Thermal conductivities of ozonide stereoisomers were assumed to be equal. Ozonide ratio peak areas used were based on at least three successive determinations on each of three separate injections. The determinations have a maximum variation of ±0.5%. Ozonide yields were determined in a similar manner using standard solutions to calibrate peak areas. Yield data were determined with a precision of ±0.5%. Results of the analyses are shown in Figures 3 and 4.

The GLPC chromatograms were also used to check for actual olefin consumption. In particular, the olefin consumptions were checked for the ozonolysis of *trans*-2,5-dimethyl-3-hexene in methylene chloride and *n*-butyraldehyde solvents. The total ozonide yield in these two solvents differs greatly (CH_2Cl_2, 1.96 mmol; *n*-butyraldehyde, 0.72 mmol). Yet the olefin consumption in these cases differs only slightly (CH_2Cl_2, 3.72 mmol; *n*-butyraldehyde, 3.59 mmol). The difference in ozonide yield is, therefore, not due to a reduced olefin consumption in the aldehyde solvent.

Ozonolysis of *trans*-2,2,5,5-Tetramethyl-3-hexene. The general ozonolysis procedure was used with the reaction solutions cooled to ca. −78 °C in a dry ice–methanol bath. The ozonolysis solutions were 5 mL of an 0.5 M solution of *trans*-2,2,5,5-tetramethyl-3-hexene in *n*-hexane, mixtures of *n*-hexane–*n*-butyraldehyde, or 100% *n*-butyraldehyde. Ozonolysis was continued to 75% of the theoretical amount required. Ozonide isomer distributions and yields were determined as described above, using column B for analytical GLPC (column temperature, 50 °C) and column C for preparative GLPC (column temperature, 65 °C). The results are shown in Figure 6.

Low-Temperature Ozonolysis of *trans*-2,5-Dimethyl-3-hexene. The general ozonolysis procedure was used with the reaction solutions cooled to −105 °C in a liquid N_2–isopentane bath. The ozonolysis solutions contained 2.5 mmol of *trans*-2,5-dimethyl-3-hexene in 5 mL of isopentane. Ozonolysis was continued until ozone was present in excess as evidenced by the appearance of a blue color (ca. 30 min). The reaction solutions were then purged with argon until the blue color was removed. At this point the reaction mixtures contained a white precipitate. The reaction mixtures were then warmed up to −98 °C, and solutions containing various amounts of *n*-butyraldehyde in isopentane (total volume of 5 mL) were added. The reaction mixtures were purged with argon continuously during addition of the aldehyde solutions. After addition of the aldehyde solutions, the reaction mixtures were allowed to warm up using the slow warmup conditions. During some of these warmups small explosions occurred which were contained within the reaction vessel. These were presumably due to rapid decomposition of the unstable trioxolane.

The reaction mixtures were analyzed by GLPC using column A (column temperature, 50 °C) to determine ozonide yields and isomer distributions. The GLPC chromatograms indicated that all of the olefin had reacted. Results of these analyses are shown in Figure 5.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE 75-23074) and to the National Institutes of Health (Grant No. ES-01934) for support of this work. We also acknowledge a helpful discussion with Professor Eric Block.

Registry No. *cis*-2,5-Dimethyl-3-hexene, 10557-44-5; *trans*-2,5-dimethyl-3-hexene, 692-70-6; *trans*-2,2,5,5-tetramethyl-3-hexene, 692-48-8; *n*-butyraldehyde, 123-72-8; *cis*-2,5-dimethyl-3-hexene ozonide, 13126-94-8; *trans*-2,5-dimethyl-3-hexene ozonide, 13126-95-9; *cis*-*n*-propylisopropylethylene ozonide, 72444-59-8; *trans*-*n*-propylisopropylethylene ozonide, 72444-60-1; *cis*-2,2,5,5-tetramethyl-3-hexene ozonide, 16187-12-5; *trans*-2,2,5,5-tetramethyl-3-hexene ozonide, 16187-11-4.

