61.2, 61.0 (CO_2CH_2, μ-CHCHR, μ-CHCHRCH), 41.7 (CH_2CH_2C-H_3), 22.4 ($CH_2CH_2CH_3$), 15.1, 14.6, 14.2 (CH_3); IR (CH_2Cl_2) 1985 (s), 1945 (w), 1785 (m), 1750 (w), 1725 (w), 1610 (w) cm^{-1}; HRMS calcd for M - CO $C_{24}H_{30}Fe_2O_6$ 526.0740, found 526.0746. Anal. Calcd for $C_{25}H_{30}Fe_2O_7$: C, 54.18; H, 5.46. Found: C, 54.15; H, 5.69.

$[C_5H_5(CO)Fe]_2(\mu$-CO)$\{\mu$-CHCH[CH(CO_2CH_3)($SO_2C_6H_5$)]-$CH_2CH_2CH_3\}$ (8). A mixture of **6** (200 mg, 0.37 mmol) and the sodium salt of methyl (phenylsulfonyl)acetate (87 mg, 0.37 mmol) in 30 mL of THF was stirred at room temperature for 0.5 h. The solution was filtered, and the THF was evaporated under vacuum. The residue was dissolved in 10 mL of CH_2Cl_2 and addition of hexane precipitated **8**, which was filtered, washed with 5 mL of hexane, and isolated as a red solid (133 mg, 60%). ^1H NMR (200 MHz, CD_2Cl_2): major isomer, δ 12.11 (d, J = 12.1 Hz, μ-CHR), 8.06-7.56 (m, C_6H_5), 4.92 (s, C_5H_5), 4.77 (s, C_5H_5), 3.47 (s, CO_2CH_3), 3.4-1.5 (complex multiplets, μ-CHC*H*($CH_2CH_2CH_3$)C*H*RR'), 0.95 (t, J = 7.3 Hz, CH_3); minor isomer, δ 11.23 (d, J = 11.8 Hz, μ-CHR), 8.06-7.56 (m, C_6H_5), 4.82 (s, C_5H_5), 4.67 (s, C_5H_5), 3.81 (s, CO_2CH_3), 3.4-1.5 (complex multiplets, μ-CHC*H*-($CH_2CH_2CH_3$)C*H*RR'), 1.01 (t, J = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 0.07 M Cr(acac)$_3$): major isomer, δ 271.2 (μ-CO), 212.5, 211.8 (CO), 180.1 (μ-CHR), 166.7 (CO_2CH_3), 141.1 (ipso-C_6H_5), 133.7 (p-C_6H_5), 128.9, 128.3 (o-, m-C_6H_5), 87.9, 87.6 (C_5H_5), 77.2 (μ-CHCHCH), 64.3 (μ-C*H*CH), 52.1 (CO_2CH_3), 40.3 ($CH_2CH_2CH_3$), 21.6 ($CH_2CH_2CH_3$), 14.2 (CH_3); minor isomer, δ 270.5 (μ-CO), 212.1, 211.7 (CO), 175.2 (μ-CHR), 166.0 (CO_2CH_3), 140.3 (ipso-C_6H_5), 133.7 (p-C_6H_5), 129.0, 128.6 (o-, m-C_6H_5), 87.8, 87.5 (C_5H_5), 78.3 (μ-CHCHCH), 59.4 (μ-C*H*CH), 52.3 (CO_2CH_3), 39.2 ($CH_2CH_2CH_3$), 22.3 ($CH_2CH_2CH_3$), 14.6 (CH_3). IR (CH_2Cl_2): 1978 (s), 1939 (w), 1782 (m), 1745 (w) cm^{-1}. HRMS: calcd for M - CO $C_{26}H_{28}Fe_2O_6S$ 580.0305, found 580.0268.

$[C_5H_5(CO)Fe]_2(\mu$-CO)$(\mu$-CHCH_2CH_3) (10)[1]. A clear solution of Li(CH_3CuCN) prepared by stirring CH_3Li (0.17 mmol) and CuCN (16 mg, 0.18 mmol) in THF at -20 °C was cooled to -78 °C and added to a stirred suspension of **1** (75 mg, 0.15 mmol) in THF (20 mL) at -78 °C. The mixture was stirred for 1 h at room temperature, and the THF was evaporated under vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, diethyl ether) to give **10** as a red solid (56 mg, 100%): ^1H NMR (270 MHz, acetone-d_6) δ 11.86 (t, J = 8.3 Hz, μ-CHR), 4.85 (s, 10 H, C_5H_5), 3.10 (dq, J = 8.1, 7.2 Hz, μ-CHCH_2), 1.47 (t, J = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M Cr(acac)$_3$) δ 273.1 (μ-CO), 214.4 (CO), 182.1 (μ-CHR), 88.2 (C_5H_5), 50.3 (μ-CHCH_2), 20.8 (CH_3).

$[C_5H_5(CO)Fe]_2(\mu$-CO)$[\mu$-CHCH(CH_3)$CH_2CH_2CH_3$] (12). A solution of Li(CH_3CuCN) prepared from CH_3Li (0.40 mmol) and CuCN (40 mg, 0.44 mmol) in THF at -20 °C was added by syringe to a stirred suspension of **6** (200 mg, 0.37 mmol) in THF (20 mL) at -78 °C. THF was evaporated under vacuum, and the residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, diethyl ether) to give **12** as a red solid (149 mg, 98%): ^1H NMR (270 MHz, CD_2Cl_2) δ 11.64 (d, J = 11.4 Hz, μ-CHR), 4.73 (s, 10 H, C_5H_5), 2.5-1.4 (multiplets, μ-CHC*H*-(CH_3)C$H_2CH_2CH_3$), 1.47 (d, J = 6.3 Hz, μ-CHCHCH_3), 0.97 (t, J = 7.2 Hz, $CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M Cr(acac)$_3$) δ 273.1 (μ-CO), 214.4 (CO), 188.2 (μ-CHR), 88.3 (C_5H_5), 58.0 (μ-C*H*CH), 45.5 ($CH_2CH_2CH_3$), 25.6 (CH_3), 21.4 ($CH_2CH_2CH_3$), 14.6 (CH_3); IR (CH_2Cl_2) 1974 (s), 1933 (w), 1772 (m) cm^{-1}; HRMS calcd for $C_{19}H_{22}Fe_2O_3$ 410.0267, found 410.0253.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged.

Registry No. **1**, 87858-04-6; **2**, 112840-90-1; **3**, 112840-91-2; **4**, 66323-99-7; **5**, 112840-92-3; **6**, 112924-67-1; **7**, 112840-93-4; **8** (isomer 1), 112840-97-8; **8** (isomer 2), 112924-68-2; **9**, 112840-94-5; **10**, 112840-95-6; **12**, 112840-96-7; $(C_4H_9)_4N^+F^-$, 429-41-4; Li(CH_3CuCN), 41753-78-0; sodium diethyl malonate, 51923-79-6; sodium methyl(phenylsulfonyl)acetate, 60729-65-9.

Homogeneous Catalysis. Conversion of 4-Pentenals to Cyclopentanones by Efficient Rhodium-Catalyzed Hydroacylation

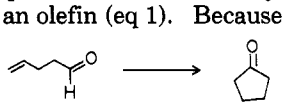
David P. Fairlie and B. Bosnich*

The Lash Miller Chemical Laboratories, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 1A1

Received October 30, 1987

A variety of complexes of the type [Rh(diphosphine)]$^+$ have been investigated as catalysts for hydroacylation, the intramolecular cyclization of 4-pentenals to cyclopentanones. All of the complexes studied effect this conversion in weakly or noncoordinating solvents at 20 °C, but the most effective catalyst was found to be the rhodium(I) species containing diphos ($(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$). This complex converts 4-pentenal at a remarkably fast rate of one turnover every 6 s at 20 °C in CH_3NO_2 and CH_2Cl_2 solutions. These catalysts are effective for 4-pentenals bearing mono substituents at the 2-, 3-, 4-, and 5-positions and disubstitution at the 3-position. Disubstitution at the 2-position slows the rate and effectiveness of catalysis considerably, and substrates having disubstitution at the terminal 5-position are not turned over by these catalysts. For the diphos catalyst, between 100 and 800 rapid turnovers are observed at 1 molar percent catalyst depending on the substrate. After this, the catalysis becomes sluggish because of substrate decarbonylation leading to the catalytically inactive [Rh(diphos)(CO)$_2$]$^+$ species. Even when the dicarbonylated species is present, catalysis continues because of substrate-induced dissociation of the carbonyl ligands. Unlike the case of hydroacylation with the [Rh(PPh_3)$_3$Cl] complex no cyclopropanes are produced with these catalysts. Double-bond migration is a competing reaction, the extent of which depends on the substrate and the diphosphine catalyst, but in general it is a minor side reaction and it is not rate-limiting.

Hydroacylation, a process having no direct organic analogy, can be induced by certain rhodium(I) complexes. The most extensively investigated form of this reaction involves the intramolecular addition of the hydrogen atom and the acyl group derived from an aldehyde moiety to the carbon atoms of an olefin (eq 1). Because hydroacylation



(1)

involves the activation of carbon-hydrogen bonds and their

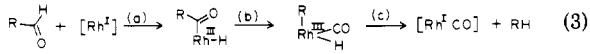
* To whom correspondence should be addressed at the Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637.

0276-7333/88/2307-0936$01.50/0

transfer to the atoms of a multiply bonded fragment, it potentially belongs to a family of reactions that may be referred to as hydrocarbonation. Such a class of reactions would involve the activation of any type of carbon–hydrogen bond and the transfer of the separated entities to a multiple bond by either an intra- or intermolecular process. The realization of *catalytic* reactions of this kind would provide distinctly new synthetic methods of wide applicability. It is because of our interest in this general class of reactions that we sought to investigate intramolecular catalytic hydroacylation. This paper describes our development of this reaction, and the following one deals with the mechanism of the catalytic process.

Hydroacylation has its origins in the observation of Tsuji[1] that aldehydes were decarbonylated by Wilkinson's catalyst (eq 2). The mechanism of decarbonylation is believed to involve the steps shown in eq 3. That al-

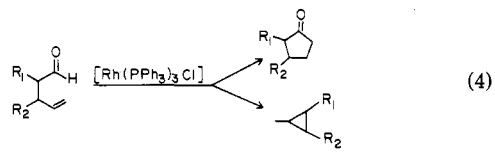
$$[Rh(PPh_3)_3Cl] + RCHO \longrightarrow RH + \underline{trans}\text{-}[Rh(PPh_3)_2CO(Cl)] + PPh_3 \quad (2)$$



(3)

dehydes are susceptible to oxidative addition (step a) was later demonstrated by Suggs,[2] who isolated and characterized the hydrido–acyl product of addition of 8-quinolinaldehyde to Wilkinson's complex. The subsequent steps, acyl decarbonylation (step b) and hydride insertion into a rhodium–carbon bond (step c), are well known.

