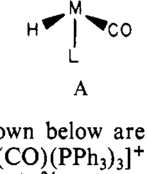
Scheme III



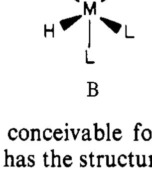
Reactions of Water Adducts with CO (Step 2). The dihydrido compounds **14b** and **15b** are rather thermally stable as far as water is present in the medium. For example, they are recovered unchanged after heating at 110 °C in aqueous pyridine for 20 h under N_2 atmosphere. A reaction of **14b** with 2,2′-bipyridine (bpy) in THF at room temperature gave $\{RhH_2(bpy)[P(i\text{-}Pr)_3]_2\}BPh_4$ (**14c**) as yellow crystals. Cis ligation of two hydrides and trans ligation of two $P(i\text{-}Pr)_3$ are readily deduced from the ^1H NMR and IR data (Table IV). The compound **14c** is also thermally stable showing no tendency to dissociate dihydrogen upon heating at 80 °C.

A facile reductive elimination of dihydride from **14b** was achieved by the reaction with CO. Thus, on introduction of CO (1 atm) into a THF solution of **14b** at room temperature, H_2 was evolved with effervescence. From the resulting solution was obtained $\{trans\text{-}Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4$ (**6b**) quantitatively, which was also isolated from the wgs reaction mixture catalyzed by **2** in pyridine. Similarly, the $P(c\text{-}C_6H_{11})_3$ compound **15b** with CO gave the corresponding carbonyl compound **7b** (Scheme III). It is to be noted that even in the presence of excess CO, the replacement of coordinated pyridine in **6b** and **7b** to give $[Rh(CO)_2L_2]^+$ does not occur.

By contrast, a reaction of **16b** with CO under similar condition employed for **14b** gave an octahedral dihydrido carbonyl compound $[RhH_2(CO)(PEt_3)_3]BPh_4$ (**18**) almost quantitatively without losing two hydrido ligands. The stereochemistry of **18** could not be determined by ^1H NMR due to the broad hydrido signal (δ −17) unresolvable even at −70 °C. The observation of two ν(Rh–H) bands (2005 and 2030 cm^{-1}), however, suggests cis arrangement of two hydrido ligands. Two possible structures A and B (L = L′ = PEt_3) shown below are conceivable for **18**. An Ir(III) congener $[IrH_2(CO)(PPh_3)_3]^+$ has the structure A, as confirmed by X-ray analysis.[24] By comparing the ν(Ir–H) bands of $[IrH_2(CO)(PPh_3)_3]^+$ (2148, 2100 cm^{-1}) with those of $[cis\text{-}IrH_2(PPh_3)_4]^+$ (2250 and 2225 cm^{-1}),[25] one could deduce that the ν(Ir–H) frequencies decrease drastically on substitution with CO of a PPh_3 ligand trans to hydride. Since the ν(Rh–H) frequencies of the Rh compounds **18** and **17b** (2015 and 2003 cm^{-1}) are comparable, it is most likely that **18** assumes the structure B rather



A



B

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Table VI. Spectral Data of Carbonyl and Related Compounds

compd	IR ν(CO),[a] cm^{-1}	^{1}H NMR (δ in ppm from Me$_4$Si)[b]
{*trans*-Rh(CO)(py)[P(*i*-Pr)$_3$]$_2$}BPh$_4$ (**6b**)	1985	1.25 (q, CH$_3$, $^3J_{H-P}$ + $^5J_{H-P}$ = 13.0 Hz, J_{H-H} = 6.5 Hz), ~1.9 (m, CH), 6.7 (m, Ph), 7.2 (m, Ph), 8.5 (m, Ph)[c]
{*trans*-Rh(CO)(py)[P(c-C$_6$H$_{11}$)$_3$]$_2$}BPh$_4$ (**7b**)	1978	
[*trans*-Rh(CO)(py)(PEt$_3$)$_2$]BPh$_4$ (**8b**)	1983	~1.15 (m, CH$_3$), ~1.60 (m, CH$_2$), 6.9 (m, Ph), 7.3 (m, Ph), 8.6 (m, Ph)[d]
trans-RhH(CO)[P(c-C$_6$H$_{11}$)$_3$]$_2$ (**9**)	1910, 1928, 1945[e] (1949)[b]	−5.9 (dt, Rh–H, J_{Rh-H} = 15.8 Hz, J_{P-H} = 20.2 Hz), 0.7–2.5 (b m, c-C$_6$H$_{11}$)
trans-RhH(CO)[P(*i*-Pr)$_3$]$_2$ (**10**)	1920, 1942[f]	−5.9 (dt, Rh–H, J_{Rh-H} = 14.3 Hz, J_{P-H} = 20.0 Hz), 1.23 (q, CH$_3$, $^3J_{H-P}$ + $^5J_{H-P}$ = 13.8 Hz, J_{H-H} = 6.9 Hz), ~2.0 (m, CH)
trans-Rh(OH)(CO)[P(*i*-Pr)$_3$]$_2$ (**11**)	1925[g]	1.27 (q, CH$_3$, $^3J_{H-P}$ + $^5J_{H-P}$ = 13.5 Hz, J_{H-H} = 6.8 Hz), ~2.3 (m, CH); −0.96 (t, OH, J_{P-H} = 5.3 Hz)
trans-Rh(OCH$_3$)(CO)[P(*i*-Pr)$_3$]$_2$ (**13**)	1925[h]	1.30 (q, CH$_3$, $^3J_{H-P}$ + $^5J_{H-P}$ = 14.0 Hz, J_{H-H} = 7.0 Hz), ~2.4 (m, CH), 3.97 (s, OCH$_3$)
[RhH$_2$(CO)(PEt$_3$)$_3$]BPh$_4$ (**18**)	1960[i]	−17 (b, Rh–H), ~1.15 (m, CH$_3$), ~2.0 (m, CH$_2$), 6.8 (m, Ph), 7.3 (m, Ph)[d]
{*trans*-Rh(*t*-BuNC)$_2$[P(*i*-Pr)$_3$]$_2$}BPh$_4$ (**19**)	2115[j]	1.38 (q, CH$_3$, $^3J_{H-P}$ + $^5J_{H-P}$ = 13.2 Hz, J_{H-H} = 6.6 Hz), ~2.3 (m, CH), 1.49 (s, *t*-Bu)[d]
[Rh(CO)$_3$P(*i*-Pr)$_3$]$_2$ (**20**)	~1950	~0.95 (b, CH$_3$), ~1.60 (b, CH)[k]
Rh$_2$(CO)$_3$[P(*i*-Pr)$_3$]$_3$ (**21**)	1732, 1769, 1957	~1.0 (m, CH$_3$), ~1.8 (m, CH)
Rh$_2$(CO)$_4$[P(*t*-Bu)$_3$]$_2$ (**22**)	1785, 1940, 1985	1.35 (d, *t*-Bu, J_{P-H} = 12.0 Hz)
Rh$_2$(CO)$_4$[PPh(*t*-Bu)$_2$]$_2$ (**23**)	1777, 1960, 1992	1.25 (d, *t*-Bu, J_{P-H} = 12.8 Hz), 7.0 (m, Ph), 8.0 (m, Ph)
Rh$_2$(CO)$_4$[P(c-C$_6$H$_{11}$)$_3$]$_2$ (**24**)	1730, 1945, 1972	
trans-Rh(CO$_2$CH$_3$)(CO)[P(*i*-Pr)$_3$]$_2$ (**25**)	1949[l]	1.28 (q, CH$_3$, $^3J_{H-P}$ + $^5J_{H-P}$ = 12.8 Hz, J_{H-H} = 6.4 Hz), 2.2 (m, CH), 3.46 (s, OCH$_3$)

[a] Measured in Nujol mull. [b] Measured in benzene-d_6. [c] Measured in THF-d_8. [d] Measured in acetone-d_6. [e] ν(Rh–H) = 1980 cm^{-1}. [f] ν(Rh–H) = 1980 cm^{-1}. [g] ν(OH) = 3644 cm^{-1}. [h] ν(C–O) = 1088 cm^{-1}. [i] ν(Rh–H) = 2005, 2030 cm^{-1}. [j] ν(C–N) = 2115 cm^{-1}. [k] Measured in benzene-d_6 under CO. [l] ν(C=O) = 1613 and ν(C–O) = 1000 cm^{-1}.

than A. Although **18** is stable at room temperature, the reductive elimination of dihydrogen took place slowly on heating at 80 °C in pyridine (Scheme III). The product obtained was **8b** which was also isolated from the wgs reaction catalyzed by **1** in pyridine.

The trans configuration of **6b** was confirmed by the virtual coupling observed for the methyl proton signal of P(*i*-Pr)$_3$ ligands (Table VI). The values of ν(CO) found for **7b** (1978 cm^{-1}) and **8b** (1983 cm^{-1}) are very close to that of **6b** (1985 cm^{-1}), which suggests a trans configuration of two phosphines in **7b** and **8b**.