Hydroformylation of Methyl Methacrylate Catalyzed by Homogeneous and Polymer-Attached Rhodium Complexes

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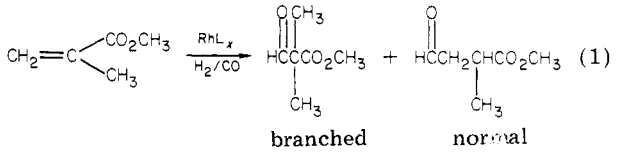
The hydroformylation of methyl methacrylate has been studied in the presence of $RhH(CO)(PPh_3)_3$ or its polymer-anchored analogue as the catalyst. The branched/normal product ratio was exceptionally sensitive to conditions, increasing as (1) [P]/[Rh] increased, (2) the pressure increased, (3) PPh_3 was replaced by $Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$, and (4) the polymer-supported phosphines replaced PPh_3 at equivalent P/Rh ratios. The branched/normal selectivity decreased as (1) $[H_2]/[CO]$ increased and (2) the temperature increased. Changing the solvent from benzene to THF or adding Et_3N had only minor effects on selectivity. The results are interpreted in terms of Wilkinson's mechanism where electronic effects control double-bond insertion into the rhodium–hydride bonds but isomerization equilibria of alkyl or acyl intermediates become more important at higher temperatures.

The hydroformylation of α,β-unsaturated esters, and in particular acrylates and methacrylates, has received much attention as a route to 1,3- and 1,4-difunctional compounds.[1-6] The product distribution in the hydroformylation of ethyl acrylate has been studied with cobalt[1,2] and rhodium[3,4] catalyst systems. The rhodium-catalyzed hydroformylation of methyl methacrylate (MMA) has been studied and the normal/branched selectivity has been found to be highly dependent on reaction conditions.[4-6] For example, Falbe[5] found the branched product (eq 1) was favored at low temperatures while the normal product dominated at high temperatures when a Rh_2O_3 catalyst was used. At 1000 atm (1:1 H_2/CO) the branched isomer accounted for ca. 85% of the product at 80 °C vs. only 13% at 150 °C. Higher pressures favored formation of the branched isomer as did the addition of phosphine ligands.



Pruett and Smith,[6] using 5% Rh/C with triphenyl phosphite ([P]/[Rh] = 6.1), found that the yield of the

(1) Y. Takegami, C. Yokokawa, and Y. Watanabe, *Bull. Chem. Soc. Jpn.*, **39**, 2430 (1966).
(2) J. Falbe, N. Huppes, and F. Korte, *Chem. Ber.*, **97**, 863 (1964).
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Table I. $RhH(CO)(PPh_3)_3$ Catalyzed Hydroformylation of Methyl Methacrylate Using 1:1 H_2/CO[a]

[P]/[Rh]	T, °C	P, psi	time, h	% convrsn	product % yield[b] branched	normal
3	80	50	22	63	25	75
3	80	100	5	58	31	69
3	80	200	18	82	57	43
3	80	400	24	100	81	19
3	80	600	4	97	93	7
3	80	800	8	100	94	6
20	80	50	23	62	48	52
20	80	100	23	87	70	30
20	80	200	23	96	80	20
20	80	400	25	99	93	7
20	80	600	23	100	96	4
20	80	800	23	100	97	3
3	80	100	5	57	31	69
6	80	100	24	90	46	54
10	80	100	23	82	53	47
15	80	100	22	93	53	47
20	80	100	23	87	70	30
25	80	100	20	96	67	33
30	80	100	22	72	64	36
40	80	100	22	64	66	34
3	25	200	48	52	99	1
3	40	200	22	59	98	2
3	60	200	23	99	90	10
3	80	200	18	82	57	43
3	100	200	21	88	14	86
3	120	200	23	61	5	95
3	30	800	91	86	99	1
3	80	800	8	100	94	6
3	150	800	6	69	16	84
20	40	200	23	58	98	2
20	60	200	23	98	96	4
20	80	200	23	96	80	20
20	100	200	22	99	57	43
20	120	200	22	100	13	87
20	150	200	18	56	2	98

[a] When [P]/[Rh] exceeds 3, the excess phosphine is added PPh_3. [b] These yields refer to the yield based on column 5. Thus, for the first entry the branched/normal ratio is 25:75 and the branched yield is 0.25 × 63%.