The presence of the hydrido–acyl intermediate in the decarbonylation mechanism suggests the possibility of intramolecular hydroacylation of 4-pentenals. This was first observed by Sakai[3] using Wilkinson's catalyst. The reaction, however, was stoichiometric, giving 30% yield of the cyclopentanone and 30% yield of the cyclopropane (eq 4). Later, Miller[4] demonstrated that the cyclization was



(4)

in fact marginally catalytic and that the turnover could be extended under ethylene pressure. Following Miller's work, Larock[5] showed that a variety of substituted 4-pentenals were turned over by Wilkinson-type catalysts. Although they were able to observe catalysis, the reactions ceased after a few turnovers due to the formation of the catalytically inactive carbonyl complex. Finally, the incisive labeling experiments of Miller[4] and the investigations of Milstein[6] clearly indicated the general outlines of the mechanism of hydroacylation. This is shown in Figure 1.

It is clear, therefore, that if this important catalytic reaction is to be made more efficient a different approach has to be adopted.

Strategy

As in all catalysis the outcome is determined by the relative rates of the individual catalytic steps and our

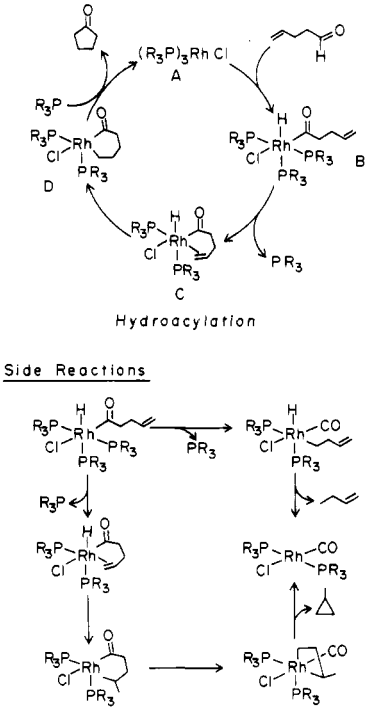
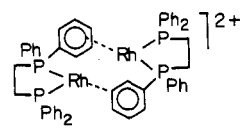


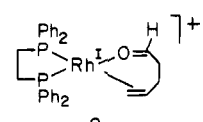
Figure 1. The proposed mechanism of hydroacylation of 4-pentenal using the $[Rh(PPh_3)_3Cl]$ catalyst and the mechanisms associated with the production of butenes, cyclopropanes, and the inactive species $[Rh(PPh_3)_2(CO)Cl]$.

strategy relies on increasing the rates of the hydroacylation steps over the rates of the competing steps that lead to side products (Figure 1). The three main steps in catalytic hydroacylation are oxidative addition (A → B), olefin insertion (C → D), and reductive elimination (D → A). In order to accelerate these steps, we rely on the effects of coordination unsaturation. It was for this reason that we chose the dimeric rhodium(I) complexes $[Rh_2(diphosphine)_2]X_2$ (X = noncoordinating anion). The dimeric diphos (1,2-bis(diphenylphosphino)ethane) complex exists as the phenyl-bridging dimer **1** in the solid state[7] and in



1

some noncoordinating solvents but as the disolvento monomer $[Rh(diphos)(solvent)_2]^+$ in coordinating solvents such as acetone or methanol. Upon addition of the 4-pentenal substrate, we expect that the dimer will split or that the weakly coordinated solvent molecules will be displaced to give the species **2** resembling the adducts formed with amino acid precursors.[8] The adduct **2** is



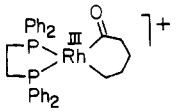
2

ideally setup for oxidative addition across the aldehyde C–H bond because of the proximal assistance of coordi-

(1) Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1965**, 3669.
(2) Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640; **1979**, *101*, 489.
(3) Sakai, K.; Ido, J.; Oda, O.; Nakamura, N. *Tetrahedron Lett.* **1972**, 1287.
(4) Lachow, C. F.; Miller, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 1281. Campbell, R. E.; Lachow, C. F.; Krishnakant, P. V.; Miller, R. G. *Ibid.* **1980**, *102*, 5824. Campbell, R. E.; Miller, R. G. *J. Organomet. Chem.* **1980**, *186*, C27.
(5) Larock, R. C.; Oertle, K.; Potter, G. *J. Am. Chem. Soc.* **1980**, *102*, 190.
(6) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1357.
(7) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055.
(8) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chim. Acta* **1979**, *37*, 2477.

nated olefin and the coordination unsaturation of the rhodium atom.[9,10] Further, we do not expect the positive charge of the complex to significantly retard C–H activation because the analogous complex $[Rh(PPh(CH_3)_2)_2(acetone)_2]^+$ rapidly decarbonylates aliphatic aldehydes.[11]

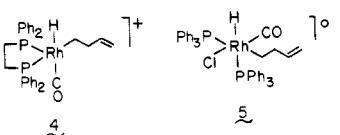
Since in the hydrido–acyl intermediate the alignment of the metal–hydride bond and the coordinated olefin is favorable, we expect hydride transfer to the coordinated olefin to be a rapid process[12] giving the metallocyclohexanone **3**. Because this intermediate is coordinatively



3

unsaturated, we expect that reductive elimination will be very rapid. The precise reasons for accelerated reductive elimination upon coordination unsaturation of rhodium(III) phosphine complexes remains to us obscure, but it is a recurring observation and it has been demonstrated for hydroacylation.[6] Thus we expect that as compared to Wilkinson's catalyst, the [Rh(diphosphine)]$^+$ catalyst will lead to more rapid oxidative addition, rapid hydride insertion, and more rapid reductive elimination.

Although coordination unsaturation is also one of the characteristics necessary for rapid decarbonylation of metal–acyl bonds,[12] we, nonetheless, expect it to be less pronounced for the [Rh(diphosphine)]$^+$ species than for the $[Rh(PPh_3)_3Cl]$ catalyst because of the accelerated hydroacylation steps of the former and also for the following reasons. The metal–carbonyl bond of the two putative decarbonylated intermediates **4** and **5**, derived from



4 **5**

[Rh(diphosphine)]$^+$ and $[Rh(PPh_3)_3Cl]$, respectively, is expected to be less stable in **4** than in **5** because the former bears a positive charge. This is not to suggest that the insertion and deinsertion rates of the [Rh(diphosphine)]$^+$ catalysts (**4** ⇌ **3**) will not be rapid but rather that the positive charge will stabilize **3** over **4**. This is consistent with the observation of "oxidatively induced migratory insertion".[13] This suppression of decarbonylation may also lead to the suppression of cyclopropane side products (Figure 1, side reactions).

Finally, the [Rh(diphosphine)]$^+$ catalysts present a new complication, which has not been reported for Wilkinson's complex. These diphosphine complexes are known to be effective in double-bond migration,[14] and this process could compete with hydroacylation. We show, however, that for most 4-pentenals, double-bond migration is much slower than hydroacylation and that the double-bond-migrated products do not interfere with catalysis.

Substrates and Catalyst Precursors

The 4-pentenals were generally prepared by Claisen rearrangement of the corresponding allyl vinyl ethers[15] which were derived from the Hg^{2+}-catalyzed vinylation of allyl alcohols.[16] Although these procedures can be tedious for the lower boiling 4-pentenals, they produce clean products in reasonable overall yields (20–30%). the alternative method involving chromium oxidation of the 4-pentenols[17] is more cumbersome and tends to give lower yields, and the products, although pure by ^1H NMR, are contaminated by trace amounts of the corresponding acids. These impurities poison the catalyst. Removal of these impurities requires careful chromatography over silica gel.

The air-stable catalyst precursor $[Rh(diphos)]_2(ClO_4)_2$[7] was isolated from the hydrogenation of a methanol suspension of $[Rh(diphos)(NBD)]ClO_4$;[18] after a few hours the orange suspension had turned yellow, indicating the formation of the dimeric product. In solution the catalyst is moderately air-sensitive and displays different characteristics according to the solvent used for dissolution.

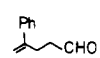
When dissolved in acetone at 11 mM in [Rh], the dimer partly dissociates to the disolvento monomer $[Rh(diphos)(acetone)_2]^+$ with about 10% remaining as the dimer. At the concentrations used for catalysis, about 10^{-3} M in [Rh], essentially all of the catalyst is in the form of the diacetonato monomer. In CH_2Cl_2 solution, the ^{31}P NMR spectrum shows a single species with equivalent phosphorus atoms and the ^1H NMR spectrum shows the absence of bridging arene groups. In view of the low coordinating power of CH_2Cl_2, we propose that the complex exists as a monomer containing a bidentate perchlorato ligand, $[Rh(diphos)ClO_4]$. The BF_4^- salt exists as a dimer in CH_2Cl_2 solutions. In CH_3NO_2 solutions, the ^{31}P NMR spectra of the catalyst precursor shows inequivalent phosphorus atoms indicating that the species retains its dimeric form in CH_3NO_2 at concentrations of ≥1 mM in [Rh]. The dimeric formulation is also indicated by the appearance of upfield ^1H NMR resonances for the bridging coordinated phenyl rings and by the ^{13}C NMR spectrum that shows two sets of eight-line signals for two inequivalent methylene carbons and a number of aromatic carbon atoms displaced to higher field. Both ^{31}P and ^1H NMR spectra show that, in CH_3NO_2 solutions, two dimeric species exist in the ratio of 7:1. We ascribe these species to the meso and racemic isomers of the dimer which arise from the fact that the phosphorus atoms bearing the bridging phenyl groups are chiral. Thus the dimer may exist as a *R,R* (or *S,S*) pair (racemic) or as a *R,S* pair (meso). These same species in the three solvents can be generated by hydrogenating solutions of $[Rh(diphos)NBD]ClO_4$. No hydrides were detected. The NMR data are collected in Table II and in the Experimental Section.

