Homogeneous Catalysis: Catalytic Intramolecular Conversion of 1,4-Dialdehydes to γ-Lactones

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A series of catalysts of the type $[Rh(diphosphine)(solvent)_2]^+$ (solvent = weakly coordinating solvent) were investigated for converting 1,4-dialdehydes and 1,4-keto aldehydes to the corresponding γ-lactones, the equivalent of the intramolecular Cannizzaro reaction. It was found that a number of these species were very effective catalysts which tolerated a high degree of steric hindrance and transformed the substrates without any detectable enolization. The carbonylated species $[Rh(diphosphine)(CO)_2]^+$ and $[Rh(diphosphine)(CO)(solvent)]^+$ are ineffective in catalysis and are the side products of intramolecular lactonization. Decarbonylation of the substrate to give these inactive carbonylated species is a minor component of the catalysis with 1,4-dialdehydes but is the major pathway for the lactonization of 1,4-ketoaldehydes. These catalysts provide a practical, mild catalytic method of converting 1,4-dialdehydes to γ-lactones. The catalysis is very rapid, occurring even at −60 °C. At −78 °C a stable substrate (η^2-aldehyde)rhodium adduct was identified and is possibly the precursor to aldehyde C−H activation. No other catalytic intermediates could be intercepted at low temperatures. The catalysis appears to be a "black box" system where, once the C−H bond is activated, none of the putative intermediates exist in detectable concentrations.

The Cannizzaro reaction is a base-promoted "disproportionation" of an aldehyde to the corresponding alcohol and acid (eq 1). Although probably mechanistically analogous, the first true disproportionation reaction was reported by Claisen (eq 2). Both of these reactions

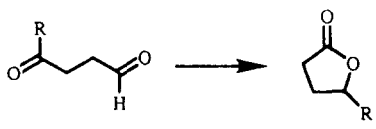
$$2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCO_2^- \quad (1)$$

$$2PhCHO \xrightarrow{MeO^-} PhCO_2CH_2Ph \quad (2)$$

are restricted to nonenolizable aldehydes; otherwise, under the required strong basic conditions, the reaction is dominated by aldol condensation. In an attempt to circumvent this problem, Tishchenko employed an amphoteric Lewis acid ($Al(OEt)_3$) as a catalyst. This refinement allowed for the use of enolizable aldehydes, but even so, aldol condensation was observed. Thus, the ideal conditions for this reaction are those that occur catalytically under neutral conditions.

A number of attempts at achieving these conditions have been reported with use of transition-metal catalysts. Under carefully controlled conditions the $[RuH_2(PPh_3)_4]$ complex acts as a relatively efficient catalyst for the intermolecular conversion of aldehydes to the corresponding esters under neutral conditions.[1] Less efficient are catalysts derived from $[Rh(H)(CO)(PPh_3)_3]$,[2] the alcoholic mixture $[RhCl_3{\cdot}3H_2O + PPh_3 + Na_2CO_3]$,[2] and the catalyst $[Rh(H)(PPh_3)_4]$.[3]

This paper describes the use of a new class of rhodium(I)-based catalysts for the intramolecular Cannizzaro reaction (eq 3). These catalysts are the same as those we



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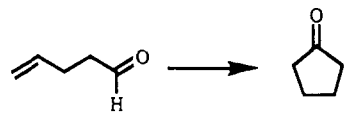
developed[4,5] for the analogous hydroacylation reaction (eq 4), and their choice was based on similar mechanistic considerations.



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Mechanism

The broad outlines of one possible mechanism for hydroacylation of an olefin and presumably also of a ketone or aldehyde is shown in Figure 1 with use of rhodium(I) catalysts. This scheme follows the conventional steps, C−H oxidative addition, olefin–hydride insertion, and reductive elimination. Alternative mechanisms might involve insertion of the double bond into the metal–acyl bond,[6] followed by hydride insertion into the metal–alkyl bond. Other mechanisms[7] seem less likely. In order for this sequence to proceed, for either mechanism, at least three vacant metal sites are required, one each for the hydride, the acyl ligand, and the olefin, aldehyde, or ketone. Further, the coordinated hydride and olefin must be mutually cis disposed. Given these requirements, we chose rhodium(I) systems of the type $[Rh(diphosphine)]^+$ in which the coordination unsaturation of the catalytic precursor is satisfied by easily displaced solvento ligands.

These catalysts were prepared as described previously[4,5,8] by hydrogenation of the $[Rh(diphosphine)(NBD)]ClO_4$ (NBD = norbornadiene) complexes. They either were isolated as the readily split aryl-bridging dimers[4,5,8] or were

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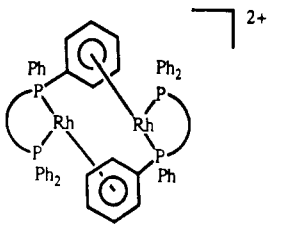
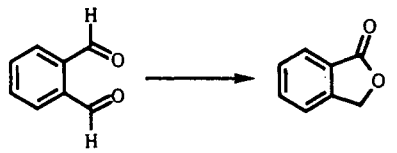
used in situ after NMR (^1H, ^{31}P) characterization.



Results

Solvent Variation. The conversion of *o*-phthaldialdehyde (1) to the corresponding lactone (eq 5) was used to investigate the general characteristics of the reaction.



