= 7.9 Hz, 2 F, CF_2). Anal. Calcd for $C_7H_9F_5OS$: C, 35.60; H, 3.84; S, 13.57. Found: C, 35.33; H, 3.76; S, 13.38.

3,3-Di[bis(perfluoroisopropoxymethyl)fluoromethoxymethyl]oxetane (12). A mixture of 3.9 g (0.067 mol) of KF, 33.4 g (0.067 mol) of ketone **10**, 7.8 g (0.032 mol) of 3,3-bis(bromomethyl)oxetane, and 75 mL of dry dimethylformamide was stirred until homogeneous and then heated at 65–70 °C for 2 days and at 80 °C for 6 h. Dilution with 500 mL of water gave a lower layer which was washed with water, dried, and distilled to afford 24.9 g (70%) of oxetane **12:** bp 85 °C (0.05 mmHg); IR 3.35 and 3.45 (saturated CH), 7.5–9 (CF, C–O), and 10.10 μm (oxetane ring); NMR (^{1}H) 4.37 (s, 1, oxetane CH_2) and 4.30 (broad s, 1, CH_2OCF); NMR (^{19}F) −78.8 (broad m, 4, CF_2O), −81.4 (m, 12, CF_3), −142.6 (m, 1, CH_2OCF), and −146.0 ppm (t of m, J_{FF} = 21.8 Hz, 2, CF_2OCF). Anal. Calcd for $C_{23}H_8F_{38}O_7$: C, 24.71; H, 0.72; F, 64.56. Found: C, 24.74; H, 0.85; F, 64.35.

Registry No.—**1**, 79-53-8; **3**, 64457-48-3; **5**, 64457-49-4; **6**, 64457-50-7; **7**, 64457-51-8; **8** (*n* = 1), 64457-52-9; **8** (*n* = 2), 64457-53-0; **9**, 64457-54-1; **10**, 64457-55-2; **11**, 64457-56-3; **12**, 64457-57-4; **13**, 64457-58-5; **14**, 64457-59-6; hexafluoroacetone, 684-16-2; 1,3-dichlorotetrafluoroacetone, 127-21-9; cyclohexane, 110-82-7; *tert*-butylmercaptan, 75-66-1; 3,3-bis(bromomethyl)oxetane, 2402-83-7.

References and Notes

(1) An often quoted example is the attack of hydroxide on trifluoromethyl iodide to give fluoroform, as described by J. Banus, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 60 (1951). For reactions of this type, formation of a charge-transfer complex has not been ruled out as an initial step.

(2) L. G. Anello, A. K. Price, and R. F. Sweeney, *J. Org. Chem.*, **33**, 2692 (1968); U. S. Patent 3 379 765 (April 23, 1968).

(3) P. Tarrant, C. G. Allison, K. P. Barthold, and E. C. Stump, Jr., "Fluorine Chemistry Reviews", Vol. 5, P. Tarrant, Ed., Marcel Dekker, New York, N.Y., 1971, p 96 ff, discuss oligomerization of hexafluoropropene epoxide to polyether acid fluorides.

(4) D. Sianesi, R. Fontanelli, and G. Caporiccio, U. S. Patent 3 513 203 (May 19, 1970), prepared the closely related ketoethers $CF_3O[CF_2CF(CF_3)O]_nCF_2COCF_3$ by a different route.

(5) F. W. Evans, M. H. Litt, A.-M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, **33**, 1837 (1968).

(6) German Patent 2 116 105 (Sept. 7, 1972).

(7) E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Am. Chem. Soc.*, **89**, 1422 (1967).

(8) E. L. Eliel, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, pp 103–106.

(9) M. H. Maguire and G. Shaw, *J. Chem. Soc.*, 2713 (1957), report the only successful reaction of this type to come to our attention. Sodium 2,4-dichlorophenoxide gave a low yield of the chloride displacement product with ethyl chlorodifluoroacetate.

Hydroformylation Catalyzed by Cis-Chelated Rhodium Complexes. Extension to Polymer-Anchored Cis-Chelated Rhodium Catalysts

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The chelating phosphine ligands $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2PPh_2$, and $Ph_2P(CH_2)_4PPh_2$ have been examined as ligands in the rhodium catalyzed hydroformylation of 1-pentene and 2-pentene. 1,2-Bis(diphenylphosphino)ethane causes a large decrease in the normal/branched (n/b) selectivity of 1-pentene hydroformylations at 60–120 °C and 100–800 psi. Increasing addition of PPh_3 causes increased n/b ratios. Hydroformylations of 2-pentene with $Ph_2PCH_2CH_2PPh_2$ exhibited low n/b selectivities which increased as pressure was lowered and temperature was raised. Using a polymer-anchored version of the catalyst (i.e., Ⓟ-$C_6H_4P(Ph)CH_2CH_2P(Ph_2)RhH(CO)L$) selectivities of 40–42% hexanal could be obtained from 2-pentene at 140 °C and 100–400 psi. The inherent propensity toward anti-Markownikoff rhodium hydride addition to a terminal double bond is lower for *cis*-phosphine chelated rhodium hydrides than for *trans*-bisphosphine–rhodium hydride complexes. This is attributed to differences in steric effects.

Phosphines and arsines have long been investigated as ligands for rhodium in the hydroformylation of olefins.[1] Detailed mechanistic investigations of hydroformylation were reported by Wilkinson et al.[2–4] using $RhH(CO)(PPh_3)_3$ as the catalyst. It has been found that rhodium complexes are more active "oxo" catalysts than cobalt compounds, permitting their use at low temperatures to give a minimum of by-products.[5] In general, rhodium-catalyzed hydroformylations are performed at temperatures from 40 to 140 °C and pressures from 50 to 1500 psi.[6] Under these conditions the selectivity to aldehydes is often greater than 99%.

Addition of tertiary phosphine ligands to rhodium-catalyzed hydroformylations greatly reduces the tendency for double bond isomerization. For example, 1-pentene was converted to 72% *n*-hexanal and 28% 2-methylpentanal in the presence of $RhH(CO)(PPh_3)_3$.[7] Similar selectivities were reported by Osborn, Wilkinson, and Yang[2] using $Rh(CO)Cl(PPh_3)_2$ and by Pruett and Smith[8] using a triphenyl phosphite–rhodium complex. Roth et al.[7] demonstrated that increasing additions of triphenylphosphine to $Rh(CO)Cl(PPh_3)_2$ resulted in a higher selectivity to *n*-heptanal from 1-hexene, while Pruett and Smith[8] observed a similar effect upon addition of excess triphenyl phosphite to $RhH(CO)(P(OPh)_3)_3$. High rates and very high terminal selectivities were observed by Brown and Wilkinson[9] when $RhH(CO)(PPh_3)_3$ was used in molten triphenylphosphine at 85–150 °C.