Catalytic Results

For catalytic hydroacylation, the catalyst could be generated in situ by hydrogenation of the $[Rh(diphos)NBD]ClO_4$ complex, or alternatively the isolated dimer $[Rh(diphos)]_2(ClO_4)_2$ could be used with the same results. The reported data refer to catalytic solutions made from the isolated dimer. Catalysis of the 4-pentenal substrate is highly sensitive to the solvent used at 20 °C. Thus in

(9) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
(10) Crabtree, R. H.; Lavin, M. E.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 1986. Crabtree, R. H.; Lavin, M. E. *J. Chem. Soc., Chem. Commun.* **1985**, 794 and references therein.
(11) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.
(12) Wojcicki, A. *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1973, Vol. 11, p 87.
(13) Wong, P. K.; Madhavaroa, M.; Marteu, D. F.; Rosenblum, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 2828.
(14) Tami, K.; Yamagata, T.; Akutagawa, S.; Kimobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.
(15) Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 6556.
(16) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828.
(17) Novak, L.; Bäan, G.; Marosfalvi, J.; Szäntay, C. *Chem. Ber.* **1980**, *113*, 2939.
(18) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

Table I. Catalyst[a] Efficiency and Substrate Specificity for Cyclization of 4-Pentenals

	Substrate	% Rh[b]	% Products; CD_3NO_2 (CD_2Cl_2) Ketone[c]	Aldehydes[d]	Olefins[e]	% Conversion[f]	Turnover Rate[g]
1.		1 (1)	 95 (95)	4 (5)	0.7 (0.3)	100 (100)	2.7×10^{-1} (3.3×10^{-1})
2.		1 (2)	 88 (89)	10 (9)	2 (2)	100 (100)	3×10^{-4}
3.		1 (1)	 98 (98)	0.5 (1)	1.5 (1)	100 (100)	(2.1×10^{-1})
4.		1 (1)	 98.5 (98)	0.5 (1)	1 (1)	100 (100)	6×10^{-2} (5×10^{-2})
5.		4	 89	7	4	89	2.6×10^{-5} [h]
6.		7 (7)	 25 (28)	68 (66)	7 (6)	89 (83)	(3.7×10^{-3})[i]
7.		1 (1)	 100 (100)	0 (0)	0.1 (0)	100 (100)	2.7×10^{-1}
8.		50 (50)	 0 (0)	0 (0)	0 (0)	0 (0)	—
9.		2 (2)	 92 (96)	4 (3)	4 (1)	100 (100)	(8.7×10^{-3})[i]
10.		10	 70	7	23	80	9.3×10^{-6} [h]
11.		1 (2)	 88 (92) cis/trans: 35/65[j]	10 (6)	2 (2)	100 (100)	8.8×10^{-2}[i] (3.6×10^{-2})
12.		2 (2)	 94 (95) cis/trans: 42/58 (66/34)[k]	4 (3)	2 (2)	100 (100)	1.2×10^{-1}
13.		2 (3)	 30 (29)	65[l] (64)[l]	5	100 (100)	(2.2×10^{-1})[i]

[a] $[Rh(dppe)]_2(ClO_4)_2$. [b] (mol of Rh/mol of substrate) × 100. Data in parentheses are for CD_2Cl_2. [c] Determined by GC (for CD_3NO_2) and 400-MHz ^1H NMR spectra. Identification was aided by ^{13}C NMR spectra (Table IV). [d] Identified (mainly 3-pentenals) and quantified by 400-MHz ^1H NMR using phenyl protons (20) of catalyst (% Rh known) as internal reference. [e] Derived from GC data. [f] % substrate consumed, deduced from ^1H NMR spectra. [g] Mol of substrate consumed/mol of Rh/s (20 °C) for 50% conversion. [h] 65 °C. [i] 35 °C. [j] Stereochemistry deduced from ^{13}C NMR spectrum. [k] Stereochemistry deduced from ^1H NMR spectra. [l] Unknown product.

CH_3CN solution no catalysis was observed presumably because of the formation of the catalytically inactive species $[Rh(diphos)(CH_3CN)_2]^+$. In methanol solutions the catalysis was severely suppressed because the substrate formed the catalytically inactive hemiacetal. In acetone solution about 20 rapid turnovers were observed before decarbonylation caused the formation of the catalytically inactive $[Rh(diphos)(CO)_2]^+$ species. After the formation of the dicarbonyl species, the hydroacylation continued but at a slower rate. We found, however, that in the CH_3NO_2 and CH_2Cl_2 solvents the catalysis proceeded quickly and with high efficiency.

As we show in the next paper, the turnover rate and turnover number depend on both the ratio of the substrate to catalyst and on the dilution at the same ratio. For consistency we have usually used a catalyst concentration of 1 mM in [Rh] and 100 mM in [substrate]. Using 1 mol % Rh and 4-pentenal in either CH_3NO_2 or CH_2Cl_2 solutions at 20 °C all of the substrate is consumed in 6 min. This represents a turnover rate of about 3×10^{-1} s^{-1} or one turnover every 6 s which is remarkably fast. The yield of cyclopentanone is 95%, and the rest is side products. These consist of double-bond migration of 4-pentenal to 3-pentenal (~4%) and to butenes (~0.7%) which result from decarbonylation. The amount of butene was determined by GC and of 3-pentenal by ^1H NMR. The presence of $[Rh(diphos)(CO)_2]^+$ after 100 turnovers was confirmed by IR [ν_{CO} 2100 (CH_2Cl_2), 2055 cm^{-1} (CH_3NO_2)] and by ^{31}P NMR.

Table I collects the data obtained for the hydroacylation of a variety of 4-pentenal substrates in CH_2Cl_2 and CH_3NO_2 solutions using the $[Rh(diphos)]^+$ catalyst. Included are the yields of the corresponding cyclopentanones and the amounts of decarbonylation and double-bond migration as well as the turnover numbers. Entries 2–5 serve to illustrate the effect of a single methyl group substituent in the various positions. Substituents at the 3- and 4-positions (entries 3 and 4) have little effect on the turnover rate or the yield compared to the parent 4-pentenal, whereas a substituent at the 2-position (entry 2) slows the turnover rate and increases the amount of double-bond migration. A single substituent at the 5-position (entry 5) slows the turnover rate even more drastically; these results refer to 65 °C and at 4% catalyst loading. *gem*-Dimethyl substitution (entries 6–8) exaggerates the steric inhibition when the two methyl groups are in the 2- and 5-positions; the latter (entry 8) gave no product even at 50% catalyst loading and the former (entry 6) generated large amounts of double-bond migration. *gem*-Dimethyl substitution at the 3-position (entry 7), however, caused no decrease in turnover rate and gave the highest yield of the product. It is intriguing that entry 8 did not decarbonylate even after extended periods at 20 °C. Decarbonylation can be induced if the catalytic solution is heated. Phenyl substituents (entries 9 and 10) follow a similar pattern to that observed for the corresponding methyl-substituted substrates. Entries 11 and 12 serve to elicit the stereoselectivity of hydroacylation. The $[Rh(diphos)]ClO_4$ catalyst shows little selectivity, and, in the case of entry 12, the selectivity is reversed upon changing from CH_2Cl_2 to CH_3NO_2 as solvents. Finally, the styrene substrate (entry 13) was expected to cyclize rapidly. It does, but the catalysis is accompanied by large amounts of unidentified side products that we suspect arise from catalyst-induced polymerization of the styrene.

Taken as a whole these results demonstrate that the $[Rh(diphos)]ClO_4$ complex is a highly efficient catalyst for the hydroacylation of 4-pentenals bearing monosubstitution in the 2-, 3-, and 4-positions and for disubstitution at the 3-position. Compared to the Wilkinson-type catalysts, the present catalyst is cleaner and is orders of magnitude faster.

Decarbonylation and Turnover Number

Although we reserve a detailed discussion of decarbonylation for the following paper, we present here some practical observations. After 100 turnovers, 4-pentenal has decarbonylated to the extent of consuming about half of the catalyst as the inactive complex $[Rh(diphos)(CO)_2]^+$ (Table I). Thus we would expect a total of about 200 turnovers before the catalyst is fully carbonylated. Indeed we find that 4-pentenal undergoes between 200 and 300 turnovers before the turnover rate becomes very slow. After 300 turnovers catalysis continues but at a rate which is at least 2 orders of magnitude slower than the initial rate. This residual catalytic activity which occurs after full carbonylation of the catalyst suggests that the CO ligands of $[Rh(diphos)(CO)_2]^+$ dissociate in the presence of excess of substrate to regenerate the active catalyst. As the amount of CO increases, however, so the turnover rate attenuates. For the substrate in entry 7 it was possible to obtain about 800 turnovers at a rate comparable to that given in Table I and a further 400 turnovers at a somewhat slower rate before catalysis essentially ceased. For most

of the 4-pentenals, the $[Rh(diphos)]^+$ catalyst in CH_2Cl_2 and in CH_3NO_2 solutions was found to produce between 100 and 1000 turnovers at an acceptable rate at 20 °C in a closed system.

Other Catalysts

Given the inhibiting effect of decarbonylation with the $[Rh(diphos)]^+$ catalyst, we investigated other diphosphine catalysts in order to determine if the turnover number could be increased. Since the turnover number depends on the relative rates of hydroacylation and of decarbonylation, we attempted to find catalysts which, relative to $[Rh(diphos)]^+$, either increased the rate of hydroacylation or decreased the rate of decarbonylation. We assume that more basic phosphines will increase the rate of hydroacylation whereas less basic phosphines will decrease this rate. It was recognized, however, that more basic phosphines will also tend to bind CO to rhodium more tightly and that it may not be possible to increase the hydroacylation rate without simultaneously increasing the decarbonylation rate. It was because of this possible correlation between hydrocarbonylation and decarbonylation rates that we investigated catalysts with increased chelate ring size; increases in chelate ring size increase the rates of catalytic hydrogenation.[19]

With these considerations in mind we investigated catalysts incorporating the following phosphines: dppp ($Ph_2P(CH_2)_3PPh_2$), dppb ($Ph_2P(CH_2)_4PPh_2$), dcpe ($(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$), dptf ($(p\text{-}CF_3C_6H_4)_2P(CH_2)_2P(C_6H_4CF_3\text{-}p)_2$), dpf ($(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2$).

The catalyst precursors of these diphosphine complexes were generated in solution by the addition of H_2 to the [Rh(diphosphine)NBD]ClO_4 complexes. In acetone solutions all of the complexes generate the $[Rh(diphosphine)(acetone)_2]^+$ ions; no hydrides were detected even after prolonged treatment with H_2. In CH_3NO_2 solutions, addition of H_2 gave a variety of product types depending on the nature of the diphosphine. The dppp and dppb complexes gave arene-bridging dimer complexes which, like the diphos analogue, exist as two diastereomeric forms. The two fluorinated diphosphine ligands, dptf and dpf, gave monomeric complexes, whereas the dcpe complex gave hydrido complexes containing both terminal and bridging hydrides that were formed even when less than stoichiometric amounts of H_2 were added in CH_3NO_2 solutions. These hydrido–dcpe complexes are, however, catalytically active for hydroacylation presumably because the substrate is hydrogenated initially. Similar patterns are observed for hydrogenation of the $[Rh(diphosphine)(NBD)]^+$ complexes in CH_2Cl_2 solutions including the formation of dimers for the dppp and dppb complexes which is not observed in CH_2Cl_2 solutions for the analogous diphos species. These conclusions are implicit in the NMR data collected in Table II where it will be noted that, for the $[Rh(diphosphine)L_2]^+$ ions, the coupling constant (J_{Rh-P}) correlates with the strength of binding of the ligand trans to phosphorus; the stronger the binding of L to Rh, the lower the value of J_{Rh-P}.[20]

The results of catalytic hydroacylation of 4-pentenal in CH_3NO_2 solution are collected in Table III. The turnover rates refer to approximately 50% of reaction because, at this stage, most catalysts are partly or fully carbonylated; thereafter, the turnover rate continuously diminishes even though the reactions go to completion in many cases. For comparison we included Miller's[4] data for the $[Rh(PPh_3)_3Cl]$ catalyst in $CHCl_3$ solution under 4 atm of ethylene, a condition which gives the highest turnover number for this catalyst. Also included are the results for the NBD and for the chloro-bridged dimer complexes of diphos. Both of these catalytic reactions are slow because, we believe, both are four-coordinate complexes that require either dissociation of the NBD ligand or chloro-bridged splitting before catalysis can occur. These processes are more difficult for these complexes than for the arene-bridged dimers. Increasing the chelate ring size reduces the overall efficiency of catalysis. The dppb catalyst decarbonylates at a comparable rate to hydroacylation, and the rate of double-bond migration is comparable to the rate of decarbonylation. The smaller ring size dppp catalyst causes less decarbonylation and less double-bond migration than the dppb catalyst, and, at 5% [Rh] loading, a 90% yield of cyclopentanone is obtained. Neither of these catalysts is as efficient as the diphos analogue.