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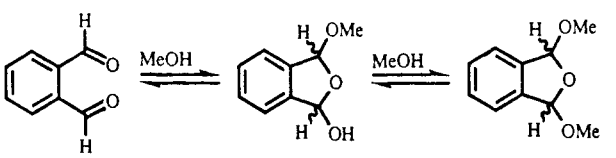
1

With use of the catalyst precursor $[Rh(diphos)]_2(ClO_4)_2$ (diphos = $Ph_2PCH_2CH_2PPh_2$) in CH_2Cl_2 solution **1** was completely and cleanly converted to the lactone in 75 min at 34 °C by employing 1.5 mol % Rh ([Rh] ≈ 2.5 mM). This corresponds to a turnover frequency of about 1.4×10^{-2} s^{-1}. The turnover frequency, however, depends on the solvent employed. Although the turnover frequency is the same in CH_3NO_2 solution as in CH_2Cl_2, the turnover frequency is 1 order of magnitude faster (1.1×10^{-1} s^{-1}) in acetone solution, it is 1 order of magnitude slower in methanol (1.8×10^{-3} s^{-1}), and no catalysis occurs in acetonitrile solution. The comparability of turnover frequency in CH_2Cl_2 and CH_3NO_2 is probably related to the fact that in these two solvents the catalyst exists[4,5] as the aryl-bridged dimer, which must be split by the substrate **1** before catalysis can occur. In acetone, however, the catalyst exists mainly as the disolvento monomer $[Rh(diphos)(acetone)_2]^+$, the acetone ligands of which are presumably easily displaced by the substrate **1**. In CH_3CN solution the catalyst exists as the species $[Rh(diphos)(CH_3CN)_2]^+$; the acetonitrile ligands are not replaced by aldehydes or ketones. Although the catalyst exists as the species $[Rh(diphos)(CH_3OH)_2]^+$ in methanol solution and the solvento ligands are easily replaced, the substrate was found to be tied up almost entirely as cyclic acetals and hemiacetals (eq 6). The origin of the catalytic retardation



(6)

in methanol solution is undoubtedly related to the diminution of dialdehyde due to acetal formation. The identification of the rhodium species in various solvents was determined by ^1H NMR spectroscopy.[4,5] These results indicate that, of the solvents tried, acetone is the solvent which gives the most efficient and rapid catalysis.

Ligand Variation. The second aspect of catalysis that we examined was the effect of varying the stereoelectronic properties of the diphosphine. The other ligands examined were as follows: dcpe = $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$, dptf = $(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(p\text{-}CF_3C_6H_4)_2$, dppp = $Ph_2PCH_2CH_2CH_2PPh_2$, dppb = $Ph_2PCH_2CH_2CH_2CH_2PPh_2$. The catalysts were prepared by hydrogenation of the isolated species [Rh(diphosphine)(NBD)]ClO_4 in acetone solutions,[4,5] giving the solvento species $[Rh(diphosphine)(acetone)_2]^+$ cleanly. All of these species are effective catalysts for conversion of **1** to the lactone. The turnover frequencies are listed in Table I.

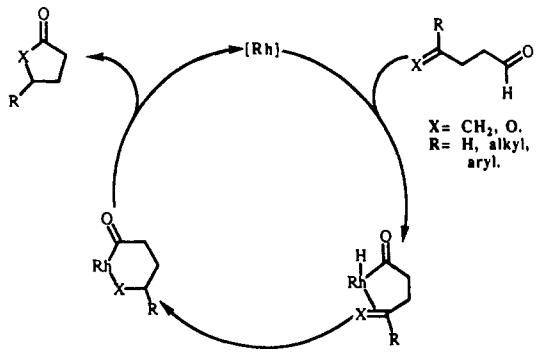


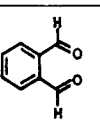
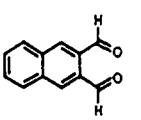
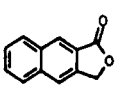
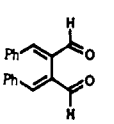
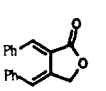
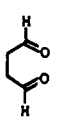
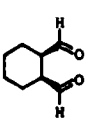
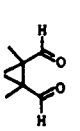
Figure 1.

Table I. Turnover Frequencies for the Conversion of *o*-Phthaldialdehyde to the Lactone by $[Rh(diphosphine)(acetone)_2]^+$

system	diphosphine	turnover freq, s^{-1} [a]
A	$Ph_2PCH_2CH_2PPh_2$	1×10^{-1}
B	$(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$	5×10^{-1}
C	$(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(p\text{-}CF_3C_6H_4)_2$	9×10^{-2}
D	$Ph_2PCH_2CH_2CH_2PPh_2$	4×10^{-1}
E	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$	3×10^{-1}

[a] Catalysis carried out in acetone at 34 °C with 1 mol % [Rh].

Table II. Rates of Catalytic Conversion of 1,4-Dialdehydes to the Corresponding Lactones with $[Rh(diphosphine)(acetone)_2]^+$

substrate	product[a]	diphosphine	[Rh], mol %	turnover freq, s^{-1}
 1		diphos	1	1×10^{-1}
		dcpe	1	5×10^{-1}
 2		diphos	1	7×10^{-1}
		dcpe	1	1×10^{-1}
 3		diphos	1	0
		dcpe	5	0
 4		diphos	2	3×10^{-5}
		dcpe	2	4×10^{-3}
 5[b]		dcpe	7	2×10^{-4}
 6		diphos	5	0
		dcpe	6	2×10^{-3}

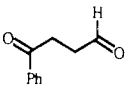
[a] All reactions were carried out in acetone solution at 34 °C. [b] Substrate contaminated with about 5 mol % *N*-methylaniline, which may have an effect on the catalysis.