Table II. Effect of H_2/CO Ratio on Selectivity in Hydroformylations of Methyl Methacrylate Catalyzed by $RhH(CO)(PPh_3)_3$ at 80 °C and 200 psi

$[H_2]/[CO]$	[P]/[Rh]	time, h	% convrsn	product % yield[a] branched	normal
0.5	3	23	96	57	43
1	3	18	82	57	43
2	3	23	99	48	52
4	3	23	99	24	76
6	3	24	99	12	88

[a] Yields refer to yields based on column 4. See Table I, footnote *b*.

branched isomer increased from 4 to 77% as the pressure increased from 110 to 2500 psi at 110 °C. A high selectivity to the branched isomer was also promoted by chelating diphosphine ligands.[4]

We have previously examined the effects of binding phosphine ligands to polymers on the selectivities of 1-pentene[7-10] and allyl alcohol[11] hydroformylations. Since

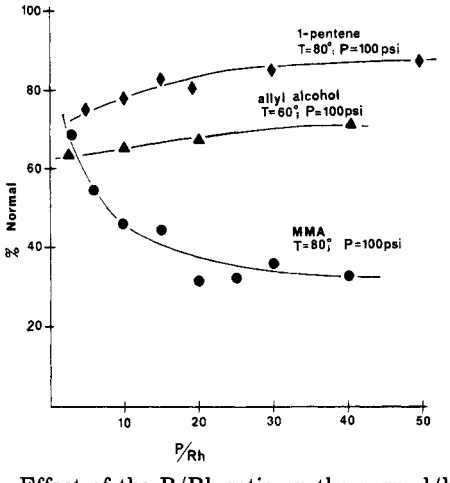


Figure 1. Effect of the P/Rh ratio on the normal/branched selectivity in hydroformylations of methyl methacrylate catalyzed by $RhH(CO)(PPh_3)_3$ at 1:1 H_2/CO and comparison with 1-pentene and allyl alcohol.

the selectivities of MMA hydroformylations were so sensitive to reaction conditions[4-6] and because polymer-anchored phosphines had large effects on the selectivities of 1-pentene hydroformylations,[7-10] we undertook a study of

(7) C. U. Pittman, Jr., and R. M. Hanes, *J. Am. Chem. Soc.*, **98**, 5402 (1976).
(8) C. U. Pittman, Jr., A. Hirao, C. Jones, R. M. Hanes, and Q. Ng, *Ann. N.Y. Acad. Sci.*, **295**, 15 (1977).
(9) C. U. Pittman, Jr., Q. Ng, A. Hirao, W. Honnick, and R. Hanes, *Colloques Internationaux CNRS*, **No. 281**, 49–94 (1978).
(10) C. U. Pittman, Jr., and A. Hirao, *J. Org. Chem.*, **43**, 640 (1978).
(11) W. D. Honnick and C. U. Pittman, Jr., submitted for publication in *J. Org. Chem.*

Table III. Effect of Solvent and Ligand on Selectivity in Hydroformylations of Methyl Methacrylate Catalyzed by $RhH(CO)(PPh_3)_3$ at 80 °C

solvent	added ligand	[ligand]/[Rh][a]	P, psi	time, h	% convrsn	product % yield[c] branched	normal
THF			200	21	95	55	45
benzene			100	5	58	31	69
benzene			200	18	82	57	43
benzene	PPh_3	3	100	24	90	46	54
benzene	PPh_3	17	100	23	87	70	30
benzene	2[b]	8.5	200	22	98	73	27
benzene	PPh_3	17	200	23	96	80	20
benzene	1[b]	1	100	23	68	59	41
benzene	Et_3N	77	100	22	56	37	63

[a] This is the added ligand/Rh ratio. In all cases $RhH(CO)(PPh_3)_3$ was charged into the reaction. [b] 1 is triphos and 2 is bis(diphenylphosphino)ferrocene. [c] Yields refer to yields based on column 6. See Table I, footnote *b*.

Table IV. Hydroformylations of Methyl Methacrylate Catalyzed by Polymer-Attached Rhodium, $(Ⓟ\text{-}PPh_2)_3RhH(CO)$, at 80 °C[a]

resin no.	% divinyl-benzene	% phosphine loading	[P]/[Rh]	P, psi	% convrsn	product % yield[b] branched	normal
3a	1	7	5	200	41	51	49
3a	1	7	5	400	29	72	28
3b	2	7	6	200	49	43	57
3c	2	16	4	200	30	46	54
3d	2	16	20	200	92	84	16
3e	1	29	3	100	20	59	41
3e	1	29	3	200	18	75	25
3e	1	29	3	400	16	92	8
3f	1	29	20	200	15	68	32
3f	1	29	20	400	65	95	5
3g	2	30	18	200	15	85	15
3g	2	30	18	400	49	95	5
3h	1	40	19	200	13	84	16
3i	1	40	31	200	60	85	15
3i	1	40	31	400	44	92	8
3j	1	61	12	200	2	86	14

[a] All reactions were run from 21 to 24 h. [b] The normal and branched yields refer to the stated percentage of the conversion. For example, in the first entry with resin 3a, the 51% yield of branched aldehyde means 51% of the 41% total conversion is branched.