A brisk dihydrogen evolution from **14b** took place immediately on addition of *t*-BuNC (5 mol/mol of **14b**) at room temperature in THF with concomitant formation of {*trans*-Rh(*t*-BuNC)$_2$[P(*i*-Pr)$_3$]$_2$}BPh$_4$ (**19**). Its trans configuration is readily deduced from the spectral data (Table VI). In view of the stability of [RhH$_2$(CO)(PEt$_3$)$_3$]$^+$ toward reductive elimination, it would be reasonable to assume that a facile dihydrogen evolution from **14b** and **15b** observed on treating with CO and *t*-BuNC proceeds through an intermediate A (L′ = pyridine) where two dihydrides and CO (or *t*-BuNC) are coplanar. This view receives support from the fact that **15b**, which readily liberates H$_2$ on treating with CO, will not form an intermediate B (L = P(c-C$_6$H$_{11}$)$_3$, L′ = py) where two bulky phosphines are forced to be cis.

Facile reductive elimination of dihydrogen from **14b** and **15b** on replacement of the electron-donating ligand (pyridine) with an electron-withdrawing one deserves comment. With the assumption that the Rh–H bond is essentially ionic,[26] the effect of electron-withdrawing ligands can be understood in terms of electronic charge transfer from hydride to metal, making the Rh–H bond less ionic and facilitating the reductive elimination of H$_2$. This effect on dimethylnickel was studied by ab initio MO-SCF-CI calculation.[27] Such a charge transfer should be more effective for the intermediate A than B. Dihydrogen evolution from stable *cis*-dihydride PtH$_2$[(*t*-Bu)$_2$P(CH$_2$)$_n$P(*t*-Bu)$_2$] (n = 2, 3) is also effected by olefins and CO.[28]

Reactions of the Rhodium(I) Hydrides with CO (Step 3). One possible route to the active species Rh(OH)(CO)L$_2$, an addition reaction of water to RhHL$_n$ followed by the substitution reaction of the adduct with CO, was described above. We consider here an alternative route: the rhodium(I) hydrides react first with CO (step 3) and subsequently with water (step 4).

A reaction of RhH[P(*i*-Pr)$_3$]$_3$ (**2**) with an excess of CO (1 atm) was examined in anhydrous pentane at room temperature. Diamagnetic orange-yellow crystals of the formula [Rh(CO)$_3$P(*i*-Pr)$_3$]$_n$ (**20**) were obtained in a high yield (80%) instead of the expected hydrido carbonyl species RhH(CO)$_n$L$_m$. At least the presence of RhH(CO)L$_2$ or RhH(CO)$_2$L$_2$ was not detected.

The IR spectrum of **20** shows the presence of terminal CO (1950 cm^{-1} (b)) and the absence of bridging CO bands. Apart from this band, no absorption was seen in the Rh–H stretching region (1900–2100 cm^{-1}). Consistently, no hydride ^{1}H NMR signal was detected in the high field region (δ 0 to −30). Since the diamagnetism precludes the monomeric form, the absence of bridging CO group in **20** invokes a direct metal–metal bonding. The PPh$_3$ analogue [Rh(CO)$_3$PPh$_3$]$_2$ has a carbonyl-bridging structure and exhibits both terminal and bridging CO bands.[29] The structure of **20** deserves scrutiny. Unfortunately, however, **20** is stable only under CO atmosphere and decomposes even under N$_2$ and even in solid state. Hence the molecular weight measurements could not be made. Tentatively we assign a dimeric structure for **20**, since formation of a polymeric form (cluster) carrying four ligands but no bridging CO is unlikely.

When freshly prepared **20** was dissolved in anhydrous pentane under a nitrogen atmosphere followed by concentration, a red crystalline compound (18%) was obtained. This was identified as Rh$_2$(CO)$_3$[P(*i*-Pr)$_3$]$_3$ (**21**) on the basis of elemental analysis and spectral data (Table VI). When 1 mol or more of free P(*i*-Pr)$_3$ was added to the solution of **20** under N$_2$, the yield of **21** was much improved (60%). The IR spectrum shows three ν(CO) bands at 1732, 1769, and 1957 cm^{-1}, and the NMR spectrum shows CH$_3$ proton signals of P(*i*-Pr)$_3$ as multiplet at δ ~1.0. A possible structure of **21** is believed to be the one shown below, containing two bridging and one terminal CO ligands (see Scheme IV).

The reaction of rhodium–hydrido compounds of bulky phosphines such as RhH[P(*t*-Bu)$_3$]$_2$ (**5**), *trans*-RhH(N$_2$)[PPh(*t*-Bu)$_2$]$_2$ (**4**), or Rh$_2$H$_2$(μ-N$_2$)[P(c-C$_6$H$_{11}$)$_3$]$_4$ (**3**) with CO in an anhydrous

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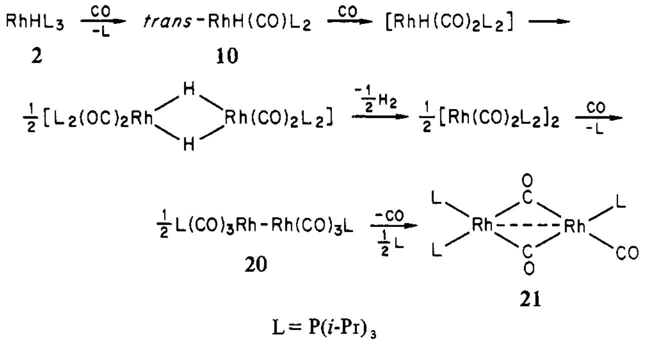
(26) Guse, M. P.; Blint, R. J.; Kunz, A. B. *Int. J. Quantum Chem.* **1977**, *XI*, 725–732.

(27) Åkermark, B.; Johansen, H.; Roos, B.; Wahlgren, U. *J. Am. Chem. Soc.* **1979**, *101*, 5876–5883.

(28) Yoshida, T.; Yamagata, Y.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.

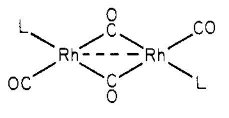
(29) Yagupsky, M.; Brown, C. K.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 937–941.

Scheme IV

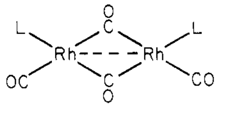


medium also results in a corresponding binuclear rhodium(0)–carbonyl compound as a yellow solid. These were not well characterized due to their extreme instability even under N_2. The chemical behavior strongly suggests that the compounds are analogous to **20**. On replacement with N_2 of CO atmosphere in a flask containing a solution of the yellow solids, binuclear rhodium(0)–carbonyl compounds $Rh_2(CO)_4L_2$ (**22**, L = P(*t*-Bu)$_3$; **23**, L = PPh(*t*-Bu)$_2$; **24**, L = P(c-C_6H_{11})$_3$) were obtained as dark red crystals. The molecular weight (687) of **22** determined cryoscopically in benzene agrees well with the required value (722). Note the different compositions of the binuclear carbonyl rhodium(0) compounds depending on the bulkiness of the phosphine ligand. Also note that **22** is the species isolated from the wgs reaction catalyzed with **5**.

The IR spectra of $Rh_2(CO)_4L_2$ indicate the presence of both terminal and bridging CO (Table VI). The observation of a single bridging ν(CO) for **22**, **23**, and **24** is consistent with the trans isomer (C). The complete absence of the geometrical isomer (D) in solution was indicated for **22** and **23** by the single *tert*-butyl ^{1}H NMR signal (Table VI). The formation of $Rh_2(CO)_2L_4$ and $Rh_2(CO)_4L_4$ was not observed, both are known for L = PPh_3.[29,30] The preferential formation of $Rh_2(CO)_3L_3$ (L = P(*i*-Pr)$_3$) and $Rh_2(CO)_4L_2$ (L = P(*t*-Bu)$_3$, PPh(*t*-Bu)$_2$, P(c-C_6H_{11})$_3$) rather than $Rh_2(CO)_nL_4$ (*n* = 2 or 4) is apparently due to the steric bulk and electronic properties of the phosphines employed.



C



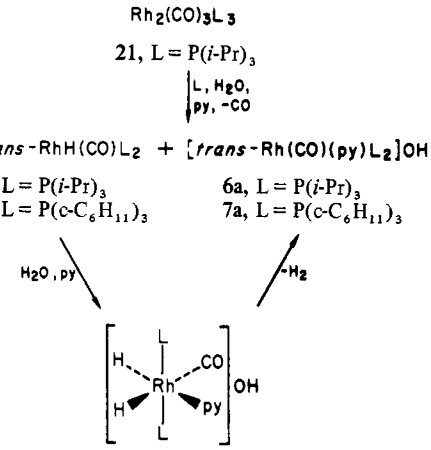
D

The hydrido carbonyl compound was found to be a species primarily responsible for the formation of $Rh_2(CO)_nL_{6-n}$ (*n* = 3, L = P(*i*-Pr)$_3$; *n* = 4, L = P(*t*-Bu)$_3$, PPh(*t*-Bu)$_2$, P(c-C_6H_{11})$_3$). Thus, on introduction of CO (1 atm) into a pentane solution of separately prepared *trans*-RhH(CO)[P(*i*-Pr)$_3$]$_2$ (**10**) at room temperature immediately precipitated **20**, which again gave **21** (60%) by replacement of the CO atmosphere with N_2. Since **2** with CO also produces **20**, we conclude that $RhH(CO)L_2$ is involved in the formation of **20**, which subsequently transforms into $Rh_2(CO)_3$[P(*i*-Pr)$_3$]$_3$ (**21**).

The reaction of $RhH(CO)(PPh_3)_3$ with CO was shown to give $RhH(CO)_2(PPh_3)_2$ which readily loses H_2, giving the CO-bridged dimer $[Rh(CO)_2(PPh_3)_2]_2$.[30] Although the corresponding RhH-$(CO)_2L_2$ was not detected in the reaction of $RhH(CO)L_2$ (L = P(*i*-Pr)$_3$) with CO, it is most likely to be involved as an incipient species leading to **21**. A plausible route to **21** is given is Scheme IV.