Recently, increased attention has been given to attaching homogeneous catalysts to polymer supports.[10–14] It is now well established that polymer-anchored $RhH(CO)(PPh_3)_3$ exhibits considerably higher selectivities than its homogeneous analogue, when the resin to which it is anchored has high P/Rh ratios and high loadings of phosphine.[12,14] At 1:1 H_2/CO, normal to branched (n/b) selectivities as high as 20:1 have been observed,[15] and by varying the H_2:CO ratios n/b selectivities up to 64:1 were achieved.[14]

Despite the extensive selectivity studies already reported, very little work describes the effect that cis-chelating phosphines exert in hydroformylation reactions. The n/b selectivity using $RhH(CO)(PPh_3)_3$ is strongly dependent on the position of equilibrium between $RhH(CO)_2(PPh_3)_2$ and $RhH(CO)_2PPh_3$.[2–4,16] This is summarized in Scheme I. The associative pathway, which leads to higher n/b selectivities,[2–4,16] proceeds mainly by anti-Markownikoff rhodium hydride addition of $RhH(CO)_2(PPh_3)_2$ to the terminal carbon. When two phosphine ligands are bound to rhodium, selectivity is higher. This suggested that a chelating ligand, such as bis(diphenylphosphino)ethane (see complex 1, Scheme II), might give high n/b selectivities because this ligand would keep two

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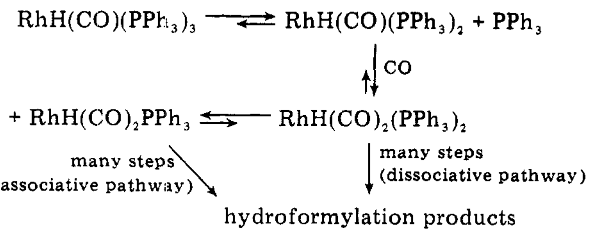
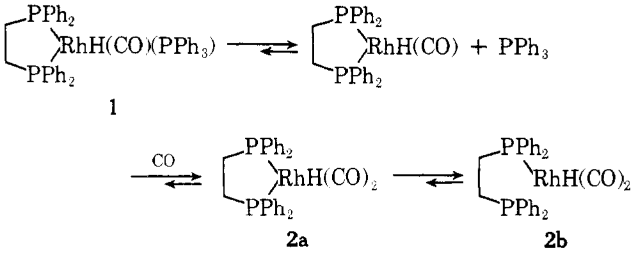
Scheme I



Scheme II



phosphines chelated to the metal. The position of equilibrium between **2a** and **2b** would greatly favor **2a**.

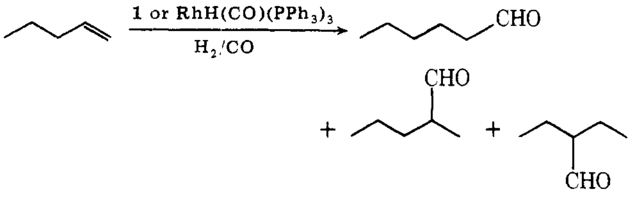
To the degree that the hydroformylation mechanisms, using $RhH(CO)(PPh_3)_3$ and **1** as catalysts, are mechanistically the same, one might postulate that **1** might be highly selective. However, the phosphine ligands in intermediate **2a** are always cis while the phosphines in $RhH(CO)_2(PPh_3)_2$ are trans. This difference in cis and trans ligand geometries may change the observed oxo chemistry. Therefore, hydroformylation studies were undertaken on both 1- and 2-pentene substrates using cis-chelating phosphines. Furthermore, polymer-anchored 1,2-diphenylphosphinoethane was prepared and used in rhodium-catalyzed hydroformylations.

Results and Discussions

Hydroformylation of 1-Pentene Catalyzed by $RhH(CO)(PPh_3)(PPh_2CH_2CH_2PPh_2)$, 1, vs. $RhH(CO)(PPh_3)_3$. Complex **1** was prepared by simple ligand exchange in benzene. Alternatively, bis(diphenylphosphino)ethane was simply added to hydroformylation reactions along with $RhH(CO)(PPh_3)_3$.

$$RhH(CO)(PPh_3)_3 + PPh_2CH_2CH_2PPh_3 \rightarrow \mathbf{1} + 2PPh_3$$

Upon dissolution, 2 mol of triphenylphosphine dissociated and, under hydroformylation conditions, the equilibria shown in Scheme II were assumed. Then **1** was used to catalyze the hydroformylation of 1-pentene at temperatures from 60 to 120 °C and pressures from 100 to 800 psi using 1:1 H_2/CO. The results are summarized in Table I. The n/b selectivity varied from 1.0 to 2.0 showing conclusively that catalysis by **1** is *far less selective* than catalysis using $RhH(CO)(PPh_3)_3$ (which under the same conditions gives n/b ratios of 3.0 to 3.5). Also, the change in selectivity with temperature was stronger at 100 psi than at either 400 or 800 psi using **1** (Table I).



The lower selectivity of **1** is partially due to the ability of this cis complex to promote double bond isomerization. Significant quantities of 2-pentene were detected during the reaction. This stands in sharp contrast to the behavior of $RhH(CO)(PPh_3)_3$ where isomerization of terminal olefins is not observed under normal hydroformylation conditions.[17] Second, the n/b ratio resulting from terminal double bond hydroformylation was inherently lower using **1**. Complex **1** is also a more active catalyst than $RhH(CO)(PPh_3)_3$. For example, cyclohexene was quantitatively converted to cyclohexanecarboxaldehyde at 85 °C, 400 psi, 1:1 H_2CO, in 20 h using complex **1**, but no aldehyde was obtained employing $RhH(CO)(PPh_3)_3$.