The results in Table I show that, first, increasing the chelate ring size by one carbon atom causes an increase

Table III. Catalytic Transformation of Substrate 7 with Use of [Rh(diphosphine)(acetone)$_2$]$^+$ [a]

diphosphine	% conversion[b]	% decarbonylation
diphos	95	35
dcpe	62	56
dptf	48	16
dppp	99	40
dppb	78	76

[a] The structure of the substrate is



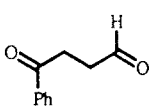
[b] With use of 5 mol % [Rh] in refluxing acetone after 18 h. % of lactone produced = % conversion − % decarbonylation.

in the turnover frequency (systems A and D) and a further increase in ring size has little effect (system E), second, electron-withdrawing groups slow down the rate (system C), and third, electron-donating groups increase the rate (system B). The dcpe catalyst is the most effective, which is further demonstrated when other 1,4-dialdehydes are used.

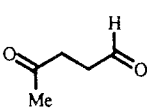
Substrate Variation. A representative collection of 1,4-dialdehydes were investigated with the diphos and dcpe catalysts. These substrates serve to illustrate the scope of catalysis. The results are collected in Table II.

The results in Table II confirm that the dcpe-derived catalyst always gives the faster rate. Neither catalyst converts **3** to the lactone after 1 day at 34 °C. It is probable that servere phenyl–phenyl interactions in the potential lactone are responsible for the lack of reactivity of **3**. Substrates **4**–**6** are converted to the lactones by the dcpe-derived catalyst, although the diphos-derived catalyst is ineffective for transforming **6**. The difference in reactivity of **6** and **4** is undoubtedly connected with the steric hindrance of the *gem*-dimethyl groups in **6**. It is significant, however, that despite this hindrance **6** does convert with the dcpe-derived catalyst, suggesting that this catalyst can tolerate a high degree of steric hindrance. The *cis*-dialdehyde **5** gives exclusively the *cis*-lactone. It is noteworthy that none of the thermodynamically more stable *trans*-dialdehyde was detected during catalysis, indicating that the dcpe-derived catalyst does not induce enolization during catalysis.

1,4-Keto Aldehydes. Given the proposed mechanism in Figure 1, 1,4-keto aldehydes also should, in the absence of competing reactions, give lactones. We have investigated the two substrates **7** and **8**. Attempts to lactonize



7



8

8 at 34 °C in acetone solution with any of the present catalysts failed. In acetone solution at 34 °C substrate **7** lactonized partially (30%) after 2 days with use of the dppp catalyst. Refluxing acetone solutions and 5 mol % [Rh] were required to promote catalysis of **7** at reasonable rates. The catalysis, however, consists of two competing paths, one of lactonization and the other of decarbonylation. The results obtained for **7** are given in Table III. Two products are formed, the lactone and propiophenone, which results from decarbonylation.

The amount of decarbonylation depends on the particular catalyst. Thus, the dppb-derived catalyst gives nearly all propiophenone and very little of the lactone, whereas the other catalysts give varying amounts of lactone. We find that at 34 °C decarbonylation occurs rapidly for **8** to give the catalytically inactive dicarbonyl species [Rh(diphosphine)(CO)$_2$]$^+$. At this temperature and in a closed vessel catalysis is essentially shut down when the decarbonylation occurs.

Table IV. Degree of Decarbonylation of Substrate 1 with Use of the [Rh(dcpe)(acetone)$_2$]$^+$ Catalyst

substrate:Rh[c]	turnover no.[a]	decarbonylation no.[b]
1000:1	500	15
500:1	450	7
200:1	200	0

[a] Number of turnovers after 6 days at 34 °C in acetone solution. [b] Number of decarbonylation events during the given number of turnovers. [c] Concentration of [Rh] is 3×10^{-3} M in acetone in all cases.

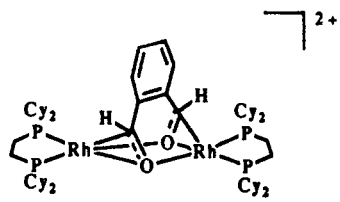
Substrate **8** is readily decarbonylated by the present catalysts, but no lactone was detected. The contrasting behavior of the 1,4-keto aldehydes compared to that of the 1,4-dialdehydes, we believe, is related to the different rates of insertion of ketones and aldehydes into the metal–hydride bond (Figure 1). Ketones are generally more difficult to reduce (with H$^-$) than are aldehydes, so that decarbonylation dominates the catalysis for 1,4-keto aldehydes. Similar arguments would probably apply if ketone insertion into the metal–acyl bond were the relevant catalytic step.

Decarbonylation of 1,4-Dialdehydes. In the case of 1,4-dialdehydes decarbonylation also occurs but to a lesser extent. We have investigated the degree of decarbonylation using substrate **1** and the catalyst [Rh(dcpe)(acetone)$_2$]$^+$ in acetone solution at 34 °C. The results are collected in Table IV. The degree of decarbonylation was measured by GC of the produced benzaldehyde. The results from Table IV show that 200 turnovers are achieved without any detectable decarbonylation of the substrate at this concentration of catalyst. At higher substrate to catalyst ratios decarbonylation is observed. After about 300 turnovers, the turnover frequency is reduced and continues to decline as the reaction proceeds. That this is caused by carbonylation of the catalyst is inferred from the observation that reaction of [Rh(dcpe)(CO)$_2$]$^+$ and 300 equiv of substrate **1** yields only 8 turnovers after 48 h at 34 °C. These turnovers are presumably caused by slow CO displacement from the fully carbonylated catalyst.