Reaction of $RhH(PPh_3)_4$ with a stoichiometric amount of CO is known to give $RhH(CO)(PPh_3)_3$.[31] *trans*-RhH(CO)[P(*i*-Pr)$_3$]$_2$ (**10**) may be prepared similarly. More conveniently, however, **10** is prepared by treating **2** with alcohols. Thus, treating **2** with CH_3OH at room temperature gave **10** in 50% yield, together with the binuclear carbonyl **21**. **21** is presumably derived via **10** through further oxidative addition of CH_3OH. The steric bulk of P(*i*-Pr)$_3$ again seems to prevent the formation of the pentacoordinate species RhH(CO)[P(*i*-Pr)$_3$]$_3$. In contrast to $RhH(CO)(PPh_3)_3$[29] which decomposes in benzene or in vacuo to give $[Rh(CO)(PPh_3)_2]_2$ with concomitant evolution of H_2, **10** is extremely stable under N_2 atmosphere and shows no tendency to form the binuclear carbonyl compounds. Therefore it is apparent that **10** is thermodynamically stable but kinetically very active toward CO and other electrophiles like CH_3OH. The analogous compound *trans*-RhH(CO)[P(c-C_6H_{11})$_3$]$_2$ (**9**) was also obtained by treating **3** with CH_3OH. The trans configuration of **9** and **10** was deduced from their ^{1}H NMR spectra; the hydrido signal appears as double triplets due to the couplings with two equivalent phosphorus atoms and a rhodium atom (Table VI).

Scheme V



Reaction of Rhodium Carbonyl with H_2O (Step 4). From the results given in the preceding section, we consider here two types of rhodium–carbonyl compounds $RhH(CO)L_2$ and $Rh_2(CO)_nL_{6-n}$ (*n* = 3, 4) as viable intermediates for the subsequent reactions with water.

The hydrido carbonyl compound **10** reacts with H_2O in pyridine at room temperature producing {*trans*-Rh(CO)(py)[P(*i*-Pr)$_3$]$_2$}OH (**6a**) which can be isolated as the BPh_4^- salt (**6b**) in 53% yield. We could detect an evolution of H_2 (70%). The formation of **6a** is readily understood as being derived through oxidative addition of H_2O to **10** to give an intermediate dihydrido carbonyl compound {RhH_2(CO)(S)[P(*i*-Pr)$_3$]$_2$}OH followed by reductive elimination of H_2. We have already demonstrated a facile H_2 evolution from {RhH_2(CO)(py)[P(*i*-Pr)$_3$]$_2$}$^+$ which is formed on introduction of CO into a solution of {$RhH_2(py)_2$[P(*i*-Pr)$_3$]$_2$}$^+$ (step 2). The oxidative addition of H_2O to the P(c-C_6H_{11})$_3$ analogue **9** also took place under a similar conditions to give {Rh(CO)(py)[P(c-C_6H_{11})$_3$]$_2$}OH (**7a**) which was again isolated as BPh_4 salt (**7b**).

The binuclear rhodium(0)–carbonyl compound **21** was found to be capable of reacting with H_2O in pyridine to give 2 mol of Rh(I) compounds. Thus, a reaction of **21** with H_2O at room temperature in the presence of excess of free P(*i*-Pr)$_3$ followed by the addition of $NaBPh_4$ gave **6b** as a sole isolatable product (64%). Evolution of H_2 (50%) was detected by the VPC analysis of the gas phase in the reaction flask. The reaction probably proceeds through a polar addition of H_2O to the Rh–Rh bond in **21**, yielding simultaneously the hydroxo compound **6a** and hydrido complex **10** (Scheme V). As described earlier in this section, the latter compound readily reacts with water in pyridine to give **6a**, via the dihydrido species $[RhH_2(CO)(S)L_2]OH$. The oxidative addition of water to rhodium(0)–carbonyl compounds resulting in the (hydrido)- and hydroxocarbonylrhodium(I) species is rather remarkable in view of the presence of more than one carbonyl ligand per Rh atom. The electron-donating trialkylphosphine appears to play an important role in keeping the metal center electron rich. This electronic effect should have been enhanced by additional free P(*i*-Pr)$_3$, as manifested in the increased catalytic activity of **21** by adding free phosphine (Table III). Additionally,

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[30] Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660–2665.

[31] Dewhirst, K. C.; Keim, W.; Reilly, C. A. *Inorg. Chem.* **1968**, *7*, 546–551.

the basic solvent pyridine could be an assisting factor, a view consistent with the facile oxidative addition of H_2O in this solvent. The same solvent effect was observed for the catalytic activity (Table II).

Reaction of *trans*-$\mathbf{Rh(OH)(CO)L_2}$ with CO (Steps 5 and 6). So far we have discussed the possible routes to the two viable intermediates $RhH(CO)L_2$ and $Rh(OH)(CO)L_2$ or $[Rh(CO)(S)L_2]OH$, which are considered to be the catalytic chain carriers. We discuss here the most important component reactions of the catalytic cycle: nucleophilic attack of OH^- on the metal carbonyl to give a M–COOH species.[6,8] Reaction of $\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}^+$ (**6b**) with OH^- was attempted in THF at room temperature. The expected hydroxycarbonyl compound $Rh(CO_2H)[P(i\text{-}Pr)_3]_2$ was not detected by IR spectroscopy of the concentrated reaction mixture, instead *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (**11**) was isolated in 70% yield. A similar reaction of **6b** with a stronger nucleophile, OCH_3^-, gave *trans*-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$ (**13**), which is extremely susceptible to hydrolysis. With a trace amount of water, **13** gives **11**, a result consistent with the known facile hydrolysis of the soft metal–OR bond.[32] The results, however, are in sharp contrast to the isoelectronic Pt(II) compound $\{trans\text{-}PtH(CO)[P(i\text{-}Pr)_3]_2\}^+$ which reacts with OR^- to give a fairly stable hydroxycarbonyl or methoxycarbonyl compound *trans*-$PtH(CO_2R)[P(i\text{-}Pr)_3]_2$ (R = H, CH_3).[6] The failure to obtain $Rh(CO_2R)[P(i\text{-}Pr)_3]_2$ (R = H, CH_3) in reaction of **6b** with OR^-

$$\underset{\mathbf{6b}}{[trans\text{-Rh(CO)(py)L}_2]\text{BPh}_4} \xrightarrow{\text{OR}^-} \underset{\begin{array}{l}\mathbf{11},\ \text{R = H, L = P}(i\text{-Pr})_3\\ \mathbf{13},\ \text{R = CH}_3,\ \text{L = P}(i\text{-Pr})_3\end{array}}{trans\text{-Rh(OR)(CO)L}_2}$$

may be ascribed to the low electrophilicity of the carbon atom of the CO ligand: compare ν(CO) or $\{trans\text{-}Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}^+$ (1985) cm^{-1}) with that of $\{trans\text{-}PtH(CO)[P(i\text{-}Pr)_3]_2\}^+$ (2058 cm^{-1}).[6] Alternatively an unfavorable equilibrium, $[Rh(CO)(py)L_2]^+ + OR^- \rightleftharpoons Rh(CO_2R)L_2 + py$, may be invoked for the failure.

The preparation of **11** from $RhCl(CO)[P(i\text{-}Pr)_3]_2$ and *n*-PrOK has been reported without spectral data except ν(CO).[33] We record the ^1H NMR spectrum of **11**; the OH resonance (δ −0.96 (t, J_{H-P} = 5.3 Hz)) and the CH_3 proton signal of $P(i\text{-}Pr)_3$ (δ 1.27 (q, $^3J_{H-P} + {}^5J_{H-P}$ = 13.5 Hz)). Evidently **11** has a trans configuration. The trans configuration of the methoxo compound **13** is also readily deduced on the basis of the ^1H NMR data (Table VI), which involves the CH_3O proton singlet signal (δ 3.97). The IR spectra of **11** and **13** show ν(OH) and ν(C—O) at 3644 and 1088 cm^{-1}, respectively. An addition of $NaBPh_4$ to a pyridine solution of **11** at room temperature gave **6b** quantitatively, suggesting that **11** is in equilibrium with a solvated ionic complex $\{trans\text{-}Rh(CO)(S)[P(i\text{-}Pr)_3]_2\}OH$ (**6a**, S = pyridine). The detection of **11** by the IR spectrum of the concentrate from the wgs reaction catalyzed by $RhH[P(i\text{-}Pr)_3]_3$ (**2**) in acetone indicates that the equilibrium lies toward left (eq 11) in a weakly coordinating solvent like acetone.

$$\underset{\mathbf{11}}{trans\text{-Rh(OH)(CO)[P}(i\text{-Pr})_3]_2} \overset{\text{S}}{\rightleftharpoons} \underset{\mathbf{6a}}{\{trans\text{-Rh(CO)(S)[P}(i\text{-Pr})_3]_2\}\text{OH}} \quad (11)$$

Evidently, in the monocarbonyl compounds **11**, **6a**, and **13**, the nucleophilic attack of OR^- (R = H, CH_3) on the CO ligand to give stable $Rh(CO_2R)[P(i\text{-}Pr)_3]_2$ was not observed. With additional CO ligands, the electrophilic properties of CO ligands should be enhanced. Thus, *trans*-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$ (**13**)

$$\underset{13}{trans\text{-Rh(OCH}_3\text{)(CO)[P}(i\text{-Pr})_3]_2} \xrightarrow{\text{CO}} \underset{\mathbf{25}}{trans\text{-Rh(CO}_2\text{CH}_3\text{)(CO)[P}(i\text{-Pr})_3]_2}$$

was treated with CO in hexane under ambient conditions. A methoxycarbonyl compound *trans*-$Rh(CO_2CH_3)(CO)[P(i\text{-}Pr)_3]_2$ (**25**) was obtained as yellow crystals (75%) together with a small amount of binuclear rhodium(0)–carbonyl compound **21**. The compound **21** must have been derived from the reaction of CO with **11** which is incipiently formed from hydrolysis of **13** with a trace of H_2O present in the reaction system, since transformation of **11** into **21** was verified as will be described shortly (Scheme VI).