Table I. Hydroformylation of 1-Pentene Catalyzed by $RhH(CO)(PPh_3)(PPh_2CH_2CH_2PPh_2)$[a]

	Yield, % (n/b), selectivity (normal), %			
psi	60 °C	80 °C	100 °C	120 °C
100	93 (2.0) 67	95 (1.9) 65	99 (1.7) 61	95 (1.0) 50
400	96 (1.9) 65	93 (2.0) 67	89 (1.8) 65	92 (2.0) 67
800	88 (1.8) 65	99 (1.8) 65	97 (1.9) 65	100 (1.8) 65

[a] 1-Pentene (1.0 mL, 9.1 mmol), rhodium (0.09 mmol), benzene (8.0 mL), 21 h, H_2/CO = 1:1.

Table II. Effect of P/Rh Ratio on Selectivity in Hydroformylations of 1-Pentene at 100 psi and 80 °C Catalyzed by $RhH(CO)(PPh_3)_3 + PPh_3$

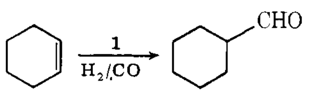
P:Rh	Conversion, %	n/b ratio	Selectivity, %
5:1	97.1	3.0	75
10:1	96.6	3.5	78
15:1	96.0	4.9	83
30:1	96.6	5.6	85
50:1	93.2	7.6	88

[a] 1-Pentene (1.0 mL, 9.1 mmol), rhodium (0.09 mmol), benzene (8.0 mL), 21 h, H_2/CO = 1:1.

Table III. Hydroformylation of 1-Pentene Catalyzed by $RhH(CO)(PPh_3)_3$ in the Presence of Excess $PPh_2CH_2CH_2PPh_2$[a]

	Yield, n/b, selectivity (normal)			
psi	60 °C	80 °C	100 °C	120 °C
100	89%, 1.2, 55%	92%, 1.1, 52%	93%, 1.0, 50%	96%, 0.9, 47%
400	68%, 1.1, 52%	97%, 1.0, 50%	97%, 1.0, 50%	99%, 1.0, 50%
800	39%, 1.0, 50%	96%, 1.0, 50%	98%, 1.0, 50%	97%, 1.0, 50%

[a] 1-Pentene (1.0 mL, 9.1 mmol), rhodium (0.09 mmol), benzene (8.0 mL), P/Rh = 21:1, 21 h, H_2/CO = 1:1.



We verified that the n/b selectivity is increased by increasing the P/Rh ratio when using $RhH(CO)(PPh_3)_3$ and excess PPh_3. This phenomenon is shown in Table II for 1-pentene reactions at 100 psi, 1:1 H_2/CO, at 80 °C. These data are presented to serve as a comparison with the effect that adding excess $PPh_2CH_2CH_2PPh_2$ to $RhH(CO)(PPh_3)_3$ has on the selectivity of 1-pentene hydroformylations (summarized in Table III). The effects of adding this cis ligand are striking. With a 9 mol excess of $PPh_2CH_2CH_2PPh_2$ (i.e., P/Rh = 21), the highest n/b ratio was only 1.2. Furthermore, over the entire matrix of conditions used, the selectivity was almost constant (0.9 to 1.2). In contrast, the selectivity climbs from 3.0 to 7.6 as excess triphenylphosphine is added (Table II). Clearly, $PPh_2CH_2CH_2PPh_2$ reduces n/b selectivity. Furthermore, by raising the $PPh_2CH_2CH_2PPh_2$/Rh ratio from 1 (Table I) to 9 (Table III) the selectivity was further de-

Table IV. The Influence of Added Bisphosphines on Selectivity in Hydroformlations of 1-Pentene with $RhH(CO)(PPh_3)_3$[a]

Phosphine	Conversion, %	n/b ratio	Normal selectivity, %
None	99	3.5	78
PPh_3	98	6.7	87
$PPh_2(CH_2)_2PPh_2$	92	1.1	52
$PPh_2(CH_2)_3PPh_2$	89	0.9	47
$PPh_2(CH_2)_4PPh_2$	93	1.2	55

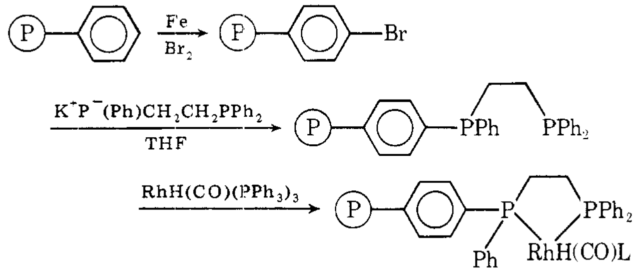
[a] 1-Pentene (1.0 mL, 9.1 mmol), rhodium (0.09 mmol), benzene (8.0 mL), P/Rh = 21:1, 100 psi (H_2/CO = 1:1), 80 °C, H_2/CO = 1:1.

Table V. Hydroformylation of 1-Pentene Catalyzed by Polymer-Anchored Catalyst 3a[a]

psi	Yield, n/b, selectivity (normal) 60 °C	80 °C	100 °C	120 °C
100	25%, 2.7, 73%	22%, 0.8, 47%	59%, 1.2, 55%	91%, 1.0, 50%
200	89%, 2.7, 73%	68%, 1.0, 50%	92%, 1.0, 50%	97%, 1.0, 50%
400	97%, 2.2, 69%	91%, 1.0, 50%	96%, 1.0, 50%	86%, 0.9, 47%
800	100%, 1.2, 55%	100%, 1.0, 50%	100%, 1.1, 52%	100%, 1.0, 50%

[a] 1-Pentene (1.0 mL, 9.1 mmol), catalyst (0.09 mmol of Rh), benzene (8.0 mL), P/Rh = 2.1:1, phosphine loading 5.7%, 21 h, H_2/CO = 1:1.

Scheme III



3a, PL = 5.7; P/Rh = 2.1
3b, PL = 22.2; P/Rh = 21

creased. This trend is just the opposite of that found upon adding excess triphenylphosphine (Table II).

To see if other chelating ligands exhibited a similar effect on hydroformylation selectivity, 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane were also studied. Representative results, summarized in Table IV, clearly establish that both of these ligands also lower the n/b selectivity.