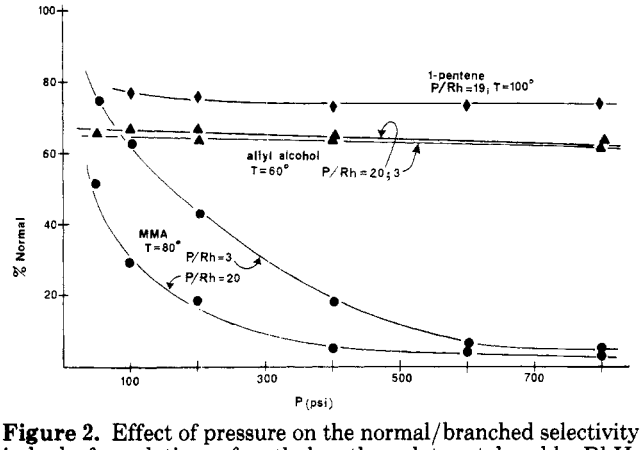


Figure 2. Effect of pressure on the normal/branched selectivity in hydroformylations of methyl methacrylate catalyzed by $RhH(CO)(PPh_3)_3$ at 1:1 H_2/CO and comparison with 1-pentene and allyl alcohol.

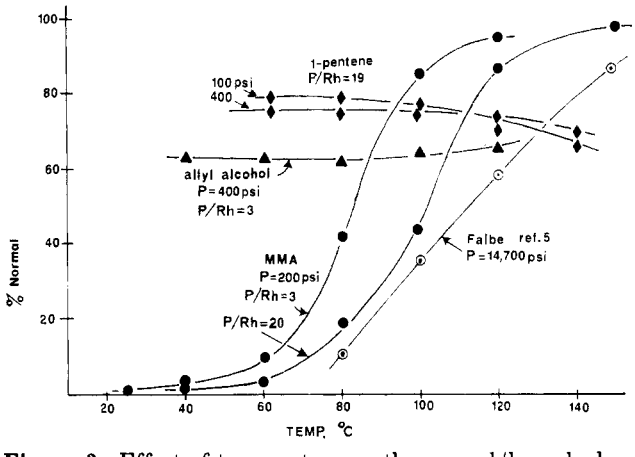


Figure 3. Effect of temperature on the normal/branched selectivity in hydroformylations of methyl methacrylate catalyzed by $RhH(CO)(PPh_3)_3$ at 1:1 H_2/CO and comparison with 1-pentene and allyl alcohol.

MMA hydroformylations catalyzed by $RhH(CO)(PPh_3)_3$ and its polymer-anchored analogues.

Results

MMA was hydroformylated according to eq 1 in high yields and the normal/branched product ratio was established by GLC. The results are summarized in Tables I–IV and Figures 1–3. At higher temperatures the aldehyde yields were sometimes lower due to competition from MMA polymerization.

Dependence of Selectivity on the P/Rh Ratio. The dependence of the normal/branched selectivity on the P/Rh ratio was studied by using $RhH(CO)(PPh_3)_3$ and added PPh_3. As the P/Rh ratio was increased from 3 to 40 the selectivity to branched product increased from 31% to 66% (at 80 °C and 100 psi). This trend is just the opposite of that observed for unfunctionalized olefins where higher P/Rh ratios lead to more normal product.[7-10]

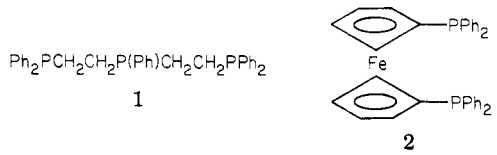
The results for MMA are displayed in Figure 1 together with results for 1-pentene and allyl alcohol. The same trend with an increase in [P]/[Rh] is observed both at 50 psi, where the branched product increases from 25% to 48% as [P]/[Rh] increases from 3 to 20, and at 400 psi where a corresponding increase in branched product from 81% to 93% occurs. Table I summarizes representative results.