Scheme VI

$$\underset{\mathbf{11, 12}}{trans\text{-Rh(OH)(CO)L}_2} \xrightarrow{\text{CO}} [\text{Rh(CO)}_2\text{L}_2]\text{OH} \longrightarrow$$

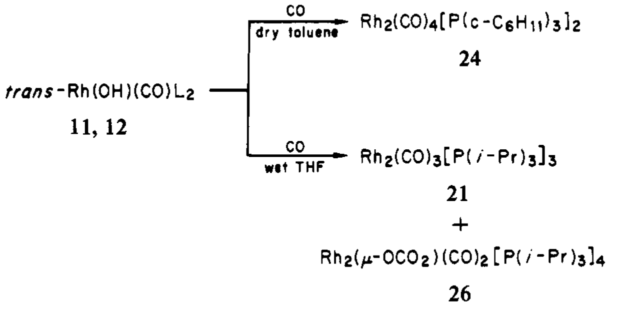
$$\text{Rh(CO}_2\text{H)(CO)L}_2 \xrightarrow{-\text{CO}_2} \underset{\mathbf{10, 9}}{trans\text{-RhH(CO)L}_2} \xrightarrow[-\frac{1}{2}\text{H}_2]{\text{CO}}$$

$$\tfrac{1}{2}\text{Rh}_2\text{(CO)}_n\text{L}_{6-n}$$

21, $n = 3$, L = $P(i\text{-}Pr)_3$

24, $n = 4$, L = $P(c\text{-}C_6H_{11})_3$

The IR spectrum of **25** shows ν(C═O) and ν(C—O) bands at 1613 and 1000 cm^{-1}, respectively, which are comparable with the corresponding values of *trans*-$PtH(CO_2CH_3)[P(i\text{-}Pr)_3]_2$,[6] $Pt(CO_2CH_3)(C_6H_{11})$(diphos),[34] and $NiCl(CO_2CH_3)(PPh_3)_2$.[35] The ^1H NMR spectrum is consistent with *trans* configuration (Table VI).



Reaction of *trans*-$Rh(OH)(CO)[P(c\text{-}C_6H_{11})_3]_2$ (**12**) with CO in dry toluene under ambient conditions did not give an expected hydroxycarbonyl complex $Rh(CO_2H)(CO)[P(c\text{-}C_6H_{11})_3]_2$, but $Rh_2(CO)_4[P(c\text{-}C_6H_{11})_3]_2$ (**24**) (30%) was obtained. A similar reaction of $Rh(OH)(CO)(PPh_3)_2$ with CO in benzene has been reported; $Rh_2(CO)_4(PPh_3)_2\cdot 2C_6H_6$ was formed with concomitant evolution of CO_2.[33] Then when we attempted the reaction with CO in the presence of H_2O, a somewhat different reaction took place. Thus, a reaction of *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (**11**) with CO in wet THF under ambient conditions gave a binuclear μ-carbonato compound $Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (**26**)[17] together with the expected $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (**21**).

A postulate that a nucleophilic attack of OH^- on the carbonyl ligand occurs in the dicarbonyl compound $[Rh(CO)_2L_2]OH$ or $[Rh(OH)(CO)_2L_2]$ leading to $Rh(CO_2H)(CO)L_2$ would account for the formation of the rhodium(0)–carbonyl compounds **21** and **24** (Scheme VI). (Hydroxycarbonyl)platinum(II) compounds *trans*-$PtH(CO_2H)[P(i\text{-}Pr)_3]_2$[6] and $Pt(CO_2H)(R)$(diphos) (R = CH_3, C_6H_9)[36] have been prepared by treating $\{trans\text{-}PtH(CO)[P(i\text{-}Pr)_3]_2\}^+$ with OH^- and by treating Pt(OH)(R)(diphos) with CO, respectively. Although we failed to detect $Rh–CO_2H$ species probably due to the strong propensity of $Rh(CO_2H)(CO)L_2$ toward β-hydrogen elimination, its involvement as a transient intermediate receives support from isolation of a closely related methoxycarbonyl compound **25**. A possible route to **26** will be described in the next section.

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[32] Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993–999.

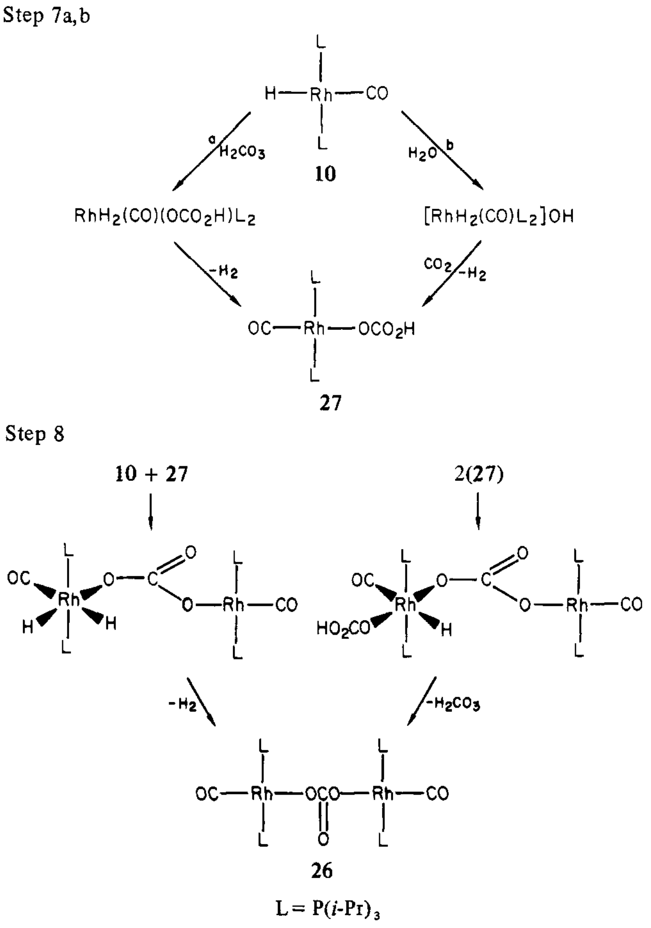
[33] Gregorio, G.; Pregaglia, G.; Ugo, G. *Inorg. Chim. Acta* **1969**, *3*, 89–93.

[34] Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750–1759.

[35] Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180–3188.

[36] Bennett, M. A.; Appleton, C. A. *J. Organomet. Chem.* **1973**, *55*, C88–C90.

Scheme VII



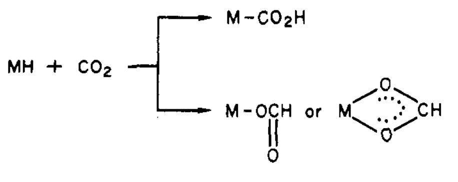
So far we have considered a direct reaction of $Rh(OH)(CO)L_2$ with CO. Alternatively, $Rh(OH)(CO)L_2$ would react first with water followed by a subsequent reaction with CO, leading to *trans*-$RhH(CO)L_2$.

$$trans\text{-}Rh(OH)(CO)L_2 \xrightarrow{H_2O} RhH(OH)_2(CO)L_2 \xrightarrow{S} [RhH(CO)(S)_2L_2](OH)_2 \xrightarrow{-S} RhH(OH)(CO_2H)L_2 \xrightarrow[-H_2O,\,-CO_2]{CO} trans\text{-}RhH(CO)L_2$$

An addition of an excess of BPh_4^- to an aqueous pyridine or THF solution of **11** obtained only **6b** but not a trace amount of a species such as $[RhH(CO)(S)_2L_2](BPh_4)_2$. Hence it appears to be reasonable to exclude this route involving an incipient oxidative addition of water. This contrasts with the facile water addition to *trans*-$RhH(CO)L_2$.

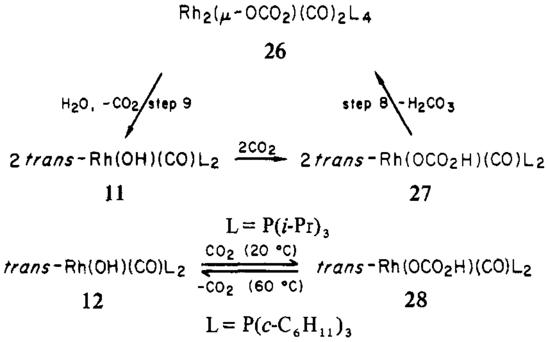
Reaction of Carbon Dioxide (Steps 7–9). In order to describe the full details of the wgs reaction, we ought to know the reaction patterns of CO_2 or H_2CO_3 with various rhodium species involved in the catalytic cycle. In this section let us focus on the CO_2 reactions with such important catalytic chain carriers as *trans*-$RhH(CO)L_2$ (**9**, **10**) and *trans*-$Rh(OH)(CO)L_2$ (**11**, **12**).