As expected, the dcpe catalyst has the fastest turnover rate of all catalysts examined; we estimate that the initial hydroacylation turnover rate is at least 20 times faster than that of the diphos analogue. This increase in hydroacylation rate, however, is also accompanied by an increase in the decarbonylation rate. Thus after about 20 turnovers the dcpe catalyst is fully carbonylated as $[Rh(dcpe)(CO)_2]^+$. Despite this, the dcpe catalyst continues to turnover at a convenient rate because of its high intrinsic rate after substrate-induced carbonyl dissociation. As the amount of CO builds up so the rate of hydroacylation becomes progressively slower. Little double-bond migration is observed with this catalyst.

Consistent with their lower electron donation the two fluorinated diphosphine catalysts decrease the rate of hydroacylation compared to the diphos analogue, the perfluoroarylphosphine being the slower. The ratio of rates of hydroacylation and of decarbonylation of these two catlaysts is about the same as for the diphos catalyst; the fluorinated diphosphine catalysts are slower versions of the unfluorinated species. Thus we have not succeeded in diverging the rates of hydroacylation and of decarbonylation with the dcpe and fluorinated catalysts; the two rates respond in the same direction and roughly in unison.

Finally, the analogous $[Rh(PPh_2CH_3)_2(acetone)_2]^+$ complex was examined to determine whether chelation was an important factor in hydroacylation. It clearly is, for we observed no hydroacylation with this catalyst. Instead we observed rapid double-bond migration of 4-pentenal to 3-pentenal. After a number of days further migration of the 3-pentenal to the 2-pentenal occurred. We could not detect any hydrides in the complex, and we presume that for this and the other catalysts double-bond migration is induced via a π-allyl mechanism.

Discussion

We have developed a vary rapid, efficient, and practical catalytic synthesis of cyclopentanones from 4-pentenals at 20 °C. For many of the substrates catalytic loadings of 1 molar percent suffice because of the high catalytic turnover rate. There is minimal competition from side reactions for the most successful catalyst $[Rh(diphos)]^+$. This catalyst is readily isolated and conveniently stored as its relatively air-stable dimer, $[Rh(diphos)]_2^{2+}$. With use of this complex in noncoordinating solvents, cyclopentanones are efficiently prepared from 2-, 3-, 4-, and 5-monosubstituted 4-pentenals as well as multisubstituted

(19) Landis, C. R.; Halpern, J. *J. Organomet. Chem.* **1983**, *250*, 485.
(20) (a) Mather, G. G.; Pidock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095. (b) Pidock, A. In *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. C., Meck, D. W., ACS Symposium Series 196; American Chemical Society: Washington, DC, 1982; p 1.

Table II. ^{31}P NMR Data (δ^a (J_{Rh-P}, J_{P-P}, Hz)) for Rhodium(I) Complexes of Chelating Diphosphines

complex[b]	solvent: acetone	CH_3NO_2	CH_2Cl_2
[Rh(diphos)NBD]$^+$	60.5 (157)	58.2 (157)	57.3 (157)
+ ≥ $2H_2$	83.5 (201)	81.5 (217, 36)[c-e]	71.3 (170)[c]
		79.4 (196, 36)[c-e]	
[Rh(diphos)]$_2^{2+}$	83.5 (201)	81.5 (217, 36)[c-e]	71.3 (170)[c]
		79.4 (196, 36)[c-e]	
+ ≥ 4CO	65.6 (121)[l]	62.8 (121)[l]	
[Rh(dppp)NBD]$^+$	19.6 (147)	17.2 (151)	15.9 (151)
+ ≥ $2H_2$	42.2 (186)	31.9 (203, 65)[c,e,f]	30.3 (202, 63)[c,e,g]
		31.0 (185, 65)[c,e,f]	30.2 (185, 63)[c,e,g]
+ ≥ 2 H_2 + ≥ 2CO	8.4 (112)[l]		
[Rh(dppb)NBD]$^+$	31.7 (154)	29.6 (154)	28.6 (154)
+ ≥ $2H_2$	54.3 (194)	43.0 (200)	41.0 (191, 57)[c,e,i]
		47.2 (208, 55)[c,e,h]	42.5 (207, 57)[c,e,i]
		41.0 (192, 55)[c,e,h]	
+ ≥ $2H_2$ + ≥ 2CO	25.4 (118)[l]		
	33.8 (80)		
[Rh(dcpe)NBD]$^+$	74.8 (153)	72.3 (156)	71.2 (153)
+ ≥ $2H_2$	102.3 (203)	87.3 (137, 7)[j]	95.5 (133, 16)[j,k]
		70.4 (117)	95.4 (132, 15)[j,k]
+ ≥ $2H_2$ + ≥ 2CO	90.0 (118)[l]		
[Rh(dpf)NBD]$^+$	25.5 (165)	23.3 (168)	22.2 (166)
+ ≥ $2H_2$	50.2 (212)	48.6 (216)	47.8 (215)
+ ≥ $2H_2$ + ≥ 2CO	27.2 (135)[l]		28.7 (132)[l]
[Rh(dptf)NBD]$^+$	61.4 (156)	59.0 (159)	57.8 (158)
+ ≥ $2H_2$	84.5 (202)	82.4 (205)	81.7 (207)
		79.5 (206)	
+ ≥ $2H_2$ + ≥ 2CO	66.7 (119)[l]		62.2 (122)[l]
[Rh(dmpe)NBD]$^+$	41.2 (155)		
+ ≥ $2H_2$	62.1 (199), 43.6 (92)		
	40.1 (124)		
+ ≥ $2H_2$ + ≥ 2CO	48.9 (113), 45.2 (116)		
	41.8 (81)		
[Rh(PPh_2CH_3)$_2$NBD]$^+$	17.6 (156)		
+ $2H_2$	41.2 (196)		
+ ≥ $3H_2$	27.8 (118)		

[a] Versus external 85% H_3PO_4. [b] Perchlorate salts. [c] No hydrides in ^1H NMR spectrum. [d] Minor diastereomer at δ 78.0 (196, 36) and 83.2 (217, 36). [e] Ratio of major:minor = 88:12. [e] Phosphorus attached to bridging arene ring, established by additional smaller coupling to rhodium through ring. [f] Second diastereomer at δ 28.9 (183, 65), position of bridging phosphorus obscured. Ratio of diastereomers ≈ 1:1. [g] Second diastereomer at δ 27.9 (201, 63)[e] and 27.8 (184, 63). Ratio "first":"second" diastereomers = 1:1. [h] Monomer:dimer (single diastereomer) = 74:26. [i] Minor diastereomer at δ 46.7 (210, 53)[e] and 39.7 (191, 55). Ratio of major:minor = 68:32. [j] Hydrides were detected by ^1H NMR in regions typical of terminal (~−8 ppm) and bridging (~−20 ppm) hydrides. [k] Major product of at least six detected. [l] [Rh(P⌒P)-$(CO)_2$]$^+$.

4-pentenals, except those which are disubstituted in the 2- or 5-positions. For these last two types of substrates steric hinderance appears to impede catalysis, particularly for disubstitution at the 5-position for which no catalysis was observed.

Compared to the previously employed complex [Rh-$(PPh_3)_3Cl$], the diphos analogue is about 10^3 times faster in turning over 4-pentenals. Moreover, in the absence of ethylene, the [Rh$(PPh_3)_3Cl$] species is barely catalytic whereas, depending on the substrate, the diphos catalyst generally gives between 100 and 800 rapid turnovers at 1 mM [Rh] before carbonylation retards, but does not extinguish, catalysis. By contrast the Wilkinson analogue is completely inactive upon monocarbonylation. Finally, the diphos catalyst produces no cyclopropanes whereas the triphenylphosphine complex gives comparable amounts of cyclopropane and cyclopentanone.

These results are in general conformity with the considerations given in the strategy section and indicate that coordination unsaturation and the forced cis arrangement of the phosphines through chelation are crucial factors favoring the present catalysts over those described previously. The precise reasons for this contrasting behavior require a detailed understanding of the mechanism of hydroacylation. This is addressed in the following paper.