We should point out, however, that the amount of decarbonylation is dependent on the catalyst concentration; the higher the concentration, the greater the amount of decarbonylation. Moreover, at higher catalyst concentrations the turnover frequency decreases not only because of increased decarbonylation but also because of the production of another catalytically inactive species when substrate **1** is used. Thus, if the concentration of [Rh(dcpe)(acetone)$_2$]$^+$ is increased from the usual concentration of [Rh] = 3×10^{-3} to 1.6×10^{-2} M, the *initial* turnover frequency decreases 9-fold with use of a 150:1 substrate 1:catalyst ratio at 34 °C. At these higher catalyst concentrations the acetone solution is deep red rather than the usual straw yellow. After 5 min of the catalysis ^{1}H and ^{31}P NMR spectroscopy shows that the solution contains 90% of a new (red) rhodium-containing species and that 25% of **1** has been lactonized. After this time catalysis continues, the amount of the red species decreases, and the carbonylated species [Rh(dcpe)(CO)$_2$]$^+$ and [Rh(dcpe)(CO)(acetone)]$^+$[4,5] begin to appear. After 1 h nearly complete conversion of the substrate had occurred. The appearance of the carbonylated catalyst early in the conversion contrast sharply with the behavior at lower catalyst concentrations (Table IV), where 200 turnovers occur without detectable decarbonylation. We have been unable

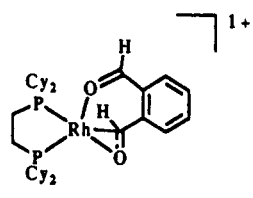
to determine precisely why the rate of decarbonylation increases with increasing concentration.

We have succeeded in isolating the red rhodium-containing species as crystals. Analytical and spectroscopic data indicate that it is a dimer. The compound is sufficiently stable at 25 °C to be isolated in the absence of substrate 1. It does, however, slowly convert the dialdehyde to the lactone. It is difficult to obtain suitable crystals for X-ray structure analysis. The crystals obtained as thin plates did not provide sufficient diffraction data for an accurate refinement of the structure but were sufficient to establish the basic geometry and bonding of the dimer. The structure contained μ-$\eta^1(O)$-η^2-aldehyde ligands as shown in **9**. At higher catalyst concentrations, the presence of **9** contributes to the retardation in the turnover frequency.



9 $^{2+}$

Mechanism. In an attempt to intercept the putative intermediates of catalysis (Figure 1), we followed the reaction at low temperatures. With use of stoichiometric amounts of substrate **1** and $[Rh(dcpe)(acetone)_2]ClO_4$ in acetone solutions none of the intermediates could be detected by ^1H, ^{13}C, or ^{31}P NMR spectroscopy at −60 °C, the lowest temperature at which catalysis commenced. Thus, intramolecular lactonization appears to yet another example of "black box" catalysis,[4,5] where the substrate enters into and the product emerges from the catalytic cycle without any intermediate being sufficiently stable to be detected. At −70 °C catalysis effectively ceases and a catalyst–substrate adduct can be detected and constitutes about 70% of the material in solution when stoichiometric amounts of substrate **1** and catalyst are used. When the temperature is raised to −60 °C, this adduct disappears and lactone begins to form. In addition to the onset of catalysis, the adduct converts to the red dimer **9**. Spectroscopic evidence defines the 1:1 adduct observed at −70 °C as having the structure **10**. The substrate is bound to the rhodium atom via η^1- and η^2-aldehyde bonds. The NMR evidence for this structure is presuasive.



10 $^{+}$

The adduct **10** exhibits a singlet at δ = 200.4 ppm for its proton-decoupled ^{13}C NMR spectrum, assigned to the σ-bound η^1-*C*HO group.[9] It is shifted 6.8 ppm upfield from the signal for the free *C*HO group of the substrate, consistent with an O-bound carbonyl. The η^2-*C*HO signal occurs at δ = 62.8 ppm and, unlike η^1-*C*HO, is coupled to rhodium ($J(^{103}Rh-^{13}C)$ = 13.8 Hz). This signal falls within the range for η^2-*C*HO species.[10] The proton-decoupled ^{13}C NMR spectrum of **10** shows six singlets in the aromatic region (δ = 145–124 ppm), consistent with the proposed unsymmetrical binding of the substrate. The proton-coupled ^{13}C NMR spectrum shows the η^1-*C*HO resonance as a doublet ($J(^1H-^{13}C)$ = 187.2 Hz); two of the six aromatic carbons are singlets, and the other four appear as doublets. The proton-coupled ^{13}C NMR spectrum for the η^2-*C*HO resonance appears as a doublet of doublets ($J(^{103}Rh-^{13}C)$ = 14 Hz, $J(^1H-^{13}C)$ = 139.7 Hz), confirming that the aldehyde is bound to both its proton and the rhodium atom. The ^1H NMR spectrum for the η^1-C*H*O aldehyde is a doublet (J = 9.6 Hz) at δ = 10 ppm, the coupling being due to either rhodium or phosphorus. This chemical shift is consistent with those of other η^1-aldehydes.[11] The ^1H NMR spectrum for the η^2-C*H*O group is observed as a broad singlet at δ = 6.9 ppm, upfield shifted from the signal for the free aldehyde by 3.60 ppm. The ^{31}P NMR spectrum shows the phosphorus atoms to be inequivalent.