The CO_2 reaction with *trans*-$RhH(CO)L_2$ (**10**, L = $P(i\text{-}Pr)_3$) is of considerable interest as two types of the reaction are possible.[37]



Treating **10** with CO_2 in wet THF (10% H_2O) under ambient conditions obtained the μ-carbonato compound **26** as the major product (60% yield) together with a smaller amount $Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$ (**31**). The formation of formato compound **31** is a "normal" CO_2 insertion into M–H bond, which appears to be by far the most common reaction scheme. The formation of this formato compound was completely suppressed by using a large excess of water; **26** could be obtained as a sole product (80% yield).

Scheme VIII



A couple of routes from **10** to **26** are conceivable. We know already that **26** is readily formed from the carbonyl bicarbonato compound $Rh(OCO_2H)(CO)[P(i\text{-}Pr)_3]_2$ (**27**) at room temperature.[17] Compounds **27** is accessible from **10** through the oxidative addition of H_2CO_3 leading to a dihydrido carbonyl bicarbonato compound $RhH_2(OCO_2H)(CO)L_2$, followed by H_2 elimination (step 7a, Scheme VII). Alternatively **27** may be formed by an oxidative addition of water to **10** to give an unstable dihydride carbonyl compound $[RhH_2(CO)L_2]OH$ (unisolatable), which releases H_2 upon reaction with CO_2 (step 7b).

Once **27** is formed, then an oxidative addition of the bicarbonato OH bond of **27** to **10** with subsequent reductive elimination of H_2 would lead to the binuclear compound **26** (step 8). An intermolecular oxidative addition of **27** may be the alternative possibility. The facile transformation of **27** without **10** into **26** has been confirmed.[17]

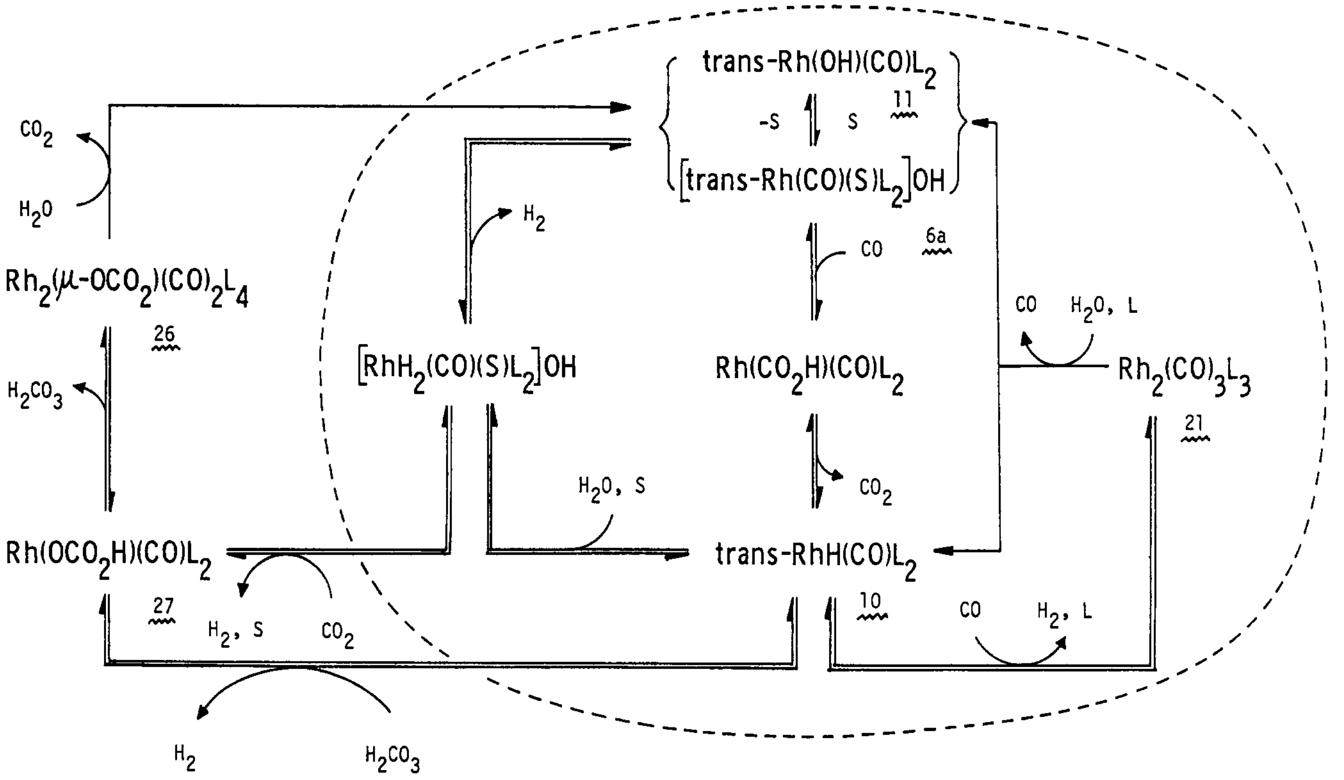
Interestingly, **26** can be hydrolyzed in aqueous pyridine or acetone regenerating **11** (step 9, Scheme VIII). Product **11** was isolated as a solvated cationic compound, $\{trans\text{-}Rh(CO)(S)[P(i\text{-}Pr)_3]_2\}BPh_4$ (**6b**; **6c**, S = acetone). A conspicuous solvent effect was observed. Thus, in pyridine the hydrolysis occurs completely at room temperature, while prolonged heating (80 °C, 5 h) is required in acetone. This hydrolysis is a rather remarkable feature consistent with the observed long life of the present catalyst system. Compounds **11**, **27**, and **26** form a cycle, implying that **11** can act as a catalyst for the hydration of CO_2. It is worth noting that a bulky phosphine ligand prevents the transformation of *trans*-$Rh(OCO_2H)(CO)L_2$ (**28**, L = $P(c\text{-}C_6H_{11})_3$) into $Rh_2(\mu\text{-}OCO_2)(CO)_2L_4$. In this case reversible decarboxylation takes place to give **12**.[17] Namely, hydroxo complexes of type **12** carrying bulky phosphine ligands can act as a CO_2 carrier.

We have reported that the CO_2 reaction of $RhHL_n$ in a wet solvent produces a *cis*-dihydrido bicarbonato compound, $RhH_2(O_2COH)L_2$ (**29**, L = $P(i\text{-}Pr)_3$; **30**, L = $P(c\text{-}C_6H_{11})_3$), and that **29** and **30** are capable of reducing CO_2 to give **27** and **28**, respectively.[17] Since the wgs reaction mixture contains CO and H_2O, the possibility of the existence of $RhHL_n$ in the reaction system is highly unlikely (steps 1–3). Therefore, this route can be neglected for the formation of such a species as **27** or **26**. However, it is to be noted that **29** and **30** serve as catalyst precursors for the wgs reaction (Table III).

Catalytic Cycle. Thus far, a series of component reactions have been described. Having elucidated these stoichiometric reactions, a discussion on the catalytic cycle is in order. Our main concern here is to draw a picture of the whole catalytic cycle. In the absence of kinetic studies we do not intend to discuss the relative kinetic importance of various component reactions.

We focus on the catalysis effected by the representative precursor $RhH[P(i\text{-}Pr)_3]_3$ (**2**). It is highly unlikely that this type of precursor carries the catalytic cycle, as it will readily be transformed into *trans*-$Rh(OH)(CO)L_2$ (**11**) or its solvated form [*trans*-$Rh(CO)(S)L_2$]OH (**6a**) through step 1 → step 2 or step

Scheme IX



L = P(*i*-Pr)$_3$

3 → step 4. Both pathways were found to be low-energy processes. As the oxidative addition of water is much facilitated in pyridine, the step 1 → step 2 may be preferred to the step 3 → step 4 in this solvent. In acetone or nonpolar solvents, the situation could be reversed.

trans-RhH(CO)L$_2$ (**10**) is another important carrier as it is formed from *trans*-Rh(OH)(CO)L$_2$ (**11**) or [Rh(CO)(S)L$_2$]OH (**6a**) by reacting with CO (see steps 5 and 6). We have shown the plausible pathway from **11** to **10** (Scheme VI) and also the route from **10** to **6a** or **11** (see step 4). In addition, a reaction of **10** with CO leading to the rhodium(0)–carbonyl compound **21** (Scheme IV) and subsequent reaction of **21** with water resulting in **6a** and **10** (Scheme V) are also an important pathway starting from **10** to give **6a**. When these elemental reactions are combined, the catalytic cycles shown in Scheme IX (the part encircled with dotted line) can be constructed. We believe that these cycles would describe the early stage of the present catalysis.