Experimental Section

All preparations and reactions of rhodium complexes were performed under Ar by using gas-tight syringes and double-ended needles. Complexes were stored under Ar at −10 °C in glass vials, with plastic caps, wrapped with parafilm, and were stable for several months except where noted. Except for certain routinely dried solvents, CH_2Cl_2 (CaH_2), THF (Na/benzophenone), and diethyl ether ($LiAlH_4$), all solvents and chemicals were distilled or recrystallized once prior to use. Deuteriated solvents were used as supplied (Aldrich). Routine ^1H NMR spectra and reported kinetic data were measured on Varian T-60 and XL-200 spectrometers. Reported NMR data (^1H, ^{13}C, ^{31}P) were derived from spectra recorded on a Varian XL-400 spectrometer. ^1H and ^{13}C NMR chemical shifts are in parts per million downfield from TMS. ^{13}C resonances were assigned on the basis of APT and DEPT experiments. ^{31}P NMR chemical shifts were measured relative to external 1% $P(OCH_3)_3$ in benzene but are reported relative to 85% H_3PO_4 (converted by adding 140.4 ppm). GLC analyses were executed on a Varian 2700 gas chromatograph (flame ionization detector) coupled to a Varian 4270 integrator. Components were separated on a QF-1 packed column (10 ft × 0.16 in. i.d., 0.25 in. o.d.; support, Chromosorb-G; 80–100 mesh). Infrared solution spectra were measured in NaCl cells on a Nicolet DX5 spectrometer. Elemental microanalyses were done by

Table III. Catalyst Efficiency for Cyclization of 4-Pentenal in Nitromethane

Catalyst[a]	% Rh[b]	% Conversion[c]	Time Required[d]	% Ketone[e]	Ratio Ketone/Olefins[f]	Turnover Rate[g]
$[Rh(PPh_3)_3Cl]$	10	65	16 h[h]	78	—	1.1×10^{-4} h
$[Rh(diphos)NBD]^+$	5	20	18 h[i]	~20	—	7×10^{-5} i
$[Rh(diphos)Cl]_2$	16	8	14 h	~85	—	1.0×10^{-5}
$[Rh(diphos)]^{+j}$	1	100	6 m	95	95	2.7×10^{-1}
$[Rh(dppp)]^+$	5	100	<7 m	~90	7	$>5\times10^{-2}$
$[Rh(dppb)]^+$	5	100	36 h[k]	~30[f]	1	1.4×10^{-2} k
$[Rh(dcpe)]^+$	1	100	24 h[k]	~80	10	$\geq5\times10^{0}$ k
$[Rh(dptf)]^+$	1	100	12 h[k]	~95	90	1.1×10^{-2} k
$[Rh(dpf)]^+$	1	100	12 h[k]	~95	40	4.7×10^{-3} k
$[Rh(PPh_2CH_3)_2(acetone)_2]^+$	1	100	50 m	0[m]	—	3.2×10^{-2}

[a] Cations are ClO_4^- salts generated in situ from NBD precursors. [b] (mol of Rh/mol of substrate) × 100. [c] Total aldehyde consumed based on ^1H NMR spectra. [d] Time required for % conversion at 20 °C. [e] Proportion of converted substrate; estimated from ^1H NMR spectra in conjunction with GC data. [f] From gas chromatography. Decarbonylation:double-bond migration ≈ 1:1. [g] For 50% conversion; mol of substrate consumed/mol of Rh/s (20 °C). [h] $CHCl_3$, 25 °C, 4 atm of ethylene; data calculated from ref 4. [i] 50 °C. [j] $[Rh(diphos)]_2(ClO_4)_2$. [k] 35 °C. [l] Also ~40% double-bond migration (3-pentenal:2-pentenal = 5:1). [m] Entirely 3-pentenal. [Rh] ≈ 1 mM.

Huffman Laboratories (Indiana).

Phosphines used is this work (1,2-bis(diphenylphosphino)ethane (diphos), 1,2-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)butane (dppb), 1,2-bis(dicyclohexylphosphino)ethane (dcpe), 1,2-bis[bis(*p*-(trifluoromethyl)phenyl)phosphino]ethane (dptf), 1,2-bis[bis(pentafluorophenyl)phosphino]ethane (dpf), triphenylphosphine (PPh_3), and diphenylmethylphosphine (PPh_2CH_3)) were purchased from Strem Chemicals; solids were recrystallized from boiling ethanol.

Rh Complexes. $[RhCl(C_2H_4)_2]_2$, prepared as described[21] from $RhCl_3$ except that ethylene bubbling was continued for 22 h (yield 86%), was converted[22] to $[Rh(NBD)_2]^+$ (ClO_4^-, BF_4^- salts) in 1:1 CH_2Cl_2/acetone. Filtration under argon through Celite, evaporation, dissolution in CH_2Cl_2(0.6 g, 4.0 mL), and treatment with THF (1.0 mL) followed by addition of hexane (1-mL aliquots) gave thick crimson-red crystalline filaments (0.5–1.5 in. long) within 2 h (95% yield): ^1H NMR (CD_2Cl_2) δ 5.67 (dd, 8 H, olefin), 4.28 (br m, 4 H, CH), 1.65 (t, 4 H, $2CH_2$); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 92.7 (d, J_{Rh-C} = 5.4 Hz, =CH), 69.9 (d, J_{Rh-C} = 4.5 Hz, CH), 56.2 (s, CH_2).

General Synthesis of [Rh(P⌒P)(NBD)]ClO_4 (P⌒P = diphos, dppp, dppb, dcpe (PPh_2CH_3)$_2$). To a stirred solution of $[Rh(NBD)_2]ClO_4$ (0.2 g, 518 μmol) in deoxygenated CH_2Cl_2 (2.0 mL) under argon was added the neat phosphine (~515 μmol) in small portions over 30 s. After being stirred for 5 min, the solution was filtered under Ar by cannula through Celite, washing the latter with CH_2Cl_2 (3 × 1 mL); the solvent was evaporated to 2 mL. Dropwise addition to this solution of dry deoxygenated diethyl ether (1 mL) either alone or following addition of dry deoxygenated THF (1 mL) gave large orange crystals in all cases upon standing. These were collected, washed (10:1 ether/CH_2Cl_2; ether), and dried under an Ar flow; yields 90 ± 5%.

[Rh(diphos)(NBD)]ClO_4: ^1H NMR (CD_3NO_2) δ 7.75–7.55 (m, 20 H, C_6H_5), 5.50 (dd, 4 H, CH=), 4.23 (br, 2 H, 2CH), 2.50 (dd, J_{P-H} = 19 Hz, J_{P-H} = 1 Hz, 4 H, PCH_2CH_2P), 1.84 (br s, 2 H, CH_2); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 134.1 (t, J = 5.8 Hz), 132.9 (s), 131.9 (t, J = 12 Hz), 130.7 (t, J = 5 Hz) (C_6H_5), 92.4 (dd, J = 5.4 Hz, olefin), 72.5 (d, J = 3.2 Hz, CH, NBD), 57.2 (s, CH_2, NBD), 27.2 (t, J_{P-C} = 24.0 Hz, $2CH_2$).

[Rh(dppp)(NBD)]ClO_4·CH_2Cl_2: ^1H NMR (CD_3NO_2) δ 7.65–7.45 (m, 20 H, C_6H_5), 4.81 (dd, J = 4.6, 1.9 Hz, 4 H, olefin), 4.02 (br s, CH, 2 H), 2.80 (br m, $2CH_2$, 4 H), 1.97 (br m, CH_2, 2 H), 1.59 (br s, CH_2, 2 H); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 134.2 (t, J = 5.4 Hz), 132.4 (s), 132.1 (t, J = 22.1 Hz), 130.4 (t, J = 4.9 Hz) (C_6H_5), 89.3 (dd, J = 10.9, 5 Hz, olefin), 70.7 (s, CH, NBD), 55.6 (s, CH_2, NBD), 25.5 (t, J = 16.5 Hz, $2CH_2$), 19.4 (s, CH_2). Anal. Calcd for $Rh_1C_{35}H_{36}Cl_3P_2O_4$: C, 53.09; H, 4.58; Cl, 13.43. No solvate: P, 8.77. Found: C, 53.14; H, 4.64; Cl, 13.30. No solvate: P, 9.24.

[Rh(dppb)]ClO_4·CH_2Cl_2: ^1H NMR (CD_3NO_2) δ 7.73–7.55 (2m, 20 H, C_6H_5), 4.59 (dd, 4 H, olefin), 3.94 (br s, 2CH, NBD), 2.62 (br m, $2CH_2$, 4 H), 1.76 (br m, $2CH_2$, 4 H), 1.56 (br s, CH_2, NBD); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 134.4 (t, J = 5.3 Hz), 133.2 (t, J = 22.7 Hz), 132.5 (s), 130.5 (t, J = 4.9 Hz) (C_6H_5), 87.3 (dd, J = 4.9, 10.8 Hz, olefin), 70.5 (d, J = 2.9 Hz, CH, NBD), 55.0 (s, CH_2, NBD), 29.6 (t, J = 14.6 Hz, $2CH_2$), 25.2 (s, $2CH_2$). Anal. Calcd for $Rh_1C_{36}H_{38}Cl_3P_2O_4$: C, 53.65; H, 4.75; Cl, 13.19. No solvate: P, 8.60. Found: C, 53.61; H, 4.75; Cl, 13.08. No solvate: P, 8.97.

[Rh(dcpe)(NBD)]ClO_4: ^1H NMR (CD_3NO_2) δ 5.70 (dd, 4 H, olefin), 4.22 (br s, 2CH, NBD), 1.20–2.20 (50 H, $4C_6H_{11}$, $2CH_2$, CH_2(NBD)); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 87.3 (dd, J = 5.2, 10.0 Hz, olefin), 72.4 (s, CH, NBD), 57.1 (s, CH_2, NBD), 36.7 (t, J = 11 Hz, CH), 30.7 (s, CH_2), 30.1 (s, CH_2), 28.2 (t, J = 6.0 Hz, CH_2), 27.9 (t, J = 5.1 Hz, CH_2), 27.1 (s, CH_2), 22.1 (t, J = 18.2 Hz, CH_2). Anal. Calcd for $Rh_1C_{33}H_{56}Cl_1P_2O_4$: C, 55.27; H, 7.87; Cl, 4.94; P, 8.63. Found: C, 54.65; H, 7.77; Cl, 5.93; P, 8.20.

[Rh(PPh_2CH_3)$_2$(NBD)]ClO_4: ^1H NMR (CD_2Cl_2) δ 7.48 (br s, 20 H, C_6H_5), 4.61 (dd, 4 H, olefin), 4.01 (br m, 2 H, 2CH, NBD), 1.57 (br, 8 H, $2CH_3$ + CH_2); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 133.7 (t, J = 5.7 Hz), 132.3 (s), 130.4 (t, J = 4.8 Hz) (C_6H_5), 85.9 (dd, J = 5.0, 11.0 Hz, olefin), 77.8 (br s, CH_3P), 69.6 (d, J = 3.1 Hz, CH, NBD), 55.0 (s, CH_2, NBD), 12.8 (t, J = 15 Hz, $2CH_2$).

[Rh(PPh_2CH_3)$_2$(acetone)$_2$]ClO_4. [Rh(PPh_2CH_3)$_2$(NBD)]ClO_4 was dissolved in deoxygenated acetone (0.1 g in 20 mL), and H_2 was bubbled through the solution for 2 min causing an orange to yellow color change. The solution was then evaporated under high vacuum to brown-yellow crystals which were stored under vacuum. ^{31}P NMR ($(CD_3)_2CO$, Table II) is consistent with the bis(acetone) complex in *acetone*. ^1H NMR (CD_3NO_2): δ 8.0–7.0 (m, C_6H_5), 7.3, 7.0, 6.95, 6.8, 6.7, 6.0, 5.2 (7t, bridging arenes), 2.5–1.0 (5d, PCH_3), 2.09 (s, acetone). Ratio of 8.0–5.0 ppm to 1.0–2.5 ppm equals 20:12, consistent with the stoichiometry "Rh(PPh_2CH_3)$_2$(acetone)". No hydrides were detected. Thus at least some dimer, $[Rh(PPh_2CH_3)_2]_2^{2+}$, is present in CD_3NO_2.