Hydroformylations of 1-Pentene Catalyzed by Polymer-Anchored 1,2-Bis(diphenylphosphino)ethane Rhodium Complexes. Reaction of brominated styrene-divinylbenzene (1%) resins with $[PPh_2CH_2CH_2PPh]^-K^+$ followed by ligand exchange with $RhH(CO)(PPh_3)_3$ gave polymer-anchored catalyst 3 (Scheme III). These resin-anchored catalysts are unique since they should exhibit greater resistance to the leaching of rhodium or migration of rhodium along a catalyst bed than previous resin-anchored rhodium catalysts.[12,14,15,19] Two resins were prepared. Catalyst **3a** had a ligand loading (i.e., PL, the percentage of resin phenyl rings substituted with the ligand) of 5.7% and a P/Rh = 2.1 (almost all resin-attached ligands are chelating a rhodium). In contrast, catalyst **3b** had a ligand loading of 22.2% and P/Rh = 21. Thus, a higher density of ligand sites was available and about 9 out of 10 of these ligands did not chelate rhodium.

Table VI. Hydroformylation of 1-Pentene by Polymer-Anchored Catalyst 3b[a]

psi	Yield, n/b, selectivity (normal) 60 °C	80 °C	100 °C	120 °C
100	61%, 2.0, 67%	96%, 2.0, 67%	95%, 2.1, 68%	100%, 1.2, 55%
200	72%, 2.0, 67%	100%, 2.0, 67%	98%, 2.1, 68%	100%, 1.0, 50%
400	100%, 2.2, 69%	100%, 2.1, 68%	100%, 2.1, 68%	99%, 1.0, 50%
800	99%, 1.0, 50%	100%, 1.0, 50%	100%, 1.0, 50%	100%, 1.0, 50%

[a] 1-Pentene (1.0 mL, 9.1 mmol), catalyst (0.09 mmol of Rh), benzene (8.0 mL), P/Rh = 21:1, phosphine loading 22.2%, 21 h, H_2/CO = 1:1.

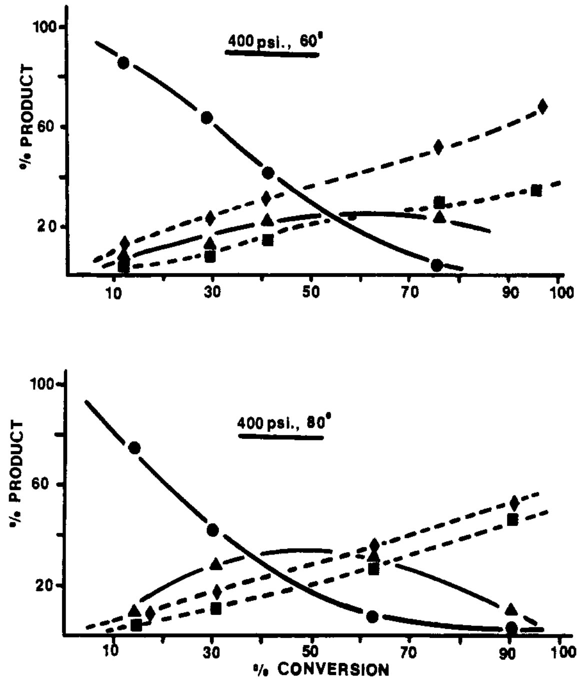


Figure 1. The product distribution as a function of conversion in hydroformylations of 1-pentene catalyzed by resin **3a**: (●) 1-pentene, (▲) 2-pentene, (◆) hexanal, (■) 2-methylpentanal.

Hydroformylations of 1-pentene were carried out using both **3a** and **3b** at 60–120 °C and 100–800 psi (summarized in Tables V and VI). As expected, based on the results with complex **1**, the n/b selectivities were low using both **3a** and **3b** over all conditions employed. For both **3a** and **3b** the selectivity decreased as either the temperature or the pressure was raised. The product distributions using **3a** are shown as a function of conversion in Table VII and Figure 1. Significant isomerization to 2-pentene occurred at both 60 and 80 °C (400 psi).

Despite the fact that a build up of 2-pentene occurs in these reactions, the n/b ratio remains constant as conversion increases. The fact that the n/b ratio does not depend on conversion implies that hydroformylation occurs mainly at the terminal double bond even when large amounts of 2-pentene are present. Thus, hydroformylation of the terminal isomer is faster than that of the internal isomers. Also, the n/b selectivity is low in terminal hydroformylation.

While other explanations may be advanced,[20] one can attribute this result to a lower propensity for anti-Markownikoff

Table VII. Product Distribution (%) as a Function of Conversion in Hydroformylations of 1-Pentene Using Catalyst 3a[a]

Cond	Conv, %	n/b	1-Pentene/ 2-pentene	1-Pentene	2-Pentene	Normal aldehyde[b]	Branched aldehyde[c]
400 psi, 60 °C	12	2.2	93/7	82.0	6.0	8.15	3.77
	29	2.2	86/14	61.8	9.8	19.73	8.76
	41	2.2	59/41	35.0	22.1	29.42	13.48
	76	2.0	7/93	1.7	22.4	50.20	25.70
	97	2.2				66.26	30.10
400 psi, 80 °C	15	1.2	90/10	76.5	8.5	8.19	6.82
	31	1.2	59/41	40.6	28.0	17.10	14.25
	63	1.2	16/84	5.9	30.8	34.53	28.77
	91	1.0	8/92	0.7	7.9	46.05	45.12

[a] 1-Pentene (1.0 mL, 9.1 mmol) catalyst (0.09 mequiv of Rh), benzene (8.0 mL), P/Rh = 2.1:1, H_2/CO = 1:1. [b] *n*-Hexanal. [c] 2-Methylpentanal.

Table VIII. Hydroformylation of 2-Pentene Catalyzed by $RhH(CO)(PPh_3)(PPh_2CH_2CH_2PPh_2)$[a]

	Yield (%), n/b			
psi	60 °C	80 °C	100 °C	120 °C
100	68, 0.12	79, 0.14	73, 0.39	90, 0.57
400	95, 0.06	92, 0.13	96, 0.17	98, 0.30
800	89, 0.06	90, 0.08	89, 0.07	95, 0.12

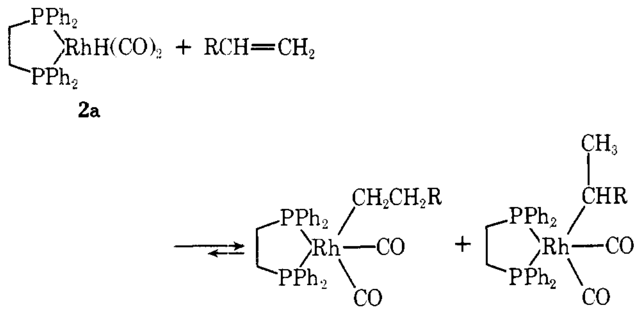
[a] 1-Pentene (1.0 mL, 9.1 mmol), rhodium (0.08 mmol), benzene (8.0 mL), 21 h, H_2/CO = 1:1.