As the wgs reaction proceeds, reaction sequences involving CO$_2$ would partake. The reactions with CO$_2$ or H$_2$CO$_3$ with the key intermediate **6a** and the transient species [Rh(CO)$_2$L$_2$]OH and Rh(CO$_2$H)(CO)L$_2$ are not associated with the production of H$_2$. On the other hand, **10** and its water adduct [RhH$_2$(CO)L$_2$]OH react with H$_2$CO$_3$ or CO$_2$ producing H$_2$ (a and b of step 7). We regard, therefore, the following reactions to be important component reactions: (1) formation of the bicarbonato compound *trans*-Rh(OCO$_2$H)(CO)[P(*i*-Pr)$_3$]$_2$ (**27**) from **10** (step 7a) or [RhH$_2$(CO)L$_2$]OH (step 7b), (2) formation of the μ-carbonato carbonyl compound **26** from **27** (step 8), and the hydrolysis of **26** to regenerate **6a** or **11** (step 9). These component reactions involving CO$_2$ or H$_2$CO$_3$ form another cycle. The whole catalytic cycles can then be depicted as shown in Scheme IX.

Since H$_2$CO$_3$ is an acid stronger than H$_2$O, step 7a would occur more readily than step 7b (Scheme VII) or 4 (Scheme V). Therefore, under a high concentration of CO$_2$, the reaction sequence step 5 → step 6 → step 7a → step 8 → step 9 would become the main avenue of catalysis. It may be worth noting that the hydrolysis of **26** is an irreversible reaction since **11** with CO$_2$ in THF does not produce **26** but **27** (Scheme VIII). This reaction of **11** with CO$_2$ is not shown in Scheme IX for clarity.

The fact that intermediates *trans*-Rh(OH)(CO)L$_2$ (**11**), *trans*-RhH(CO)L$_2$ (**9**), Rh$_2$(μ-OCO$_2$)(CO)$_2$L$_4$ (**26**), and RhH$_2$(O$_2$COH)L$_2$ (a precursor of Rh(OCO$_2$H)(CO)L$_2$ (**27**)[17]) show comparable catalytic activities (*L* = P(*i*-Pr)$_3$, Table III) for the wgs reaction strongly supports the proposed cycles (Scheme IX). Interestingly, the PPh$_3$ analogue *trans*-Rh(OH)(CO)(PPh$_3$)$_2$[33,38] shows a lower activity, while *trans*-RhCl(CO)(PPh$_3$)$_2$ is totally inactive. Another piece of support for the proposed mechanism is the formation of Rh$_2$(μ-OCO$_2$)(CO)$_2$[P(*i*-Pr)$_3$]$_4$ (**26**) from **2**, H$_2$O, and CO. Thus a prolonged stirring of an aqueous THF solution of **2** under CO (1 atm) at room temperature gave **26** (20% yield).

The difference in catalysis between two isoelectronic systems RhHL$_3$ and PtL$_3$[6] for the wgs reaction deserves comment. The most distinct difference between two systems is the solvent effect exerted on the catalytic activity. Thus, the catalytic activity of Pt[P(*i*-Pr)$_3$]$_3$ was approximately 8 times higher in acetone than in pyridine, while the situation is reversed for RhHL$_n$ (Table II). The observed solvent effect for Pt[P(*i*-Pr)$_3$]$_3$ has been shown to be associated with the CO activation process. The formation of {*trans*-PtH(CO)[P(*i*-Pr)$_3$]$_2$}OH through the reaction of {*trans*-PtH(S)[P(*i*-Pr)$_3$]$_2$}OH (S = solvent) with CO in strongly coordinating pyridine is not so facile as in acetone. Similarly replacement of the coordinated pyridine with CO in {*trans*-Rh(CO)(py)[P(*i*-Pr)$_3$]$_2$}$^+$ (**6b**) does not occur at least under ambient conditions. Since an equilibrium exists between {*trans*-Rh(CO)(S)[P(*i*-Pr)$_3$]$_2$}OH and *trans*-Rh(OH)(CO)[P(*i*-Pr)$_3$]$_2$ (**11**), a direct reaction of the latter with CO may constitute an alternative route to {Rh(CO)$_2$[P(*i*-Pr)$_3$]$_2$}OH, a process requiring no solvent participation. The observed solvent effect described above suggests the reaction of the neutral species **11** with CO to be a preferred pathway (Scheme VI). The hydrolysis of Rh$_2$(μ-OCO$_2$)(CO)$_2$[P(*i*-Pr)$_3$]$_4$ (**26**) producing {*trans*-RhCO)(S)[P(*i*-Pr)$_3$]$_2$}OH showed a similar solvent effect as observed for the catalysis by RhH[P(*i*-Pr)$_3$]$_3$ (**2**). The hydrolysis of **26** in acetone,

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(37) (a) Eisenberg, R.; Hendrikson, D. E. *Adv. Catal.* **1979**, *28*, 79–172. (b) Voplin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313–386.

(38) Vaska, L.; Peno, J., Jr. *J. Chem. Soc. D* **1971**, 418–419.

therefore, is considered to be one of the high activation energy-requiring processes.

Another distinct difference is the relative catalytic activities observed for the metal–carbonyl clusters $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (**21**) and $Pt_3(CO)_3[P(i\text{-}Pr)_3]_4$ both of which are produced from direct reaction of $RhHL_3$ and PtL_3 with CO, respectively. In contrast to the relatively inactive $Pt_3(CO)_3[P(i\text{-}Pr)_3]_4$, the rhodium–carbonyl cluster (**21**) shows a considerable activity. When free $P(i\text{-}Pr)_3$ is added to **21**, the activity could be enhanced to as much as twice the original activity.

Concluding Remarks

Rhodium(I) hydrides, $RhHL_n$ (L = trialkylphosphine), have been shown to serve as catalyst precursors for the wgs reaction, without further additives. A remarkable feature is their capability of transferring two electrons to a water molecule, generating OH^- and coordinated H^-, realized in the formation of ionic complexes such as *cis*-$[RhH_2(py)_2L_2]OH$. The rhodium(I) hydrides can thus be regarded as *built-in base* catalysts, in sharp contrast to the metal–carbonyl or carbonyl cluster catalysts previously reported. It is noteworthy that in spite of the hydridic character of the hydride ligand of $RhHL_n$, the protolysis with water of the original Rh(I)–H bond does not occur.

Facile H_2 evolution from the water adduct *cis*-$[RhH_2(py)_2L_2]OH$ occurs only when treated with electron-withdrawing substrates such as CO or RNC. The reaction of the adduct with CO leads to one of the key intermediates, *trans*-$Rh(OH)(CO)L_2$, or its solvated form [*trans*-$Rh(CO)(S)L_2]OH$. Another key intermediate, *trans*-$RhH(CO)L_2$, with CO forms Rh(0) dimers $Rh_2(CO)_nL_{6-n}$. Remarkably the carbonyl dimers are nucleophilic enough to undergo oxidative addition of water regenerating *trans*-$RhH(CO)L_2$ together with [*trans*-$Rh(CO)(S)L_2]OH$. $RhH(CO)L_2$ is also capable of reducing water to give H_2, the product being [*trans*-$Rh(CO)(S)L_2]OH$. The oxidation of CO to CO_2 occurs in the reaction of *trans*-$Rh(OH)(CO)L_2$ with CO, regenerating *trans*-$RhH(CO)L_2$ through an intermediate of $Rh(CO_2H)(CO)L_2$. A catalytic cycle can be constructed with these elemental reactions.

We found an important role of CO_2 produced for the H_2 generation. The reaction of $RhH(CO)L_2$ with H_2CO_3 is presumably involved in one of the catalytic cycles as the reaction generates H_2 and a bicarbonato compound, $Rh(OCO_2H)(CO)L_2$. The latter subsequently transforms into a μ-carbonato dimer, $Rh_2(\mu\text{-}OCO_2)(CO)_2L_4$, which in turn can react with water, regenerating *trans*-$Rh(OH)(CO)L_2$ or its solvated form. These results support that *trans*-$Rh(OH)(CO)L_2$ and *trans*-$RhH(CO)L_2$ are the major catalytic chain carriers.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dinitrogen or argon. ^1H NMR spectra were recorded on JEOL JNM-4H-100 or JNM-C-60HL spectrometer and IR spectra recorded on a Hitachi Model 295 spectrometer. Literature methods were employed for preparations of $RhH(PEt_3)_n$ (n = 3, 4),[19] *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$,[39] $RhH[P(t\text{-}Bu)_3]_2$,[23] $RhH[P(i\text{-}Pr)_3]_3$,[23] $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$,[23] *trans*-$Rh(OH)(CO)L_2$ (L = $P(c\text{-}C_6H_{11})_3$,[17] PPh_3[33,38]), $Rh_2(\mu\text{-}O_2CO)(CO)_2[P(i\text{-}Pr)_3]_4$,[17] $RhH_2(O_2COH)L_2$ (L = $P(c\text{-}C_6H_{11})_3$, $P(i\text{-}Pr)_3$),[17] $Rh(OCO_2H)(CO)L_2$ (L = $P(i\text{-}Pr)_3$, $P(c\text{-}C_6H_{11})_3$), and $Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$.[17] Satisfactory elemental analyses for C, H, and N have been obtained for all new compounds described herein except {*trans*-$Rh(CO)(acetone)[P(i\text{-}Pr)_3]_2$}$BPh_4$ (**6c**) which was characterized by IR spectrum and by transformation into the pyridine analogue **6b**.