Dependence of Selectivity on Pressure and H_2/CO Ratio. The dependence of selectivity on pressure (at 1:1 H_2/CO) in MMA hydroformylations is illustrated in Figure 2 for P/Rh ratios of 3 and 20, respectively. Increasing the pressure results in a large increase selectivity in to the branched product at both low and high P/Rh ratios. This pressure dependence of the selectivity is in the same direction as that observed for both 1-pentene[7-10] and allyl alcohol,[11] both of which are also shown in Figure 2 for comparison. However, the sensitivity of the selectivity to pressure is much greater for MMA. Table I lists representative results. At constant total pressure, the selectivity to the normal product increases as $[H_2]/[CO]$ increases. Table II summarizes representative results at 80 °C, 200 psi, and [P]/[Rh] = 3. As $[H_2]/[CO]$ increases from 0.5 to 6 (i.e., as the CO partial pressure decreases) the normal selectivity enlarges from 43% to 89%.

Dependence of Selectivity on Temperature. Increasing temperature results in an increased selectivity toward the normal product in MMA hydroformylations. This is true at both low and high P/Rh ratios. For example, at [P]/[Rh] = 3 and 200 psi, only 1% of the normal isomer is obtained at 25 °C compared to 95% at 120 °C. Similarly, at [P]/[Rh] = 20 and 200 psi, the normal isomer yield increases from 2% to 98% as the temperature is raised from 40 to 150 °C. These results are shown in Figure 3 where they are compared to similar studies on 1-pentene and allyl alcohol. As temperature is increased, there is a small decrease in the selectivity to the normal product for 1-pentene and a small increase for allyl alcohol. In both, the temperature dependence on the selectivity is far less than that found for MMA. The isomer distribution for MMA found by Falbe[5] in Rh_2O_3-catalyzed hydroformylations at 14 700 psi are also shown in Figure 3 for comparison.

Effect of Solvent and Added Ligands. The selectivity of MMA hydroformylations was studied in both benzene and THF. Very little difference resulted upon changing the solvent when the $RhH(CO)(PPh_3)_3$ catalyst system was used. At 80 °C and 200 psi, the selectivity to the branched product was 57% in benzene and 55% in THF.

Two chelating phosphines were compared with triphenylphosphine (Table III). These were triphos, **1**, and bis(diphenylphosphino)ferrocene, **2**. When **1** and **2** were

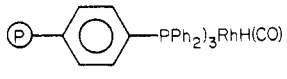


1 2

compared at equal P/Rh ratios, triphos resulted in higher selectivities to the branched product. For example, at 80 °C, 100 psi, and [P]/[Rh] = 6, the selectivity to the branched product increased from 45% using PPh_3 to 59% using triphos. However, the opposite effect was found with bis(diphenylphosphino)ferrocene. At 80 °C, 200 psi, and [P]/[Rh] = 17, the selectivity to the branched product was 73% using **2** compared to 80% using PPh_3.

In contrast to the addition of phosphine, which resulted in increased branched selectivities, the addition of triethylamine had little effect. When a 77-fold excess of triethylamine ([N]/[Rh] = 77) was employed at 80 °C and 100 psi, the selectivity to branched product increased only to 36.8% from 31% when no amine was present. This may be compared to 66% branched product when [P]/[Rh] = 40 at the same conditions. Representative results are summarized in Table III.

Use of Polymer-Supported $RhH(CO)(PPh_3)_2$. A series of styrene–divinylbenzene resin-anchored catalysts, **3a–i**, was prepared as described previously.[7-10,12] These are tabulated along with the results of hydroformylations catalyzed by the resins in Table IV. Resins were employed with both 1% and 2% divinylbenzene, phosphine loadings (the fraction of the resins' phenyl rings substituted with PPh_2 groups) from 7% to 61%, and P/Rh ratios of 3.0 to 31. We recently discussed the role of variations in phosphine loading, [P]/[Rh], cross-link density, and chain mobility on the selectivity of α-olefin hydroformylations;[7-9] therefore that discussion will not be repeated here. The rates, in general, were slower with the polymer-supported catalysts vs. the homogeneous catalysts when compared at equivalent temperatures, pressures, and P/Rh ratios. This effect is most pronounced when high phosphine loadings are combined with large amounts of rhodium in the polymer. This situation creates a high cross-link density and the polymers's swelling ratio decreases (see last entry in Table IV).