Species **10** is stable at −78 °C for over 18 h. It is attractive to suggest that **10** is the first step along the trajectory for rhodium addition to the C–H bond of the aldehyde, particularly since Roper[12] has demonstrated such a transformation in the solid state. We should point out, however, that the observation of the η^2-CHO binding does not necessarily imply that this species is part of the catalytic cycle, even though it exists only at very low temperatures and disappears when catalysis commences. Whatever the case, it is clear that C–H activation is a facile process with these catalysts because catalytic turnover is observed at −60 °C.

Discussion

It is clear from the foregoing results that the [Rh(diphosphine)]$^+$ species are effective catalysts for converting 1,4-dialdehydes to γ-lactones under mild, neutral conditions. Moreover, the problem of enolization encountered with other catalysts has been circumvented. That incorporation of bidentate phosphines is one of the crucial factors in making the present catalysts effective is evidenced by the fact that we find that Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$, is an ineffective lactonization catalyst. It only leads to decarbonylation of the substrate.

Although decarbonylation has been suppressed, but not eliminated, with the present catalysts for 1,4-dialdehydes, it dominated the catalysis of 1,4-keto aldehydes. It is significant, however, that the catalysts will tolerate a high degree of steric hindrance in 1,4-dialdehyde substrates.

We note, finally, that the exploitation of the catalysis is hampered by the fact that there are no simple methods of generating nonaromatic 1,4-dialdehydes. The aliphatic 1,4-dialdehydes are sensitive molecules, being prone to both acid- and base-induced condensation and to ready hydration in protic oxygenated solvents. It is noteworthy that the present catalysts tolerate such sensitive species.

Experimental Section

The solvents CH_2Cl_2 (CaH_2), THF (Na/benzophenone), Et_2O ($LiAlH_4$), acetone (3-Å molecular sieves), DMSO (CaH_2), benzene (CaH_2), MeOH ($(MeO)_2Mg$), ethyl acetate (CaH_2), and pentane (CaH_2) were distilled from their appropriate drying agents under dry N_2 and stored under N_2 before use. The solvents used for the reactions involving rhodium compounds were first deoxygenated by bubbling argon through them for 20 min. The deu-

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terated solvents were used as supplied (Aldrich Gold Label). ^1H NMR spectra were recorded on a Varian T-60 continuous-wave or a Varian XL-400 Fourier transform spectrometer. ^1H NMR chemical shifts were measured in ppm relative to a tetramethylsilane internal reference. ^{31}P NMR spectra were recorded on a Varian XL-400 Fourier transform spectrometer operating at 161.9 MHz. ^{31}P NMR chemical shifts were measured in ppm relative to a $P(OMe)_3$ external reference (1% in benzene solution) but are reported in ppm relative to 85% H_3PO_4 (converted by adding 140.4 ppm). ^{13}C NMR spectra were recorded on a Varian XL-400 Fourier transform NMR spectrometer operating at 100.6 MHz. ^{13}C NMR chemical shifts were measured in ppm relative to a tetramethylsilane external reference. GLC analysis was carried out on a Varian 2700 gas chromatograph equipped with a flame ionization detector coupled to a Varian 4270 peak integrator. Components were separated on a QF-1 packed column (10 ft × 0.16 in. internal diameter and 0.25 in. outer diameter; support Chromosorb-G, 80–100 mesh). Infrared spectra were obtained in NaCl cells on a Varian DX5 Fourier transform spectrometer with solvent suppression. Melting points were obtained on a Fischer-Johns melting point apparatus and are uncorrected. Microelemental analyses were performed at Huffman Laboratories (Indiana).

Rhodium Compounds. All preparations and reactions of rhodium compounds were carried out under argon with use of standard Schlenk techniques. The rhodium compounds were stored under argon at −10 °C in glass vials with plastic caps wrapped with Parafilm.

The diphosphine ligands 1,2-bis(dicyclohexylphosphino)ethane (dcpe), 1,2-bis[bis(*p*-(trifluoromethyl)phenyl)phosphino]ethane (dptf), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), and 1,4-bis(diphenylphosphino)butane (dppb) were supplied by Strem Chemicals and were recrystallized from boiling ethanol under argon prior to use $[Rh(C_2H_4)_2Cl]_2$,[4,5,13] $[Rh(NBD)_2]ClO_4$,[4,5,14] $[Rh(dcpe)(NBD)]ClO_4$,[4,5] $[Rh(dptf)(NBD)]ClO_4$,[4,5] $[Rh(dppe)(NBD)]ClO_4$,[4,5,8] $[Rh(dppp)(NBD)]ClO_4$,[4,5] $[Rh(dppb)(NBD)]ClO_4$,[4,5] and $[Rh(dppe)]_2(ClO_4)_2$[4,5,8] were synthesized by literature procedures.