Table IX. Hydroformylation of 2-Pentene Catalyzed by $RhH(CO)(PPh_3)_3$[a]

	Yield (%), n/b			
psi	60 °C	80 °C	100 °C	120 °C
100	87, 0.10	90, 0.23	91, 0.38	79, 0.49
400	98, 0.04	97, 0.10	93, 0.13	94, 0.27
800	94, 0.03	99, 0.04	100, 0.05	100, 0.06

[a] 1-Pentene (1.0 mL, 9.1 mmol), rhodium (0.09 mmol), benzene (8.0 mL), 21 h, H_2/CO = 1:1.

rhodium hydride addition of **2a** relative to $RhH(CO)_2(PPh_3)_2$. Since anti-Markownikoff addition of $RhH(CO)_2(PPh_3)_2$ to olefins is due largely to a steric effect,[16] we suggest that **2a** is less sterically hindered than its trans counterpart $RhH(CO)_2(PPh_3)_2$.


2a

Resin **3a** catalyzed the isomerization of 1-pentene to 2-pentene in the presence of high CO pressures. Thus, after 20 h at 80 °C and 400 psi of carbon monoxide, 40% of 1-pentene was converted to 2-pentene. This contrasts with $RhH(CO)(PPh_3)_3$ where isomerization is inhibited by the presence of carbon monoxide.[4,21]

Resins **3a** and **3b** were readily filtered from product solutions and recycled, often with little loss of activity. For example, catalyst **3a** proved to be very active even after 20 recycles at 600 psi and 80 °C. Remarkably, the filtrations used to separate the resin catalyst from the products were performed in air! At high temperatures, however, the activities of both **3a** and **3b** dropped after each cycle. For example, the yields of aldehydes obtained from reactions conducted at 120 °C, 400 psi, and 21 h with resin **3a** were 86, 73, 50, and then 15% (at 72 h) on successive recycles. The n/b selectivity remained constant.

Hydroformylation of 2-Pentene Catalyzed by $RhH(CO)(PPh_3)(PPh_2CH_2CH_2PPh_2)$, 1, and by $RhH(CO)(PPh_3)_3$. Published kinetic data on the hydroformylation of internal olefins with phosphine-substituted rhodium complexes is skimpy. The most detailed information available is for $RhH(CO)(PPh_3)_3$ at 25 °C and 1 atm[22] where 2-pentene hydroformylation was about 25 times slower than that of 1-pentene. When internal olefins were hydroformylated at 70–100 °C, terminal aldehydes were not obtained from phosphine–rhodium catalysts.[22,23] Thus, isomerization using phosphine–rhodium catalysts is markedly repressed below 100 °C.[23-26] Using $RhCl(CO)(PPh_3)_2$, Roth et al.[7] observed no terminal product in 2-pentene hydroformylations at 70 °C, but upon increasing the temperature to 150 °C the amount of *n*-hexanal increased to 36.8%. Excess triphenylphosphine reduced the amount of normal isomer to 16.1% at 150 °C. Excess triphenylphosphine caused the same effect in *cis*-2-butene hydroformylations catalyzed by Rh_2O_3.[23]

Since **1** exhibited a high isomerization activity (relative to $RhH(CO)(PPh_3)_3$), we though it might be a superior catalyst for the terminal hydroformylation of internal olefins. This would require (1) a rapid internal to terminal isomerization rate relative to internal hydroformylation, (2) significantly faster reaction at the terminal (versus internal) double bond, and (3) a high inherent n/b selectivity when the terminal double bond was hydroformylated. We felt that the first two criteria might hold. Thus, hydroformylations of 2-pentene were carried out employing $RhH(CO)(PPh_3)(PPh_2CH_2CH_2PPh_2)$, **1**, at 60–120 °C and 100–800 psi (results in Table VIII).

The n/b selectivities using **1** were low. However, the yield of *n*-hexanal increased as the temperature was raised from 60 to 120 °C at each pressure. In fact, 36% normal product was obtained at 120 °C and 100 psi. Raising the temperature increased the isomerization rate faster than the rate of internal hydroformylation. At temperatures from 60 to 120 °C, the selectivity to *n*-hexanal decreased as the pressure was increased. Either the rate of isomerization decreased as carbon monoxide pressure increased[21] or the rate of internal olefin hydroformylation increased relative to isomerization.

To compare the effect of the 1,2-bis(diphenylphosphino)ethane to that of triphenylphosphine, the selectivities in rhodium-catalyzed 2-pentene hydroformylations were obtained at the same conditions (see Table IX). The trends are similar. The amount of terminal product increases as temperature is raised, but the amount of terminal product is less with $RhH(CO)(PPh_3)_3$. At 100 °C and 100 psi a n/b selectivity

Table X. Hydroformylation of 2-Pentene Catalyzed by $RhH(CO)(PPh_3)_3$ in the Presence of Excess PPh_3[a]

psi	Yield (%), n/b 60 °C	100 °C	120 °C
100	40, 0.06	85, 0.03	74, 0.10
400	49, 0.05	100, 0.03	99, 0.09
800	66, 0.03	100, 0.05	100, 0.08

[a] 2-Pentene (1.0 mL, 9 mmol), rhodium (0.09 mmol), benzene (8 mL), P/Rh = 21:1, 21 h, H_2/CO = 1:1.

Table XI. Hydroformylation of 2-Pentene Catalyzed by $RhH(CO)(PPh_3)_3$ in the Presence of $PPh_2CH_2CH_2PPh_2$[a]

psi	Yield (%), n/b 60 °C	80 °C	100 °C	120 °C
100	28, 0.00	55, 0.00	72, 0.00	62, 0.10
400	9, 0.00	36, 0.00	61, 0.00	78, 0.02
800	7, 0.00	12, 0.00	65, 0.00	90, 0.00

[a] 2-Pentene (1.0 mL, 9.1 mmol), rhodium (0.09 mmol), benzene (8.0 mL), P/Rh = 21:1, 21 h, H_2/CO = 1:1.