The wgs Reaction. Typically, to a 100-mL stainless-steel autoclave containing a solution of catalytic precursor (0.1 mmol) in pyridine or acetone (5.0 mL) was charged H_2O (2.0 mL) and CO (20 Kg/cm^2) successively. After being heated at the specified temperature (50–150 °C) for 18 h, the mixture was cooled to room temperature. The gas was introduced through a needle valve into a thick-rubber balloon in order to trap all the gaseous products. The H_2 content was quantitatively analyzed by VPC (activated charcoal, 1.8 m, 80 °C; carrier gas, Ar) by using N_2 as an internal calibrant. For the analysis of CO_2, the balloon was connected with a flask containing an aqueous $Ba(OH)_2$ solution. After the complete absorption (overnight), the excess of $Ba(OH)_2$ remained was back-titrated with an oxalic acid solution. Additionally, an excess of a $Ba(OH)_2$ solution was added to the liquid phase in the autoclave to determine the CO_2 content dissolved in the liquid. For the quantitative analysis of CO_2 produced, we have established a more convenient method. Thus, the following empirical correlation was found for the VPC area of CO unreacted and CO_2 produced (activated charcoal, 1.8 m, 90 °C; carrier gas, He).

CO_2 (mmol) = $82 \times [CO_2]/([CO_2] + [CO])$ where $[CO_2]$ and $[CO]$ are the corresponding area. This equation is only applicable for the wgs reaction carried out in a 100-mL autoclave containing 7.0 mL of aqueous pyridine under an initial CO pressure of 20 Kg/cm^2.

Isolation of Rhodium Compounds from the wgs Reaction. (I) *trans*-$[Rh(CO)(py)L_2]BPh_4$ (6b, L = $P(i\text{-}Pr)_3$; 7b, L = $P(c\text{-}C_6H_{11})_3$; 8b, L = PEt_3). A wgs reaction mixture carried out by using $RhH[P(i\text{-}Pr)_3]_3$ (0.058 g, 0.1 mmol) in pyridine (5.0 mL) and H_2O (2.0 mL) under CO (20 Kg/cm^2) at 100 °C was cooled to room temperature and degassed. To a yellow solution remained was added $NaBPh_4$ (0.050 g, 0.146 mmol), and the mixture was concentrated in vacuo to give crystals, which were washed with H_2O and recrystallized from toluene–THF to give {*trans*-$Rh(CO)(py)[P(i\text{-}Pr)_3]_2$}$BPh_4 \cdot 2C_6H_5CH_3$ (0.07 g, 70%). A similar treatment of the water gas shift reaction mixture effected by $RhH_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ and $RhH(PEt_3)_3$ in pyridine gave **7b** (50%) and **8b** (85% yield), respectively.

(II) *trans*-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$ (9). A pale yellow solution obtained from the wgs reaction mixture effected by $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ (0.135 g, 0.1 mmol) in acetone was concentrated in vacuo. The solid residue was recrystallized from hexane to give **9** as yellow crystals (0.08 g, 58%). The formation of **9** was confirmed by the hydrido NMR signal.

(III) *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (11). A pale yellow solution obtained after degassing of the wgs reaction mixture effected by $RhH[P(i\text{-}Pr)_3]_3$ under a similar condition as (I) but in acetone (5.0 mL) was concentrated in vacuo to dryness. The IR spectrum of oily solid residue showed the formation of **11** (ν(CO) 1925 and ν(OH) 3644 cm^{-1}).

(IV) $Rh_2(CO)_4[P(t\text{-}Bu)_3]_2$ (22). An orange-red solution obtained from the wgs reaction mixture effected by $RhH[P(t\text{-}Bu)_3]_2$ (0.100 g, 0.2 mmol) in acetone was concentrated, and the residue was recrystallized from toluene and hexane to give **22** as red crystals in 60% yield.

Oxidative Addition of Water to Rhodium(I)–Hydrido Compounds. (I) {$RhH_2(py)_2[P(i\text{-}Pr)_3]_2$}$BPh_4$ (14b). To a pyridine solution (5 mL) of $RhH[P(i\text{-}Pr)_3]_3$ (0.23 g, 0.4 mmol) was added H_2O (1 mL) and $NaBPh_4$ (0.17 g, 0.5 mmol) successively at room temperature. The colorless solution was concentrated in vacuo, and the residue was recrystallized from a mixture of toluene and THF to give **14b** as colorless crystals (0.2, g, 76%), mp 140 °C dec.

(II) {$RhH_2(py)_2[P(c\text{-}C_6H_{11})_3]_2$}$BPh_4$ (15b). A similar reaction of $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ (0.27 g, 0.2 mmol) with H_2O (5 mL) in the presence of $NaBPh_4$ (0.17 g, 0.5 mmol) in pyridine (50 mL) gave **15b** as yellow crystals (0.18 g, 40%), mp 170 °C dec.

(III) $[RhH_2(PEt_3)_4]BPh_4$ (17b). A solution of $RhH(PEt_3)_4$ (0.29 g, 0.5 mmol) in pyridine (10 mL) containing excess of free PEt_3 (0.72 g, 6 mmol) was treated with H_2O (2 mL) followed by the addition of $NaBPh_4$ (0.18 g, 0.53 mmol). The orange solution was concentrated in vacuo, and the residue was recrystallized from THF–MeOH containing free PEt_3 to give pale yellow crystals (0.21 g, 47%), mp 95 °C dec.

(IV) $[RhH_2(PEt_3)_3]BPh_4$ (16b). This compound was prepared by a similar method employed as above but in the absence of free PEt_3. Recrystallization from pyridine–MeOH gave $[RhH_2(PEt_3)_3]BPh_4 \cdot {}^1/_2C_5H_5N$ as orange crystals (60%), mp 115 °C dec. By contrast, recrystallization from THF–MeOH gave $[RhH_2(PEt_3)_3]BPh_4$ as pale yellow crystals (80%), mp 120 °C dec.

Alternatively $[RhH_2(PEt_3)_3]BPh_4 \cdot {}^1/_2C_5H_5N$ was obtained by recrystallization of $[RhH_2(PEt_3)_4]BPh_4$ from pyridine–MeOH in the absence of free PEt_3.

Reaction of the Water Adducts with CO, *t*-BuNC, and 2,2′-Bipyridine. (I) {$Rh(CO)(py)[P(i\text{-}Pr)_3]_2$}$BPh_4$ (6b). To a solution of {$RhH_2(py)_2[P(i\text{-}Pr)_3]_2$}$BPh_4$ (0.18 g, 0.2 mmol) in THF (2 mL) was introduced CO (1 atm) at room temperature. A vigorous H_2 gas evolution was observed. Addition of toluene (5 mL) to the mixture gave pale yellow crystals. Recrystallization from toluene–THF gave an analytically pure **6b** containing 2 mol of toluene as the crystallization solvent (0.16 g, 80%); mp 155 °C dec.

(II) {$RhH_2(bipy)[P(i\text{-}Pr)_3]_2$}$BPh_4$ (6c). A mixture of {$RhH_2(py)_2[P(i\text{-}Pr)_3]_2$}$BPh_4$ (0.225 g, 0.25 mmol) and 2,2′-bipyridine (0.117 g, 0.75 mmol) in THF (10 mL) was stirred at room temperature for 5 h. The bright yellow solution was concentrated in vacuo, and the residue was recrystallized from a mixture of THF and toluene to give {$RhH_2(bipy)[P(i\text{-}Pr)_3]_2$}$BPh_4 \cdot C_6H_5CH_3$ as yellow crystals quantitatively, mp 150 °C dec.

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(39) Hoffman, P. R.; Yoshida, T.; Okano, T.; Otsuka, S.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 2462–2466.

(III) $\{Rh(CO)(py)[P(c\text{-}C_6H_{11})_3]_2\}BPh_4$ (7b). This compound was prepared in a similar manner to I by treating $\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}BPh_4$ with CO. The concentrated mixture was recrystallized from THF–MeOH to give yellow crystals (65%), mp 198 °C dec.

(IV) $[RhH_2(CO)(PEt_3)_3]BPh_4$ (18). A solution of $[RhH_2(PEt_3)_3]BPh_4$ (0.15 g, 0.19 mmol) in THF (5 mL) was stirred under CO (1 atm) at room temperature for 10 h. The yellow solution was concentrated in vacuo to 2 mL, and MeOH was added to give **18** as pale yellow crystals (0.15 g, 98%), mp 85 °C dec.

(V) $[Rh(CO)(py)(PEt_3)_2]BPh_4$ (8b). A solution of $[RhH_2(CO)(PEt_3)_3]BPh_4$ (0.24 g, 0.3 mmol) in pyridine (10 mL) was heated at 80 °C for 30 h. The recrystallization from THF–MeOH of the concentrated residue gave yellow crystals (0.1 g, 75%), mp 104–108 °C dec.

(VI) $\{trans\text{-}Rh(t\text{-}BuNC)_2[P(i\text{-}Pr)_3]_2\}BPh_4$ (19). To a solution of $\{RhH_2(py)_2[P(i\text{-}Pr)_3]_2\}BPh_4$ (0.225 g, 0.25 mol) in THF (10 mL) was added *t*-BuNC (0.10 g, 1.25 mmol) at room temperature. Immediately, a vigorous H_2 evolution took place. Addition of MeOH (7 mL) to the concentrated solution gave bright yellow crystals quantitatively, mp 199–200 °C dec.