Organic Reactions. All organic reactions were carried out under dry N_2. All reagents were either distilled or recrystallized prior to use. *o*-Phthaldialdehyde (**1**) was used as supplied by Sigma Chemicals. 2,3-Naphthalenedicarboxaldehyde[15] (**2**), 2,3-bis(Z-benzylidene)-1,4-butanedial[16] (**3**), succindialdehyde[17] (**4**), 2,2,3,3-tetramethylsuccindialdehyde[18] (**6**), 4-oxo-4-phenylbutanal[19] (**7**), and 4-oxopentanal[19] (**8**) were prepared by literature procedures. Substrates **4** and **6** contained 2,5-dimethoxytetrahydrofuran (62%) and 2-(2-methylpropen-1-oxy)-2-methylpropanal (as well as a polymeric material) (48% total) as impurities, respectively. *cis*-1,2-Cyclohexanedicarboxaldehyde (**5**) could only be prepared in low yields (3%) and with *N*-methylaniline (5%) as an impurity, by a modified reduction of *cis*-*N*,*N*′-dimethyl-*N*,*N*′-diphenyl-1,2-cyclohexanedicarboxamide[20] with $LiAlH(OEt)_3$.[20,21]

Catalysis with $[Rh(dppe)]_2(ClO_4)_2$. Typically $[Rh(dppe)]_2(ClO_4)_2$ (1 mg, 0.83 μmol) and the solid substrate (166 μmol) were weighed into an NMR tube that was then capped with a rubber septum and flushed with argon for 60 s. The solvent (0.6 mL) was then syringed into the tube, forming a yellow-orange solution. The reaction was monitored at 34 °C by ^1H NMR spectroscopy.

The procedure was modified for liquid substrates by syringing in the required amount after the catalyst precursor was dissolved.

In all catalytic runs the reactions remained homogeneous. The validity of the ^1H NMR analysis was checked for *o*-phthaldialdehyde in two ways. First, the concentrations of substrate and product were determined by integration against a known concentration of bis(cyclopentadienyl)iron(II), $[FeCp_2]$, as an internal standard. The results were the same with or without the standard. Second, the catalytic conversion was carried out on a preparative scale and the product was isolated. Thus, **1** (0.40 g) and $[Rh(dppe)]_2(ClO_4)_2$ (0.0358 g) in acetone solution (35 mL) were stirred under argon for 18 h at 25 °C. The solvent was then removed under reduced pressure to give dark-brown crystals, which were dissolved in CH_2Cl_2–hexane (30 mL, 1:1) and passed through a Florisil plug to remove the catalyst. The clear, colorless eluent was pumped down at 12 mm to give a pale yellow oil, which upon further evaporation at 1 mm and 25 °C crystallized exothermically to give 0.39 g (98%) of the lactone, mp 72 °C. The product was identical with an authentic sample of the lactone by ^1H NMR spectroscopy TLC (alumina), and melting point. It is therefore reasonable to assume that the NMR analysis is valid for the other dialdehydes.

Catalysis with $[Rh(P\frown P)(NBD)]ClO_4$, Where P⌒P = dcpe, dptf, dppp, dppb. The same procedure as that in the previous section was employed except that the $[Rh(P\frown P)(NBD)]ClO_4$ catalyst precursor had to be hydrogenated by syringing in 4 equiv of H_2/mol of Rh for the reaction to commence. Liquid substrates were syringed in after the hydrogenation; otherwise, the hydrogenation was carried out in the presence of substrate. No evidence of substrate hydrogenation was observed.

The reactions with the phenyl keto aldehyde **7** in refluxing acetone were carried out with the same procedures as above, only on a larger scale (23.6 μmol of Rh atoms), and hydrogenation of the catalyst precursor was accomplished by bubbling H_2 through the solution for 3 min.

Product Analysis. Qualitative and quantitative analysis was carried out by ^1H NMR spectroscopy. Substrates **1**, **2**, and **4**–**8** gave known γ-lactones, the identities of which were confirmed by comparison of experimental with published spectra (Table V). For 2,2,3,3-tetramethylsuccindialdehyde (**6**) the product, 2,2,3,3-tetramethyl-γ-butyrolacetone, is a known compound,[26] and its presence was deduced from its ^1H NMR spectrum. The large amounts of impurities present in the substrate discouraged attempts to isolate the product for further identification. Gas–liquid chromatography was used to identify and quantify the decarbonylation side reaction products for substrates **1**, **7**, and **8**. The retention times were compared to those of authentic samples. Typically 0.1–0.5-μL samples of product solution were injected on the column. Initial temperatures of 50–80 °C (flow rate 18 mL/min) were required to separate the decarbonylated substrate (benzaldehyde, propiophenone and methyl ethyl ketone, respectively) from the solvent peaks. These came off with retention times of 5–10 min. The temperature was then raised to 200 °C at a rate of 15 °C/min to drive off the substrates and lactones with retention times from 13 to 28 min.

The stereochemistry of the product from the lactonization of **5** was confirmed as cis by comparison of the high-field ^{13}C and ^1H NMR spectra to those of an authentic sample.[22]

Reaction of $[Rh(dcpe)(acetone)_2]ClO_4$ with 40 Equiv of the Methyl Keto Aldehyde 8. This reaction was prepared by using the standard procedure with $[Rh(dcpe)(NBD)]ClO_4$ (19.6 mg, 27.3 μmol), acetone-d_6 (0.4 mL), and the methyl keto aldehyde **8** (0.111 g, 1112 μmol). The ^{31}P NMR spectrum of the mixture was recorded 5 min after mixing. The composition of the resulting solution according to the integrated intensities of the corresponding peaks was 13.2% $[Rh(dcpe)(CO)_2]^+$, 42.9% $[Rh(dcpe)(CO)(acetone)]^+$, and an unidentified species with inequivalent phosphorus atoms at δ 92.33 (br d, J_{Rh-P} = 158.6 Hz, J_{P-P} not measurable), 87.81 (br d, J_{Rh-P} = 143.6 Hz, J_{P-P} not measurable) for the remainder.