Specific Synthesis of [Rh(P⌒P)(NBD)]ClO_4 (P⌒P = dptf, dpf). Complexes were prepared by dissolving $[Rh(NBD)_2]ClO_4$ (0.1 g, 259 μmol) in CH_2Cl_2 (2 mL) and adding acetone (20 mL) and phosphine (260 μmol). After being stirred (5 min), the solution was filtered under argon by cannula through Celite (washing with acetone) and evaporated to 20 mL, and addition of dry deoxygenated diethyl ether (30 mL) precipitated orange-yellow crystals that were collected, washed (ice-cold acetone, ether), and stored at −10 °C under Ar.

[Rh(dpf)(NBD)]ClO_4: ^1H NMR (CD_3NO_2) δ 5.54 (dd, J = 4.3, 1.9 Hz, olefin, 4 H), 4.19 (br s, CH, 2 H), 3.16, 3.09 (br s, $2CH_2$, 4 H), 1.88 (br s, CH_2, 2 H); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 149.5 (m), 147.0 (m), 144.4 (m), 141.1 (m), 138.6 (m), 103.9 (m) (C_6F_5), 93.0 (d, J = 4.4 Hz, olefin), 72.2 (s, CH, NBD), 56.9 (s, CH_2, NBD), 28.8 (m, $2CH_2$). Anal. Calcd for $Rh_1C_{33}H_{12}Cl_1F_{20}P_2O_4$: C, 37.62; H, 1.14; Cl, 3.37; F, 36.10; P, 5.89. Found: C, 37.65; H, 1.21; Cl, 3.38; F, 35.82; P, 6.45.

[Rh(dptf)(NBD)]ClO_4: ^1H NMR (CD_3NO_2) δ 7.87 (m, C_6H_4, 16 H), 5.63 (dd, J = 4.5, 2.2 Hz, olefin, 4 H), 4.27 (brs, 2CH), 2.67, 2.62 (2br s, $2CH_2$, 4 H), 1.87 (br s, CH_2, 2 H); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 135.9 (t), 134.9 (t, J = 16.1 Hz, CH), 134.2 (q, J = 32.6 Hz, CF_3), 127.5 (br d, J = 4.2 Hz, CH), 126.6 (s), 123.9 (s) (C_6H_4), 94.3 (dd, J = 4.7, 9.7 Hz, olefin), 73.2 (d, J = 2.2 Hz, CH, NBD), 57.7 (s, CH_2, NBD), 27.0 (t, J = 23 Hz, $2CH_2$). Anal. Calcd for $Rh_1C_{37}H_{28}Cl_1F_{12}P_2O_4$: C, 46.04; H, 2.90; Cl, 3.68; F, 23.64; P. 6.43. Found: C, 46.26; H, 3.07; Cl, 3.68; F, 22.90; P. 6.82.

[Rh(diphos)]$_2$(ClO_4)$_2$·CH_3OH.[7] H_2 was slowly bubbled through a glass pipette into a suspension of [Rh(diphos)(NBD)]ClO_4 (0.3 g) in deoxygenated CH_3OH (4.0 mL). After 2 h the orange solid become yellow and the supernatant was almost colorless. (In some preparations the supernatant was dark brown-yellow). The mixture was cooled in an ice bath before transferring by cannula under Ar onto a fine sinter. The yellow

(21) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.
(22) Schenck, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.

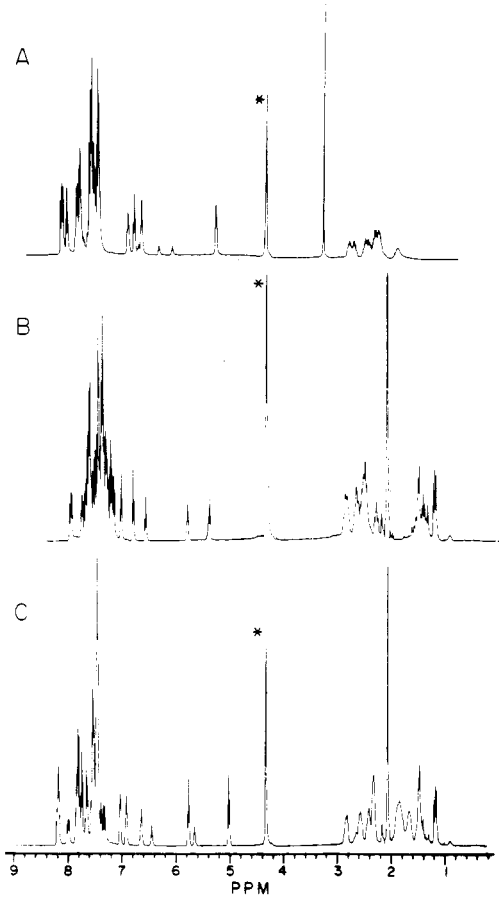


Figure 2. The 400-MHz ^1H NMR spectra of the arene-bridging dimers $[Rh(diphos)]_2(ClO_4)_2$ (A), $[Rh(dppp)]_2(ClO_4)_2$ (B), and $[Rh(dppb)]_2(ClO_4)_2$ (C) in nitromethane solutions. The species B and C were generated in situ by hydrogenation of the corresponding norbornadiene precursors. These spectra contain the signals due to norbornane.

complex was washed with ice-cold CH_3OH (3 × 1 mL) and pentane (3 × 1 mL) and dried by passing argon over it for 5–10 min before storing under Ar at −10 °C; yield 0.26 g (97%). Anal. Calcd for $Rh_2C_{53}H_{52}Cl_2P_4O_9$: C, 51.60; H, 4.24; Cl, 5.74; P, 10.04. Found: C, 51.42; H, 4.07; Cl, 5.45; P, 9.76.

Characterization of $[Rh(\widehat{P\,P})]_2(ClO_4)_2$ ($\widehat{P\,P}$ = diphos, dppp, dppb). Figure 2A displays the complex ^1H NMR spectrum for a solution of $[Rh(diphos)]_2(ClO_4)_2$, isolated from CH_3OH, in CD_3NO_2. The integration ratio for signals in the regions 5.0–9.0; 3.0–3.5, and 2.2–3.0 ppm is 40:3:8, and these are assigned to aromatic, methanol methyl, and methylene protons, respectively. The proportion of methanol is consistent with the elemental analyses above. The triplet ^1H resonances at 5.4, 6.7, 6.8, and 6.9 ppm as well as at 6.15, 6.4, and 6.75 ppm are ascribed to some of the bridging arene ring protons of major and minor diastereomers, respectively, of $[Rh(diphos)]_2(ClO_4)_2$. The ratio of diastereomers (~7:1) agrees with that determined (Table II) by ^{31}P NMR spectroscopy. In CD_2Cl_2, however, all of these ^1H signals attributed to bridging arenes vanish leaving only two aromatic resonances at 7.6 and 7.8 ppm. The ^{13}C NMR spectrum for $[Rh(diphos)]_2(ClO_4)_2$ in CD_3NO_2 shows two eight-line signals (ddd), centered at δ 30.65 and 31.67 (J_{Rh-C} = 37.1, 36.1 Hz; J_{C-P_1} = 3.3, 3.5 Hz; J_{C-P_2} = 15.2, 14.7 Hz), for inequivalent methylene carbons of diphos, bridging arene carbon resonances at 90–112 ppm, and other phenyl signals at 125–140ppm.

Parts B and C of Figure 2 show the resulting spectra for solutions of $[Rh(dppp)(NBD)]ClO_4$ and $[Rh(dppb)(NBD)]ClO_4$, respectively, in CD_3NO_2 after H_2 was bubbled through the solutions for 2 min (>2H_2/Rh). No hydrides were detected. Clearly, as in Figure 2A, a number of bridging arene resonances appear between 5.0 and 8.5 ppm in both cases and there are too many signals to be accounted for by single isomers of $[Rh(dppp)]_2^{2+}$ and $[Rh(dppb)]_2^{2+}$. We conclude from the number and relative proportions of these resonances, together with the more complex ^{31}P NMR data (Table II), that parts B and C of Figure 2 each represent two diastereomers of $[Rh(dppp)]_2^{2+}$ and $[Rh(dppb)]_2^{2+}$, respectively.

$[Rh(diphos)Cl]_2$. $[Rh(C_8H_{12})Cl]_2$ (0.2 g, 0.406 mmol) was dissolved in deoxygenated toluene (3.0 mL) at 60–70 °C under Ar. To the stirred solution was added dppe (0.32 g, 0.804 mmol) in toluene (4 mL) dropwise over $^3/_4$ h under argon. During the second half of the addition a yellow crystalline precipitate had formed in the orange solution. Prolonged heating (3 h, 125 °C oil bath) intensified the orange color and produced an orange crystalline precipitate. Hexane (4 mL) was added, and the solution was cooled over 1 h to −78 °C. Crystals were collected by filtration, washed (6 × 15 mL of hexane, 4 × 10 mL of pentane), and stored under Ar: yield 0.31 g (71%); ^1H NMR (CD_2Cl_2) δ 7.85–7.20 (br m, 20 H, C_6H_5), 2.07 (br d, $J_{P-\beta-CH_2}$ = 20 Hz, 4 H); ^{31}P NMR (CD_2Cl_2) δ 74.2 (J_{Rh-P} = 198 Hz). Anal. Calcd for $Rh_2C_{52}H_{48}Cl_2P_4$: C, 58.18; H, 4.51; Cl, 6.60; P, 11.54. Found: C, 58.01; H, 4.53; Cl, 6.84; P, 11.44.

Aldehyde Substrates. 4-Pentenal was prepared by two methods. The chromium oxidation of 4-pentenol[17] consistently gave a product which, after distillation (40% yield), was pure by ^1H NMR spectroscopy but failed to cyclize rapidly under catalytic conditions unless further purified by chromatography on silica gel (eluent 1:1 pentane/ether). This treatment considerably reduced the recovery of the volatile aldehyde (25%). Pure 4-pentenal (64%) was more conveniently obtained by distillation (bp 99–102 °C) of the product from Claisen rearrangement[15] of allyl vinyl ether; the latter was prepared by the Hg^{2+}-catalyzed vinylation of allyl alcohol.[16]

4-Pentenal: ^1H NMR (CD_3NO_2) δ 9.74 (t, J = 1.6 Hz, 1 H, CHO), 5.82–6.02 (m, 1 H, =CH), 5.00–5.15 (m, 2 H, $=CH_2$), 2.34–2.63 (m, 4 H, CH_2).