Table XII. Hydroformylation of 2-Pentene by Polymer-Anchored Catalyst 3a[a]

psi	Yield (%), n/b 60 °C	80 °C	100 °C	120 °C	140 °C
100	28, 0.45	56, 0.48	71, 0.66	78, 0.68	91, 0.72
200	15, 0.39	74, 0.46	62, 0.65	51, 0.66	98, 0.69
400	63, 0.15	91, 0.14	97, 0.43	95, 0.64	100, 0.69
800	100, 0.05	100, 0.20	96, 0.29	100, 0.43	100, 0.66

[a] 2-Pentene (1.0 mL, 9.1 mmol), catalyst (0.09 mmol of rhodium), benzene (8.0 mL), P/Rh = 21:1, phosphine loading 5.7%, 21 h, H_2/CO = 1:1.

Table XIII. Hydroformylation of 2-Pentene by Polymer-Anchored Catalyst 3b[a]

psi	Yield (%), n/b 60 °C	80 °C	100 °C	120 °C
100	22, 0.11	44, 0.11	63, 0.16	88, 0.29
200	53, 0.08	74, 0.08	95, 0.12	86, 0.28
400	80, 0.06	99, 0.08	100, 0.10	93, 0.29
800	100, 0.03	93, 0.06	98, 0.13	95, 0.22

[a] 2-Pentene (1.0 mL, 9.1 mmol), catalyst (0.09 mmol of Rh), benzene (8.0 mL), P/Rh = 21:1, phosphine loading 22.2%, 21 h, H_2/CO = 1:1.

of 0.38 was achieved. Thus, at mild conditions, isomerization does become competitive with internal hydroformylation.

The addition of excess triphenylphosphine (Table X) or excess 1,2-bis(diphenylphosphino)ethane (Table XI) inhibits isomerization in 2-pentene hydroformations. Only branched products were obtained when $Ph_2PCH_2CH_2PPh_2$ was used at 60–100 °C and 100 to 800 psi. Traces of *n*-hexanal were found at 120 °C and 100 or 400 psi. Excess triphenylphosphine reduced the amount of normal product but did not eliminate it, as was the case using the chelating ligand.

Hydroformylations of 2-Pentene Catalyzed by Polymer-Anchored 1,2-Bis(diphenylphosphino)ethane rhodium Complexes. Resin catalysts **3a** and **3b** were employed in 2-pentene hydroformylations at 60–140 °C and 100–800 psi. High aldehyde yields were obtained in all cases except at 100–200 psi and 60–80 °C where partial conversion occurred at 21 h. Surprisingly, the n/b selectivities for resin **3a** (Table XII) were higher than those of 1 (Table VIII), although the trends were the same. The selectivity increased with increasing temperature using **3a** and **3b** (Tables XII and XIII)

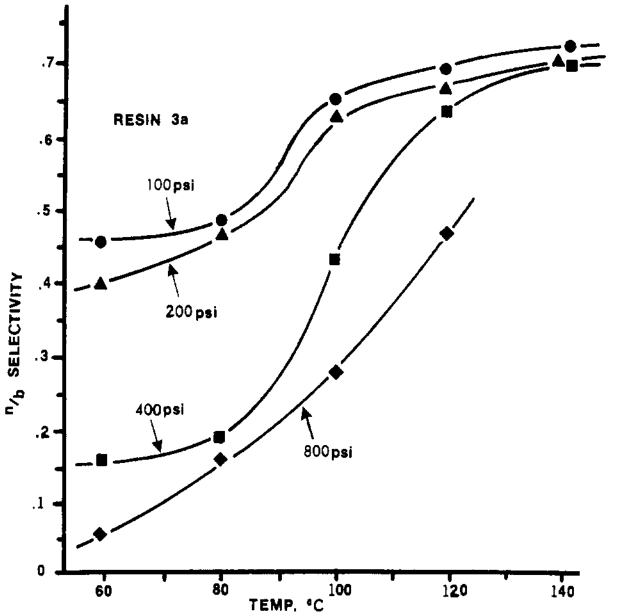


Figure 2. The normal to branched product selectivity as a function of temperature in 2-pentene hydroformylations catalyzed by resin 3a.

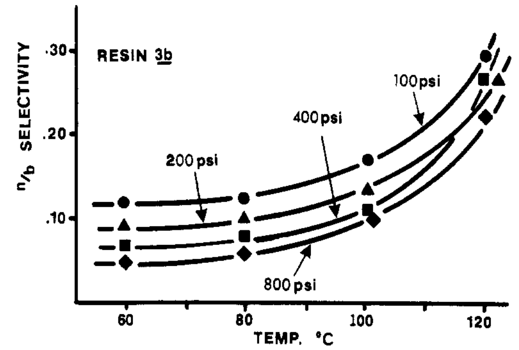


Figure 3. The normal to branched product selectivity as a function of temperature in 2-pentene hydroformylations catalyzed by resin 3b.

and decreased as the pressure was raised with resin **3a**. Figures 2 and 3 plot selectivity vs. temperature for resins **3a** and **3b** at different pressures. The highest selectivity achieved was n/b = 0.72 using **3a** at 100 psi and 140 °C. This corresponds to a 42% yield of *n*-hexanal from 2-pentene. *Thus, the selectivity to normal product was greater at 140 °C than that reported for* $Rh(CO)Cl(PPh_3)_2$ *at 200 °C.* Unfortunately, the temperature dependence of selectivity levels off above 120 °C suggesting that further temperature increases will have only a modest effect at raising the n/b ratio.

The terminal selectivity of **3b** in 2-pentene hydroformylations (Table XIII) was lower than that of **3a.** Since excess $Ph_2PCH_2CH_2PPh_2$ suppresses isomerization, the low selectivity of **3b** with its 22% ligand loading and P/Rh = 21 is not surprising. Thus, more internal hydroformylation is expected with **3b.** This agrees with the observation (Table V and VI) that resin **3a** is less selective than **3b** in 1-pentene hydroformylations (i.e., isomerization to 2-pentene plays a larger role when **3a** is the catalyst).