Reaction of *o*-Phthaldialdehyde with $[Rh(dcpe)(CO)_2]^+$. $[Rh(dcpe)(CO)_2]ClO_4$ was prepared by bubbling CO for 20 s through a solution of $[Rh(dcpe)(acetone)_2]ClO_4$ (29.6 μmol) in acetone (0.7 mL) (prepared as described previously). ^{31}P NMR $[(CD_3)_2CO]$: δ 90.97 (d, J_{Rh-P} = 118 Hz). IR $[(CD_3)_2CO]$: ν (C≡O) 2085.6, 2035.5 cm^{-1}. Argon was then bubbled through the solution

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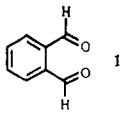
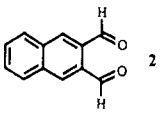
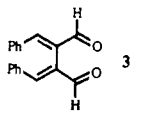
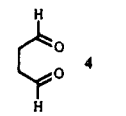
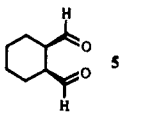
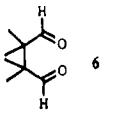
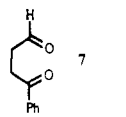
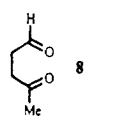
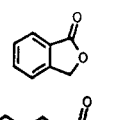
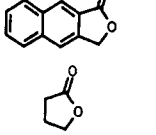
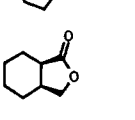
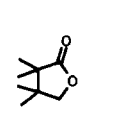
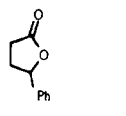
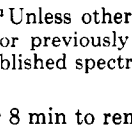
Table V. ^{1}H NMR Data of Substrates and Products

compd	solvent	spectrum,[a] δ
 1	$(CD_3)_2CO$	9.72 (s, 2 H, C*H*O), 8.08–7.66 (m, 4 H, aromatic)
 2	$CDCl_3$	10.54 (s, 2 H, C*H*O), 8.40–7.68 (m, 6 H, aromatic)
 3	$CDCl_3$	9.66 (s, 2 H, C*H*O), 7.62 (s, 2 H, vinylic), 7.55–7.07 (m, 10 H, aromatic)
 4	$CDCl_3$	9.96 (s, 2 H, C*H*O), 3.78 (s, 4 H, aliphatic)
 5	$(CD_3)_2CO$	9.70 (s, 2 H, C*H*O), 2.96–2.64 (m, 2 H, bridging C*H*), 2.10–1.10 (m, 8 H, ring protons)
 6	$(CD_3)_2CO$	9.60 (s, 2 H, C*H*O), 1.10 (s, 12 H, CH_3)
 7	$CDCl_3$	9.94 (s, 1 H, C*H*O), 8.10–7.12 (m, 5 H, aromatic), 3.32 (t, J = 6 Hz, 2 H, $-CH_2-$), 2.90 (t, J = 6 Hz, 2 H, $-CH_2-$)
 8	$(CD_3)_2CO$	9.75 (s, 1 H, C*H*O), 2.70 (m, 4 H, $-CH_2CH_2-$), 2.32 (s, 3 H, CH_3)
	CD_2Cl_2	8.00–7.36 (m, 4 H, aromatic), 5.33 (s, 2 H, $-CH_2O-$)[b]
	$(CD_3)_2CO$	8.53–7.55 (m, 6 H, aromatic), 5.57 (s, 2 H, $-CH_2O-$)[c]
	$(CD_3)_2CO$	4.22 (t, J = 7.4 Hz, 2 H, $-CH_2O-$), 2.39–2.12 (m, 4 H, $-CH_2CH_2CO-$)[b]
	$(CD_3)_2CO$	4.28 (m, 1 H, $-CH_2O-$), 3.98 (m, 1 H, $-CH_2O-$), 2.78 (m, 1 H, bridging C*H*), 2.58 (m, 1 H, bridging C*H*), 2.12–1.16 (m, 8 H, ring protons)[d]
	$(CD_3)_2CO$	3.96 (s, 2 H, $-CH_2O-$), 1.04 (s, 6 H, 2 CH_3), 1.00 (s, 6 H, 2 CH_3)
	$(CD_3)_2CO$	7.34 (s, 5 H, aromatic), 5.52 (t, J = 7 Hz, 1 H, $-CH(Ph)O-$), 2.81–1.82 (m, 4 H, $-CH_2CH_2CO-$)[b]

[a] Unless otherwise stated, ^{1}H NMR data recorded at 60 MHz. [b] For previously published spectra, see ref 24. [c] For previously published spectrum, see ref 25. [d] Recorded at 400 MHz.[22]

for 8 min to remove all of the free CO. The mixture was then transferred by a double-ended needle to an NMR tube containing *o*-phthaldialdehyde (1; 1200 mg, 9151 μmol, 310 equiv). The ^{31}P NMR spectra were recorded after both 5 min and 1 week; both contained $[Rh(dcpe)(CO)_2]ClO_4$ as the only detectable species in solution. The ^{1}H NMR spectrum recorded 48 h after mixing showed that 6 turnovers had occurred.