Other aldehydes, also obtained via the Claisen rearrangement as reported in the literature, were the following. **2-Methyl-4-pentenal**:[23] 23% yield; bp 115–118 °C (lit. bp 118 °C); ^1H NMR (CD_3NO_2) δ 9.59 (d, J = 1.4 Hz, 1 H, CHO), 5.80 (m, 1 H, =CH), 5.0–5.1 (m, 2 H, $=CH_2$), 2.4–2.5 (m, 2 H, CH_2), 1.6 (m, 1 H, CH), 1.07 (d, J = 6.9 Hz, 3 H, CH_3). **3-Methyl-4-pentenal**:[23] 37% yield; bp 121–123 °C (lit. bp 118–119 °C (739 mm)); ^1H NMR (CD_3NO_2) δ 9.66 (t, J = 2.1 Hz, 1 H, CHO), 5.84 (m, 1 H, =CH), 5.00 (dd, J = 10.2, 17.4 Hz, 2 H, $=CH_2$), 2.77 (m, 1 H, CH), 2.42 (dddd, 2 H, CH_2), 1.06 (d, J = 6.7 Hz, 3 H, CH_3). **4-Methyl-4-pentenal**:[24] 24% yield; bp 101–104 °C (lit. bp 100–103 °C (758 Torr)); ^1H NMR (CD_3NO_2) δ 9.70 (t, J = 1.6 Hz, 1 H, CHO), 4.65–4.80 (m, 2 H, $=CH_2$), 2.5–2.6 (m, 2 H, CH_2CH_2CHO), 2.33 (t, 2 H, CH_2C=), 1.75 (m, 3 H, CH_3). ***trans*-4-Hexenal**:[25] 18% yield; bp 68–70 °C (110 mm) (lit. bp 42–44 °C (15 Torr)); product was further purified by chromatography on silica gel, eluting with 5–10% CH_2Cl_2/hexane; ^1H NMR (CD_3NO_2) δ 9.67 (t, J = 1 Hz, 1 H, CHO), 5.48 (m, 2 H, CH=CH), 2.47 (m, 2 H, CH_2), 2.3 (m, 2 H, CH_2), 1.63 (m, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 204.7 (C=O), 130.9, 127.2 (CH=), 44.4, 26.1 (CH_2), 14.1 (CH_3). **5-Methyl-4-hexenal**:[26] 22% yield; bp 90 °C (100 mm) (lit. bp 90 °C (100 Torr)); product was purified by chromatography on silica gel, eluting with 25–50% CH_2Cl_2/hexane; ^1H NMR (CD_3NO_2) δ 9.68 (t, J = 1.6 Hz, 1 H, CHO), 5.12 (tsept, J = 7.2, 1.5, 1.3 Hz, 1 H, =CH), 2.45 (dt, J = 7.2, 1.6 Hz, 2 H, CH_2CHO), 2.29 (dt, J = 6.8, 7.1 Hz, 2 H, CH_2CH=), 1.66 (dd, J = 7.9, 1.0 Hz, 6 H, $(CH_3)_2$). **3,3-Dimethyl-4-pentenal**:[27] 88% yield; bp 128–130 °C; ^1H NMR (CD_3NO_2) δ 9.66 (t, J = 3.0 Hz, 1 H, CHO), 5.97 (dd, J = 17.6, 10.7 Hz, 1 H, =CH), 5.03 (dd, J = 17.5, 1.2 Hz, 1 H, =CH), 5.00 (dd, J = 10.6, 1.2 Hz, 1 H, =CH), 2.34 (d, J = 2.9 Hz, 2 H, CH_2CHO), 1.14 (s, 6 H, $(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 204.9 (C=O), 148.1 (CH=), 112.0 (H_2C=), 55.5 (CH_2), 27.7 ($(CH_3)_2$), 37.0 ($C(CH_3)_2$).

4-Phenyl-4-pentenal was prepared by refluxing β-phenylallyl alcohol (18 g, 134 mmol) with $Hg(OAc)_2$ (5 g) in butyl vinyl ether

(23) Montgomery, L. K.; Matt, J. W.; Webster, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 923.
(24) Vig, O. P.; Vig, B.; Anand, R. C. *Indian J. Chem.* **1969**, *7*, 1112.
(25) Crandall, J. K.; Mayer, C. F. *J. Org. Chem.* **1970**, *35*, 3049.
(26) Marbel, R.; Saucy, G. *Helv. Chim. Acta* **1967**, *50*, 2095.
(27) Boeckman, R. K., Jr.; Koo, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 7146.

Table IV. NMR Data for Cyclopentanones

	$^{13}C\{^1H\}$ NMR data[a,b]	^1H NMR data[a]
	221.9 (C=O), 39.0 (CH_2), 24.2 (CH_2)	1.94 (m, 4 H, CH_2CH_2C=O), 2.11 (m, 4 H, CH_2C=O)
	223.3 (C=O), 45.0 (CH), 38.3, 32.9, 21.6 (CH_2), 14.5 (CH_3)	1.06 (d, J = 6.8 Hz, 3 H, CH_3), 1.40–2.30 (4m, 7 H, $3CH_2$ + CH)
	221.6 (C=O), 47.5, 39.4, 32.4 (CH_2), 33.0 (CH), 20.6 (CH_3)	1.10 (d, J = 6.4 Hz, 3 H, CH_3), 1.43–2.33 (4m, 7 H, $3CH_2$ + CH)
	220.1 (C=O), 141.1, 129.8, 129.8, 128.0 (C_6H_5), 56.8 (CH), 39.1, 33.0, 21.9 (CH_2)	1.9–2.5 (m, 7 H, $3CH_2$ + CH), 7.2–7.8 (m, 5 H, C_6H_5)
	216.5 (C=O), 157.7, 142.2, 140.5, 140.1 (C_6H_5), 55.8 (CH), 58.8, 52.1, 44.6 (CH_2)	1.95–2.61 (m, 6 H, $3CH_2$), 3.4–3.5 (m, 1 H, CH), 7.2–7.4 (m, 5 H, C_6H_5)
	225.2 (C=O), 39.2, 37.6, 19.5 (CH_2), 21.8 (CH_3),[c] (>C<)	0.98 (s, 6 H, $(CH_3)_2$), 1.80 (t, 2 H, CH_2), 1.89 (m, 2 H, CH_2), 2.2 (t, J = 7.5 Hz, 2 H, CH_2)
	221.2 (C=O), 54.0, 38.1, 37.8 (CH_2), 28.5 (CH_3), 37.3 (>C<)	1.09 (s, 6 H, $(CH_3)_2$), 1.79 (t, 2 H, J = 7.8 Hz, $CH_2CH_2C(CH_3)_2$) 1.99 (s, 2 H, $C(CH_3)_2CH_2CO$), 2.24 (t, 2 H, J = 7.8 Hz, CH_2CH_2CO)
	208.7 (C=O), 157.2, 138.4, 135.9, 128.5, 128.3, 124.3 (C_6H_4), 37.1, 26.8 (CH_2)	2.61–2.66 (m, 2 H, CH_2), 3.14–3.17 (m, 2 H, CH_2), 7.3–8.0 (m, 4 H, C_6H_4)
 trans	221.6 (C=O), 45.0 (CH), 46.3, 32.4, 27.5 (CH_2)[a] 220.0 (C=O), 44.2 (CH), 45.9, 31.7, 26.7 (CH_2)[d]	1.10–2.40 (m, 14 H, $6CH_2$ + 2CH)
 cis	219.5 (C=O), 36.8 (CH), 43.9, 28.4, 23.6 (CH_2)[a] 217.8 (C=O), 35.9 (CH), 43.5, 27.7, 22.8 (CH_2)[d,e]	1.20–2.45 (m, 14 H, $6CH_2$ + 2CH)
 trans	220.6, 210.5 (C=O), 45.1, 38.6 (CH), 48.0, 45.6, 42.8, 28.5 (CH_2), 29.9, 18.7 (CH_3)[a] 218.6, 208.3 (C=O), 44.2, 37.8 (CH), 47.6, 45.2, 42.3, 27.6 (CH_2), 30.0, 18.5 (CH_3)[d]	1.12 (d, J = 6.2 Hz, 3 H, CH_3CH), 2.10 (s, 3 H, CH_3), 1.7–2.6 (m, 10 H, $4CH_2$ + 2CH)
 cis	219.5, 210.4 (C=O), 40.5, 34.0 (CH), 48.0, 42.6, 42.4, 25.5 (CH_2), 29.9, 14.7 (CH_3)[a] 217.6, 208.3 (C=O), 39.6, 33.2 (CH), 47.5, 42.1, 42.0, 24.7 (CH_2), 30.0, 14.5 (CH_3)[d]	0.92 (d, J = 7.0 Hz, 3 H, CH_3CH), 2.10 (s, 3 H, CH_3), 1.5–2.6 (m, 10 H, $4CH_2$ + 2CH)

[a] δ, TMS/CD_3NO_2; 400-MHz spectra. [b] Assignments based on APT/DEPT experiments. [c] Not clearly observed. [d] δ, TMS/CD_2Cl_2; 400-MHz spectra. [e] δ, TMS/$CDCl_3$: 227, 43.4, 35.8, 27.8, 22.6 ppm. Clark, D. A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1979**, *101*, 3567.

(200 g, 2 mol) for 17 h. The mixture was then cooled, stirred with 10% Na_2CO_3 (100 mL) for 30 min, filtered through filter paper, and distilled: yield 40%; bp 123–126 °C; ^1H NMR (CD_3NO_2) δ 9.71 (t, J = 7 Hz, 1 H, CHO), 7.31–7.49 (m, 5 H, C_6H_5), 5.13, 5.37 (2s, 2 H, $=CH_2$), 2.86 (t, 2 H, CH_2C=), 2.62 (m, 2 H, CH_2CHO). β-Phenylallyl alcohol was obtained from the reaction of $LiAlH_4$ with β-phenyl allyl acetate,[28] and the latter was prepared by oxidation of α-methylstyrene with selenium dioxide.[29]

5-Phenyl-4-pentenal was similarly made by refluxing phenyl vinyl carbinol[30] (11.4 g, 85 mmol) with $Hg(OAc)_2$ (5 g) in butyl vinyl ether (116 g, 1.16 mol) for 19 h. The solution was cooled, washed with 10% Na_2CO_3 (4 × 100 ml), dried over $MgSO_4$, and distilled: 28% yield; bp 122 °C (14 mm); bp 77–79 °C (0.1 mm); ^1H NMR (CD_3NO_2) δ 9.75 (t, J = 1.5 Hz, 1 H, CHO), 7.2–7.45 (m, 5 H, C_6H_5), 6.3–6.6 (m, 2 H, CH=CH), 2.62–2.66 (m, 2 H, CH_2), 2.51–2.55 (m, 2 H, CH_2); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 204.3 (C=O), 139.1, 131.8, 130.5, 130.0, 128.5, 127.3 (C_6H_5, C=C), 44.1, 26.6 (CH_2).