The selectivity of **3b** (Table XIII) is higher than that of its soluble analogue, 1 (Table XI), at the same P/Rh ratio (21:1). For example, 10–20% normal product was obtained using **3b** at 100–120 °C and 100–800 psi despite its excess of ligand (P/Rh = 21). Linear product formation was more effectively suppressed with 1. This may be attributed to the restricted

Table XIV. Product Distribution (%) as a Function of Conversion in Hydroformylations of 2-Pentene Using Catalyst 3a[a]

Cond	Conv, %	n/b	1-Pentene/ 2-pentene	1-Pentene	2-Pentene	Normal aldehyde[b]	Branched aldehyde[c]
200 psi, 80 °C	7.3	0.59	6/94	5.3	87.4	2.71	4.61
	26	0.52	4/96	3.2	70.5	8.98	17.35
	51	0.47	7/93	3.4	46.0	16.18	34.42
	74	0.46	10/90	2.5	23.6	23.41	50.43
	94	0.51	11/89	0.7	5.4	31.08	62.20
400 psi, 80 °C	35	0.15	0.1/99.9	0.06	64.9	4.46	30.58
	52	0.20	0.5/99.5	0.2	47.4	9.00	43.41
	76	0.16	3/97	0.8	23.6	10.43	65.17
	91	0.14	10/90	0.8	8.0	11.29	79.84

[a] 1-Pentene (1.0 mL, 9.1 mmol), catalyst (0.09 mmol of Rh), benzene (8.0 mL), P/Rh = 21:1, H_2/CO = 1:1. [b] n-Hexanal. [c] 2-Methylpentanal and 2-ethylbutanal.

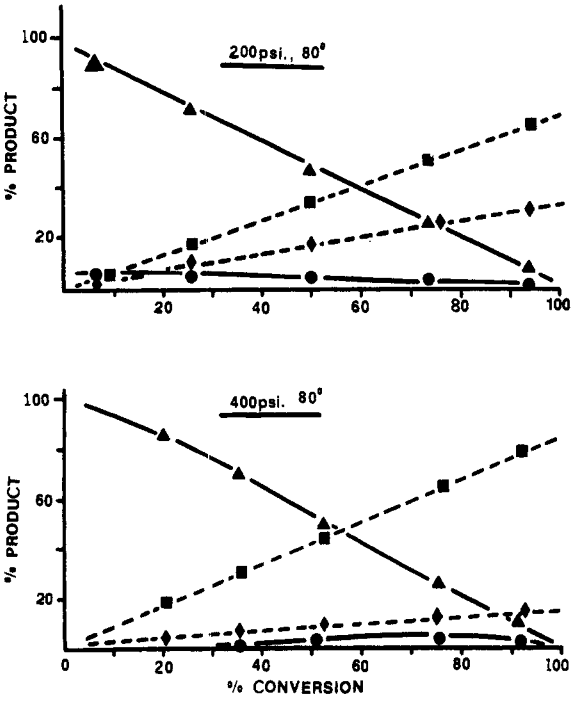


Figure 4. The product distribution as a function of conversion in hydroformylations of 2-pentene catalyzed by resin **3a**: (●) 1-pentene, (▲) 2-pentene, (◆) hexanal, (■) 2-methylpentanal.

ligand mobility within the **3b** polymer matrix. At 22% ligand loading, the ligand concentration available to rhodium is lower than that available to the same P/Rh in the homogeneous solutions. This is an example of partial matrix isolation.[27,28]

The rate of 2-pentene hydroformylations decreased as excess 1,2-bis(diphenylphosphino)ethane was added. The rates were often greater using **3b** than using **1** (homogeneous) at P/Rh = 21. Again, this is a manifestation of ligand matrix isolation.

Product distributions as a function of conversion for 2-pentene reactions at 200 and 400 psi are summarized in Table XIV and Figure 4. At 400 psi and 80 °C, the amount of 1-pentene observed never reached 1%. When the pressure was reduced to 200 psi at 80 °C, as much as 5% 1-pentene was detected early in the reaction. However, this level decreased steadily as conversion increased. The n/b ratio was independent of conversion.

Conclusions

Using chelating phosphine ligands in rhodium-catalyzed 1-pentene hydroformylations sharply decreases the n/b selectivity. The isomerization activity is greater with 1,2-bis(diphenylphosphino)ethane (relative to PPh_3). The n/b selectivity is reduced during reaction at the terminal double bond. The hydroformylation activity for internal double bonds is greater using complex 1 than with $RhH(CO)(PPh_3)_3$. Yields of terminal product from 40 to 45% may be obtained from 2-pentene at temperatures from 120 to 140 °C using a polymer-anchored 1,2-bis(diphenylphosphino)ethane complex. However, this system cannot match the high n/b ratios for internal olefins, given by modified cobalt catalysts. For example, $Co_2(CO)_6(PBu_3)_2$ gives as much *n*-heptanal from 2-hexene as from 1-hexene.[29] Slaugh and Millineaux[1] have noted good yields for terminal products with cobalt systems, and Asinger, Fell, and Rupilius[30] found 76% terminal product could be obtained from *trans*-4-octene. Finally, phosphine modified cobalt catalysts, at 190 °C, gave >80% nonanol from 2-octene.[31] The high selectivity of phosphine-modified cobalt catalysts results in part from the higher steric hindrance encountered in the production of branched isomers.

Rhodium complexes of cis-chelating phosphines have a lower regioselectivity for anti-Markownikoff rhodium hydride addition than either phosphine modified cobalt catalysts or $RhH(CO)(PPh_3)_3$. This probably results from the lower steric demand of the cis ligand during rhodium hydride addition.

Experimental Section

Benzene and toluene were dried over CaH_2 for at least 24 h and distilled under nitrogen. Similar care was taken to dry all solvents. Nitrogen, hydrogen, and carbon monoxide were obtained commercially (99 + %) and used as received. $RhH(CO)(PPh_3)_3$ and the bisphosphine ligands ($PPh_2(CH_2)_nPPh_2$, $n = 2, 3$, and 4) were obtained from Strem or Pressure Chemical Co.

Preparation of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$. The title compound was prepared from phenylphosphine and diphenylvinylphosphine sulfide by base-catalyzed addition of $C_6H_5PH_2$ across the vinyl group, followed by $LiAlH_4$ reduction of the sulfide according to the method of King.[32] A 40% yield, bp 210–215 °C (0.2 mmHg), was obtained. The product had an NMR spectrum identical with that reported.[33]