[(Rh(dcpe))$_2$(*o*-phthaldialdehyde)](ClO$_4$)$_2$ (9). [Rh(dcpe)(NBD)]ClO_4 (100 mg, 139.6 μmol) was partially dissolved in acetone (6.0 mL), forming a red-orange solution. H_2 was bubbled through the solution until a straw yellow homogeneous solution resulted.[23] The mixture was cooled to −60 °C and the excess H_2 removed by evacuating the flask and refilling it with argon twice. The mixture was then transferred via a double-ended needle to a −60 °C solution of *o*-phthaldialdehyde (1; 18.93 mg, 141 μmol) in acetone (1 mL), forming a deep red solution. The mixture was warmed to 0 °C over 1 h. Crystallization at 0 °C was induced by the addition of 3 mL of diethyl ether. Two 0.5-mL portions of diethyl ether were added at 30-min intervals. After a further 30 min 2 mL of diethyl ether was added. The mixture was kept for 30 min more at 0 °C; the red-brown crystals were collected under argon. The solid was washed with two 0.5-mL portions of −60 °C acetone and three 1-mL portions of diethyl ether and dried under 0.01 mmHg vacuum; yield 0.083 g (86%). ^{1}H NMR [$(CD_3)_2CO$]: δ 8.07–8.05 (m, 2 H, aromatic), 7.76–7.69 (m, 2 H, aromatic), 7.14–7.13 (br s, 2 H, μ-$\eta^1(O)$-η^2-C*H*O groups), 2.6–0.1 (m, 48 H, dcpe). ^{13}C NMR [$(CD_3)_2CO$]: δ 140.9 (s, aromatic), 132.4 (s, aromatic), 130.7 (s, aromatic), 108.9 (d, J_{Rh-C} = 15.2 Hz, μ-$\eta^1(O)$-η^2-CHO groups). ^{31}P NMR [$(CD_3)_2CO$]: δ 97.2 (dd, J_{Rh-P} = 185.2 Hz, J_{P-P} = 19.9 Hz), 93.0 (dd, J_{Rh-P} = 153.2 Hz, J_{P-P} = 20.1 Hz). IR (CH_2Cl_2): no bands in the carbonyl region and a strong band at 1100.0 cm^{-1}, which may be ClO_4^- stretch. Anal. Calcd for $Rh_2C_{60}H_{102}Cl_2P_4O_{10}$: C, 52.07; H, 7.43; Cl, 5.12; P, 8.95. Found: C, 52.05; H, 7.38; Cl, 5.37; P, 8.36.

Low-Temperature Stoichiometric Reaction of [Rh(dcpe)(acetone)$_2$]ClO$_4$ and *o*-Phthaldialdehyde (1). [Rh(dcpe)(NBD)]ClO_4 (15.0 mg, 21 μmol) in acetone-d_6 (0.6 mL) was hydrogenated as described in the preceding procedure. The ^{31}P NMR spectrum showed that the solution contained only [Rh(dcpe)(acetone)$_2$]ClO_4 (δ 102.3 (d, J_{Rh-P} = 203 Hz)). The mixture was cooled to −78 °C and quickly transferred by double-ended needle to an NMR tube (also cooled to −78 °C) containing *o*-phthaldialdehyde (1; 2.8 mg, 21 μmol). A dark red solution resulted. The tube was removed briefly from the bath (~5 s) for mixing. The ^{1}H NMR spectrum of the solution at −78 °C showed that 68% of the substrate and catalyst had been combined to generate the η^2-η^1 adduct **10**. This adduct is stable for over 18 h at this temperature and was characterized by ^{1}H, ^{13}C, ^{13}C{^{1}H}, and ^{31}P NMR spectroscopy. ^{1}H NMR [$(CD_3)_2CO$]: δ 10.03 (d, J = 9.6 Hz, 1 H, η^1-C*H*O), 8.16–7.78 (m, 4 H, aromatic), 6.94 (br s, 1 H, η^2-C*H*O), 2.6–0.1 (m, 48 H, dcpe). ^{13}C NMR [$(CD_3)_2CO$]: δ 200.46 (s, η^1-CHO), 145.92 (s, Ar*C*- CHO), 138.72 (s, Ar*C*-H), 136.87 (s, Ar*C*-CHO), 132.31 (s, Ar*C*-H), 128.45 (s, Ar*C*-H), 128.09 (s, Ar*C*-H), 62.83 (d, J_{Rh-C} = 13.8 Hz, η^2-CHO), 36.1–25 (m, dcpe). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$]: δ 200.46 (d, J_{H-C} = 187.2 Hz, η^1-CHO), 145.92 (s, Ar*C*-CHO), 138.99 (d, J_{H-C} = 110 Hz, Ar*C*-H), 136.75 (s, Ar*C*-CHO), 132.14 (d, J_{H-C} = 171.35 Hz, Ar*C*-H), 128.43 (d, J_{H-C} = 166.35 Hz, Ar*C*-H), 128.10 (d, J_{H-C} = 160.25, Ar*C*-H), 62.76 (dd, J_{Rh-C} = 14.1 Hz, J_{H-C} = 139.7 Hz, η^2-CHO), 36.1–25 (m, dcpe). ^{31}P NMR [$(CD_3)_2CO$]: broad hump at −78 °C. At −60 °C the peaks sharpened but the material disappeared before a proper spectrum could be obtained; thus, the following data are approximate: δ 93.0 (dd, J_{Rh-P} = 157 Hz, J_{P-P} = 22 Hz), 90.6 (dd, J_{Rh-P} = 173 Hz, J_{P-P} = 20 Hz).

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

(23) Care must be taken not to use a large excess of H_2 at these high [Rh]'s. Otherwise a yellow solid precipitates that we believe to be an oligomer of the formula $([Rh(dcpe)(H)_2]ClO_4)_n$, consisting of hydride bridges.

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