The following aldehydes were prepared as reported. **2,2-Dimethyl-4-pentenal**:[31] 10% yield, bp 63–64 °C (90 mm) (lit. bp 124–125 °C); ^1H NMR (CD_2Cl_2) δ 9.46 (s, 1 H, CHO), 5.72 (m, 1 H, =CH), 5.04–5.09 (m, 2 H, $=CH_2$), 2.20 (m, 2 H, CH_2), 1.03 (s, 6 H, $(CH_3)_2$). **o-Formylstyrene**:[32] 54% yield; bp 61.5 °C (0.1 mm) (lit. bp 70–75 °C (1 Torr)); ^1H NMR (CD_3NO_2) δ 10.24 (s, 1 H, CHO), 7.5–7.8 (m, 5 H, C_6H_4, CH=), 5.77 (dd, J = 11.2, 1.2 Hz, =CH), 5.50 (dd, J = 17.4, 1.2 Hz, =CH); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 194.3 (C=O), 141.5, 135.2, 134.8, 134.3, 132.5, 129.4, 128.5, 119.8 (C=C, C_6H_5). **7-Oxo-5-isopropenylhept-2-one**:[33] 31% yield; product was purified by chromatography on silica gel (9:1 hexane/ethyl acetate eluent); ^1H NMR (CD_3NO_2) δ 9.61 (t, J = 2.1 Hz, 1 H, CHO), 4.80, 4.83 (2s, 2 H, $=CH_2$), 2.61–2.73 (m, 1 H, CH), 2.38–2.49 (m, 4 H, $2CH_2$), 2.08 (s, 3 H, CH_3), 1.66 (m, 5 H, CH_3 + CH_2); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 210.3 (C=O, ketone), 204.3 (C=O, aldehyde), 147.9 (=C), 113.2 (H_2C=), 48.3, 41.8, 27.8 (CH_2), 42.1, 18.9 (CH_3).

(2-Methylenecyclohexyl)acetaldehyde was prepared via Wittig reaction of the corresponding keto acetal:[34] 62% yield, bp 86 °C (20 mm) (lit.[35] bp 82 °C (14 Torr)); ^1H NMR (CD_3NO_2) δ 9.68 (t, J = 2.1 Hz, 1 H, CHO), 4.52, 4.69 (2s, 2 H, $=CH_2$), 1.2–2.7 (m, 11 H, $5CH_2$ + CH); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 204.8 (C=O), 153.5 (=C<), 106.3 ($=CH_2$), 47.7 (CH_2CHO), 38.9 (CH), 36.6, 35.6, 29.7, 26.2 (CH_2). The keto acetal was obtained[36] (56% yield) from reaction of the dicyclohexylimine carbanion with $ICH_2CH(OC_2H_5)_2$.

Catalysis Method. All solvents were purged with Ar (10 min) immediately prior to use. Typically $[Rh(dppe)]_2(ClO_4)_2$ (1.10 mg, 1.8×10^{-6} mol of Rh) was weighed into an NMR tube and capped with a rubber septum. Argon was blown into the tube via needle

(28) Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 1886.
(29) Hatch, L. F.; Patton, T. L. *J. Am. Chem. Soc.* **1954**, *76*, 2705.
(30) Ramsden, H. E.; Leebrick, J. R.; Rosenberg, S. D.; Miller, E. H.; Walburn, J. J.; Balint, A. E.; Cserr, R. *J. Org. Chem.* **1957**, *22*, 1602.
(31) Groenewegen, P.; Kallenberg, H.; Gen, A. v. d. *Tetrahedron Lett.* **1978**, 491.
(32) Dale, W. J.; Starr, L.; Strobel, C. W. *J. Org. Chem.* **1961**, *26*, 2225.
(33) Wolinsky, J.; Barker, W. *J. Am. Chem. Soc.* **1960**, *82*, 636.
(34) Burk, L. A.; Soffer, M. D. *Tetrahedron* **1976**, *32*, 2083.
(35) Cresson, P. *Bull. Soc. Chim. Fr.* **1964**, 2629.
(36) Larchevêque, M.; Valette, G.; Cuvigny, T. *Tetrahedron.* **1979**, *35*, 1745.

for 60 s, before 0.7 mL of solvent (CD_2Cl_2 or $MeNO_2$-d_3) was added. The tube was reweighed, 4-pentenal (15.87 mg, 1.89×10^{-4} mol) was added by syringe, and the ^1H NMR spectrum was recorded without delay. By rapidly scanning the region 2.8–1.6 ppm downfield of TMS, we could monitor the transformation of aldehyde methylene protons to cyclopentanone methylene protons several times before cyclization was complete (6 min, 20 °C; ≤3 min, 35 °C).

Alternatively the weighed catalyst precursor, [Rh(P⌒P)(NBD)]ClO_4 ($\sim 10^{-6}$ mol), in deoxygenated solvent was hydrogenated, by syringing in 3–4 equiv of H_2/mol of Rh, prior to substrate addition as described above. The identity of the rhodium complexes, formed in situ prior to aldehyde addition, was determined by ^{31}P NMR spectroscopy in separate experiments employing a 10-fold greater concentration of Rh. The complex [Rh(dpf)(NBD)]ClO_4 was unique in resisting hydrogenation and required H_2 bubbling for 5–10 min even in acetone for complete removal of NBD.

Product Analyses. When reactions were complete, as assessed by 60-MHz ^1H NMR spectroscopy, the high-field ^1H and ^{13}C NMR spectra were recorded. Of these data (Table IV) the latter were especially useful for unambiguous qualitative identification of cyclopentanone products, while the former spectra permitted both qualitative and quantitative product analysis. Note that certain pairs of 4-pentenal substrates (Table IV, entries 2 and 5, 3 and 4, 6 and 8) give common cyclopentanones, thus aiding their identification. The ^{13}C resonance for the carbonyl of cyclopentanones (Table IV) was especially diagnostic, being displaced 10–20 ppm downfield of aldehyde carbonyls.

Unreacted substrate and aldehyde products arising from double-bond migration were clearly identified in 400-MHz ^1H NMR spectra, and they were quantified, by integration relative to the 20 aromatic protons of the catalyst of known [Rh], with estimated accuracy of $<\pm 0.3\%$. By this method quantitation of the ketone products was also possible, but the error in reported numbers is higher (±2–3%); the trace amounts of olefin decarbonylation products were observed in the ^1H NMR spectra but could not be quantitatively determined. On the other hand, gas–liquid chromatography on nitromethane solutions gave reproducible analyses for olefins and cyclopentanones (estimated accuracy ≤0.2%), but determination of aldehydes was usually unreliable due to partial overlap with the solvent. Typically 0.2–0.5-μL samples of product solutions were injected into the chromatograph (column temp ≈ 80 °C, isothermal; flow rate = 25 mL/min), and retention times were as follows: olefins (~2 min), solvent (6–8 min), aldehydes (12–17 min), cyclopentanones (20–40 min). Note that 1- and 2-butenes were not distinguishable by these analyses.

Stereochemistry of the product from cyclization of **12** (Table I) was determined from the ^1H NMR spectrum, using information reported elsewhere[37] for the cis isomer. At 20 mol % Rh as [$Rh(PPh_3)_3Cl$], the *cis*-cyclopentanone product is favored over the trans product in CH_2Cl_2, CH_3NO_2, and acetone (90:1). For the product from **11**, a ^1H–^{13}C NMR correlation experiment established that proton resonances for cis CH and trans CH were at δ 2.31 and 1.55, respectively, in CD_3NO_2. However, the stereochemistry could not be determined by ^1H NMR because those positions were obscured by other signals. A gated $^{13}C\{^1H\}$ NMR experiment (in which the NOE was suppressed by using long delays, $10T_1$, with decoupler off between pulses) resulted in each isomer having all ^{13}C resonances of equal intensity allowing, in conjunction with footnote *e* (Table IV), unambiguous determination of the isomeric ratio.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, Esso Petroleum, and the Bickell Foundation.

Registry No. dptf, 98815-27-1; dpf, 76858-94-1; [Rh(NBD)$_2$]ClO_4, 60576-58-1; [Rh(diphos)(NBD)]ClO_4, 32799-34-1; [Rh(dppp)(NBD)]ClO_4, 112790-16-6; [Rh(dppb)]ClO_4, 112712-01-3; [Rh(dcpe)(NBD)]ClO_4, 112681-84-2; [$Rh(PPh_2CH_3)_2$(NBD)]ClO_4, 32799-81-8; [$Rh(PPh_2CH_3)_2$(acetone)$_2$]ClO_4, 112681-86-4; [Rh(dpf)(NBD)]ClO_4, 112681-88-6; [Rh(dptf)(NBD)]ClO_4, 112681-90-0; [Rh(diphos)], 112681-96-6; [Rh(diphos)Cl]$_2$, 53204-14-1; [$Rh(PPh_3)_3Cl$], 14694-95-2; [Rh(dppp)]$^+$, 112681-91-1; [$Rh(C_8H_{12})Cl]_2$, 12092-47-6; [Rh(dcpe)]$^+$, 112681-92-2; [Rh(dptf)]$^+$, 112681-93-3; [Rh(dpf)]$^+$, 112681-94-4; 4-pentenal, 2100-17-6; 2-methyl-4-pentenal, 5187-71-3; 3-methyl-4-pentenal, 1777-33-9; 4-methyl-4-pentenal, 3973-43-1; *trans*-4-hexenal, 25166-87-4; 2,2-dimethyl-4-pentenal, 5497-67-6; 3,3-dimethyl-4-pentenal, 919-93-7; 5-methyl-4-hexenal, 764-32-9; 4-phenyl-4-pentenal, 51758-24-8; 5-phenyl-4-pentenal, 51758-25-9; (2-methylenecyclohexyl)acetaldehyde, 3991-38-6; 7-oxo-5-isopropenylhept-2-one, 7086-79-5; *o*-formylstyrene, 28272-96-0; β-phenylallyl alcohol, 6006-81-1; phenyl vinyl carbinol, 4393-06-0; butyl vinyl ether, 111-34-2; cyclopentanone, 120-92-3; 2-methylcyclopentanone, 1120-72-5; 3-methylcyclopentanone, 1757-42-2; 2,2-dimethylcyclopentanone, 4541-32-6; 3,3-dimethylcyclopentanone, 20500-49-6; 3-phenylcyclopentanone, 64145-51-3; 2-phenylcyclopentanone, 1198-34-1; *cis*-2-octahydroindenone, 5689-04-3; *trans*-2-octahydroindenone, 16484-17-6; *cis*-3-methyl-4-(3-oxobutyl)cyclopentanone, 112790-18-8; *trans*-3-methyl-4-(3-oxobutyl)cyclopentanone, 112790-17-7; 2,3-dihydroindan-1-one, 83-33-0; 3-pentenal, 5604-55-7; 2-pentenal, 764-39-6.

(37) Sakai, K.; Ishiguro, Y.; Funakoshi, K.; Ueno, K.; Suemune, H. *Tetrahedron Lett.* **1984**, *25*, 961.