Preparation of Cis-Chelated Resin Catalyst 3. A dry THF solution (100 mL) containing $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ (15.7 g, 49 mmol) was added slowly to a suspension of potassium metal (14 g, 359 mmol) in dry THF (100 mL) under nitrogen. A yellow precipitate appeared immediately. Stirring was continued 2 days at 22 °C under nitrogen and unreacted potassium was then removed. The solution was transferred, under nitrogen, to a rapidly stirred THF slurry of brominated styrene–1% divinylbenzene resin beads (6.4 g, 20.78% Br, 34% of rings brominated, 16.6 mg-atoms of bromine per g). This reaction was stirred under nitrogen 72 h and unreacted $KP(C_6H_5)CH_2CH_2P(C_6H_5)_2$ was hydrolyzed in deoxygenated acetone–water (3:1, 1 L). The resin beads were washed successively in 1-L each of the following nitrogen-purged solvents: acetone, water, benzene, and methanol. The beads were dried at 22 °C (0.1 mmHg) for several days. Analysis found 7.71% P which corresponded to 22.2% of the phenyl rings containing a bound $P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ group. Aliquotes of the polymer were then swollen in benzene and reacted with the desired amount of $RhH(CO)(PPh_3)_3$ to effect phosphine exchange. Using various ratios of polymer to $RhH(CO)(PPh_3)_3$, the P/Rh of the resin could be varied. The resulting polymers (i.e., **3a** and **3b**) were then extracted (soxhlett) with benzene and dried under vacuum. Hydroformylations of 1-pentene or 2-pentene using **3a** or **3b** were carried out as described below.

Hydroformylations of 1-Pentene by Resin-Anchored Catalysts. Hydroformylations were carried out in 150 cm^3 stainless steel pressures bombs (dried at 120 °C overnight and purged with nitrogen while cooling). The resin catalyst (0.09 mmol of Rh) was added with benzene (8 mL) and 1-pentene (1.0 ml, 9.1 mmol). The bomb was cooled (ice bath), pressurized with carbon monoxide (400 psi), and allowed to equilibrate 5 min before venting to atmospheric pressure. This procedure was repeated twice. The bomb was raised to the desired pressure with equal amounts of hydrogen and carbon monoxide (or the appropriate amounts of each in cases where a 1:1 ratio was not used). The bomb was placed in a preequilibrated oil bath and vigorously shaken for the desired reaction time. The reactions were conducted at a constant pressure by connecting the reaction bomb to a gas reservoir via stainless steel tubing (coiled to permit shaking) and a pressure control valve. Thus, the pressure to the bomb remained constant while the pressure in the gas reservoir dropped. Kinetics were easily monitored by measuring the pressure change in the reservoir (known volume) by means of a pressure transducer connected to a recorder. Thus, pressure vs. time plots were directly obtained during the reaction. This system is described elsewhere in detail.[18]

Upon completion, the bomb was cooled and gases were then vented. The reaction solution was quantitatively analyzed by VPC. The resin was recovered (filtration), washed (extracted), and dried under vacuum before being recycled. The products, hexanal and 2-methylpentanal, were isolated by preparative VPC and analyzed by NMR and IR. They were identical with authentic samples. Product yields were routinely obtained by analytical GLC using electronic integration.

Comparison of Homogeneous and Resin-Anchored Catalysts. The polymer-anchored and homogeneously catalyzed reactions were compared using equal solution volumes, equivalent amounts of rhodium, equal 1-pentene/Rh ratios, and the same 1-pentene/benzene ratios. The reactions were always compared at equal temperatures, pressures, P/Rh ratios, and H_2/CO ratios. However, even when conducted this way, they are not completely analogous because the swollen volume of the resin does not fill the entire solution volume. Thus, rhodium and phosphorus are confined to the swollen polymer's volume using anchored-catalysts as opposed to the entire solution volume in homogeneous runs. For this reason, selectivity was directly compared at equivalent "concentrations" in several cases. In one case, where resin **3a** occupied 20% of the reaction solution's volume, the concentration of rhodium in the homogeneous reaction was increased by a factor of five (to 5.0×10^{-2} M HpRh). Now the local concentration of phosphine and rhodium in the resin was quite close to that in the homogeneous reaction. Selectivities did not depend upon the concentration of catalyst at the conditions studied in this paper.

Preparation of $RhH(CO)(PPh_3)(PPh_2CH_2CH_2PPh_2)$, 1. To a 300 mL Schlenk flask (under nitrogen) was added 1.836 g (2 mmol) of $RhH(CO)(PPh_3)_3$, 0.796 g (2 mmol) of $PPh_2CH_2CH_2PPh_2$, and 200 mL of benzene. The reaction mixture was heated to reflux with stirring for 3 days. Then, benzene was evaporated in vacuo and the residue was extracted with hot *n*-hexane followed by drying to give a yellow-grey solid. Anal. Calcd: Rh, 12.98; C, 68.19. Found: Rh, 12.82; C, 68.63.

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Registry No.—**1**, 64611-33-2; $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$, 33355-58-7; $BhH(CO)(PPh_3)_3$, 64665-44-7; PPh_3, 603-35-0; $PPh_2(CH_2)_2PPh_2$, 1663-45-2; $PPh_2(CH_2)_3PPh_2$, 6737-42-4; $PPh_2(CH_2)_4PPh_2$, 7688-25-7; $KP(C_6H_5)CH_2CH_2P(C_6H_5)_2$, 64611-28-5; styrenedivinylbenzene polymer, 9003-70-7; 1-pentene, 109-67-1; 2-pentene, 109-68-2.

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(16) Wilkinson[3] demonstrated that $(PPh_3)_3RhH(CO)$ was converted to an equilibrium mixture of $(PPh_3)_2RhH(CO)_2$, $(PPh_3)RhH(CO)_2$, and $[Rh(CO)_2(PPh_3)_2]_2$ in solution in the presence of CO. He then postulated that hydroformylation proceeded through one of two paths, depending on the conditions.[4] In the associative pathway, olefin first coordinates to $(PPh_3)_2RhH(CO)_2$ followed by rapid metal hydride addition across $>C{=}C<$. In the dissociative pathway, PPh_3 is lost from $(PPh_3)_2RhH(CO)_2$ giving $(PPh_3)RhH(CO)_2$ which coordinates with olefin followed by fast metal hydride addition. The selectivity is determined in the metal hydride addition step. For both electronic and steric reasons,[4] the dissociative pathway, where $(PPh_3)RhH(CO)_2$ adds across the olefin, is less selective than the associative path where $(PPh_3)_2RhH(CO)_2$ adds across the olefin. At higher phosphine concentrations, Wilkinson[4] postulated (because the equilibrium would favor formation of $(PPh_3)_2RhH(CO)_2$) that the associative pathway was increasingly favored, thus accounting for the increased selectivity at high phosphine concentrations. The associative pathway may be criticized for requiring a 20-electron intermediate unless it is viewed as a direct rhodium hydride addition to an uncoordinated olefin.

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