Reaction of Water Molecule with *trans*-$RhH(CO)L_2$ ($L = P(i\text{-}Pr)_3$, $P(c\text{-}C_6H_{11})_3$). (I) $\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4{\cdot}2C_6H_5CH_3$ (6b). To a solution of *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ (0.15 g, 0.33 mmol) in pyridine (10 mL) was added H_2O (1.5 mL) and $NaBPh_4$ (0.137 g, 0.4 mmol) successively at room temperature, and the mixture was stirred for 0.5 h. VPC analysis of the gaseous phase showed the formation of H_2 (70% yield). The yellow solution was concentrated in vacuo, and the residue was recrystallized from toluene–THF to give the titled compound (0.18 g, 53%) as pale yellow crystals. Recrystallization from THF–MeOH gave an analytically pure sample.

(II) $\{Rh(CO)(py)[P(c\text{-}C_6H_{11})_3]_2\}BPh_4$ (7b). A similar treatment of *trans*-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$ with H_2O followed by the addition of $NaBPh_4$ as above gave the titled compound (55%) as yellow crystals.

Reaction of Water Molecule with $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (Vide Infra). To a red solution of $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (0.04 g, 0.063 mmol) in pyridine (5 mL) containing $P(i\text{-}Pr)_3$ (0.08 g, 0.5 mmol) was added H_2O (2 mL) at room temperature to give a yellow solution. VPC analysis of gaseous phase indicated a H_2 formation in 50% yield. After addition of $NaBPh_4$ (0.05 g, 0.146 mmol), the mixture was concentrated. Recrystallization of the residue from toluene–THF gave **6b** (0.083 g, 64%).

Preparation of *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (11). A solution of $\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4{\cdot}2C_6H_5CH_3$ (0.17 g, 0.16 mmol) in THF (5 mL) was treated with KOH powder (0.28 g, 5.0 mmol) at room temperature for 2 h. After concentration, the residue was extracted with toluene. When extract was concentrated, **11** was obtained as pale yellow crystals (0.053 g, 70%), mp 155 °C dec. Alternatively, **11** was prepared by hydrolysis of *trans*-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$ in THF in 80% yield.

Preparation of *trans*-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$ (13). A mixture of *trans*-$\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4{\cdot}2C_6H_5CH_3$ (0.15 g, 0.15 mmol) and CH_3ONa (0.054 g, 1.0 mmol) in THF (3 mL) was stirred at room temperature for 1 h. When reaction mixture was concentrated, the residue upon recrystallization from hexane gave **13** as pale yellow crystals (0.035 g, 50%), mp 115 °C dec.

Preparation of *trans*-$RhH(CO)L_2$. (I) *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ (10). To a solution of $RhH[P(i\text{-}Pr)_3]_3$ (0.35 g, 0.6 mmol) in hexane was added CH_3OH (1 mL) at room temperature. After removal of dark red crystals of $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (0.03 g) by filtration, the filtrate was concentrated to 2 mL and the concentrate was cooled at −20 °C to give yellow crystals of **10** (0.15 g, 53%), mp 70 °C dec.

(II) *trans*-$RhH(CO)[P(c\text{-}C_6H_{11})_3]_2$ (9). This compound was prepared by a similar method as described above as yellow crystals (70%), mp 210 °C dec.

Reaction of Rhodium(I)–Hydrido Compounds with CO. (I) $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (21). To a solution of $RhH[P(i\text{-}Pr)_3]_3$ (0.175 g, 0.3 mmol) in pentane was bubbled CO at room temperature for 1 min. The reaction mixture was concentrated to 3 mL in vacuo, and the concentrate was cooled at −20 °C under CO to give $[Rh(CO)_3P(i\text{-}Pr)_3]_2$ (**20**) as yellow crystals (0.085 g, 81%). This compound was stable only under CO but decomposed rapidly under N_2 or under vacuum. Thus, recrystallization of $[Rh(CO)_3P(i\text{-}Pr)_3]_2$ (0.1 g) from pentane under N_2 gave the title compound as red crystals (0.02 g, 18%), mp 70 °C dec. Alternatively, **21** was obtained in 60% yield by a reaction of *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ with CO in pentane at room temperature followed by substitution of CO atmosphere by N_2.

(II) $Rh_2(CO)_4L_2$ (22, $L = P(t\text{-}Bu)_3$; 23, $PPh(t\text{-}Bu)_2$; 24, $P(c\text{-}C_6H_{11})_3$). To a solution of $RhH[P(t\text{-}Bu)_3]_2$ (0.17 g, 0.3 mmol) in hexane (10 mL) was bubbled CO at room temperature for 5 min to precipitate yellow crystals. While the yellow crystals were stable under a CO atmosphere, a rapid color change occurred upon replacement of CO with N_2 to give red solids. Recrystallization from toluene–hexane under N_2 gave $Rh_2(CO)_4[P(t\text{-}Bu)_3]_2$ (**22**) as dark red crystals (0.085 g, 79%). Molecular weight determined cryoscopically in benzene (687) agreed with the required value (722).

A similar reaction of *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ and $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ with CO gave the corresponding $Rh_2(CO)_4L_2$ ($L = PPh(t\text{-}Bu)_2$, mp 289 °C dec; $L = P(c\text{-}C_6H_{11})_3$, 220 °C dec) as dark red crystals.

Reaction of *trans*-$Rh(OH)(CO)L_2$ with CO. (I) *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$. To a solution of *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$ (0.03 g, 0.06 mmol) in THF (5 mL) containing H_2O (0.1 mL) was bubbled CO for 1 min at room temperature to give an orange solution. The color changed to red on replacing the CO atmosphere with N_2 through bubbling. The IR spectrum of the concentrated residue showed the formation of $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ (**21**) (1957, 1768, and 1730 cm^{-1}) and a carbonyl carbonato compound $Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (**26**) (1934, 1533, 1300, and 1275 cm^{-1}).[17]

(II) *trans*-$Rh(OH)(CO)[P(c\text{-}C_6H_{11})_3]_2$. A solution of *trans*-$Rh(OH)(CO)[P(c\text{-}C_6H_{11})_3]_2$ (0.20 g, 0.28 mmol) in toluene (10 mL) was stirred under CO (1 atm) at room temperature for 2 h to give a yellow solution. The yellow solution was treated with N_2 to give a red solution, from which $Rh_2(CO)_4[P(c\text{-}C_6H_{11})_3]_2$ (**24**) (0.05 g, 30%) was obtained on concentration.

Preparation of *trans*-$Rh(CO_2CH_3)(CO)[P(i\text{-}Pr)_3]_2$ (25). A solution of *trans*-$Rh(OCH_3)(CO)[P(i\text{-}Pr)_3]_2$ (0.16 g, 0.33 mmol) in hexane (10 mL) was stirred under CO (1 atm) at room temperature for 10 min. Concentration of the mixture gave yellow crystals together with a small amount of red crystals of $Rh_2(CO)_3[P(i\text{-}Pr)_3]_3$ as detected by the characteristic $\nu(CO)$ bands (1732 and 1768 cm^{-1}) due to the bridging carbonyl ligands. An analytically pure sample of **25** was obtained by recrystallization of the yellow crystals from hexane (126 mg, 75%), mp 103–106 °C dec.

Reaction of $RhH[P(i\text{-}Pr)_3]_3$ with CO in the Presence of H_2O. A mixture of $RhH[P(i\text{-}Pr)_3]_3$ (0.18 g, 0.3 mmol) and H_2O (0.1 mL) in THF (10 mL) was treated with CO (1 atm) for 30 h at room temperature. The concentrated residue was recrystallized from heptane to give $Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (**26**) (0.03 g, 20%).

Reaction of *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ with CO_2 in Aqueous THF. A solution of *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ (0.23 g, 0.5 mmol) in THF (10 mL) containing H_2O (1 mL) was stirred under CO_2 (1 atm) at room temperature for 20 h. The IR spectrum of the concentrated residue indicates the formation of $Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (**26**) and a formate compound $Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$ (**31**) (1633 cm^{-1}).[17] Recrystallization from ether gave pure **26** (0.14 g, 60%). A similar reaction of *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ with CO_2 in the presence of a large excess of H_2O gave **26** as a sole product (80%) and the formation of the formate compound was not detected.

Hydrolysis of $Rh_2(\mu\text{-}OCO_2)(CO)_2[P(i\text{-}Pr)_3]_4$ (26). A mixture of **26** (0.23 g, 0.24 mmol) and $NaBPh_4$ (0.18 g, 0.53 mmol) in 10% aqueous pyridine (10 mL) was stirred at room temperature for few minutes. The concentrated mixture was recrystallized from THF–toluene to give $\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4{\cdot}2C_6H_5CH_3$ (**6b**) quantitatively.

Under similar conditions but in aqueous acetone, the rate of hydrolysis of **26** was extremely slow and the carbonate compound recovered quantitatively after being stirred at room temperature for 10 h. The hydrolysis, however, occurs at higher temperature. Thus, the hydrolysis at 80 °C for 5 h gave $\{Rh(CO)(acetone)[P(i\text{-}Pr)_3]_2\}BPh_4$ (**6c**) in 50% yield. The IR spectrum shows $\nu(CO)$ of the CO and acetone at 1978 and 1678 cm^{-1}, respectively. The coordinated acetone in **6c** is readily displaced by pyridine to give **6b** on dissolution in pyridine.

Hydrolysis of $Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$ (31). A similar hydrolysis of $Rh(O_2CH)(CO)[P(i\text{-}Pr)_3]_2$ (0.18 g, 0.36 mmol) in aqueous pyridine, and subsequent treatment with $NaBPh_4$ gave $\{Rh(CO)(py)[P(i\text{-}Pr)_3]_2\}BPh_4$ quantitatively.

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