3

The resin-bound catalysts were more selective to the branched product, vs. the homogeneous catalyst, when compared at equivalent P/Rh ratios. For example resin **3e** (29% phosphine loading, [P]/[Rh] = 3) gave 75% branched product at 80 °C and 200 psi vs. only 57% for the homogeneous case. As the concentration of phosphine in the polymer increases (i.e., as the phosphine loading increases), one would expect that ligand equilibria occurring during the reaction would favor more highly phosphinated rhodium species.[8,9] Thus, it is not surprising that at similar P/Rh ratios, resins containing higher phosphine loadings give higher branched product yields. This is illustrated in Table IV by comparing resin **3h** (40% phosphine loading, [P]/[Rh] = 19) to resin **3f** (29% phosphine loading, [P]/[Rh] = 20). At 80 °C and 200 psi, resin **3h** gave 84% branched product vs. 68% for **3f**.

Discussion

We have previously investigated the rhodium-catalyzed hydroformylation of 1-pentene[7-10] and allyl alcohol[11] and interpreted the effects of temperature, pressure, P/Rh ratio, H_2/CO ratio, and chelating diphosphine ligands on isomer distribution by the mechanism originally proposed by Wilkinson.[13,14] In this mechanism, olefin coordinates to rhodium followed by insertion into a rhodium–hydride bond to form an alkylrhodium species. Then CO insertion into the alkyl species generates an acylrhodium species which, subsequently, oxidatively adds hydrogen and eliminates an aldehyde molecule. The normal-to-branched selectivity depends upon the relative rates of olefin insertion to give the normal or branched alkyl complexes.[13,14]

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(14) C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970).

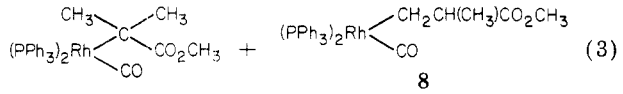
Conceivably, the relative rates of CO insertion and the position of equilibrium between normal and branched alkyl complexes (and acyl complexes) could also play a role in selectivity, depending on the balance existing between all the rate constants.

The phosphine equilibria depicted in eq 2 play an im-

$$\underset{\mathbf{4}}{RhH(CO)(PPh_3)_2} \overset{\overset{+CO}{\longrightarrow}}{\underset{-CO}{\longleftarrow}} \underset{\mathbf{5}}{RhH(CO)_2(PPh_3)_2} \overset{\overset{-PPh_3}{\longrightarrow}}{\underset{+PPh_3}{\longleftarrow}} \underset{\mathbf{6}}{RhH(CO)_2(PPh_3)} \quad (2)$$

portant role in the selectivity. If selectivity is determined by the insertion of the double bond into the rhodium–hydride bond, then the olefin complexes of species 4 and 6 would control selectivity. Species 4, and its olefin complex, have a more "hydridic" rhodium–hydride bond than does either 6 or its olefin complex. Thus, the methyl methacrylate complex of 4 would, on electronic grounds, prefer to give the branched alkyl complex 7 upon insertion (eq 3). Obviously, steric effects operate to favor the

$$RhH(CO)(PPh_3)_2(CH_2{=}C(CH_3)COOCH_3) \rightleftharpoons$$

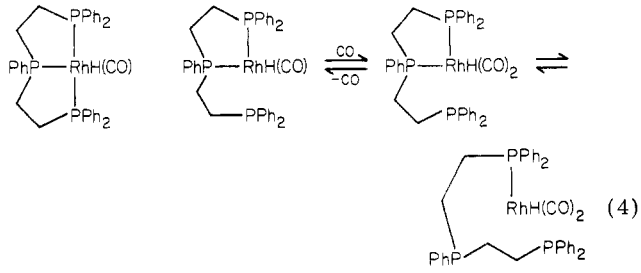


$$\underset{\mathbf{7}}{} + \underset{\mathbf{8}}{} \quad (3)$$

formation of terminal alkyl complex 8. If electronic effects predominate, then one would expect that a higher P/Rh ratio would shift equilibrium 2 toward the left favoring 4 and, therefore, favor the branched aldehyde. This is in accord with our findings. Electronic, not steric, effects seem to predominate as suggested previously.[15]

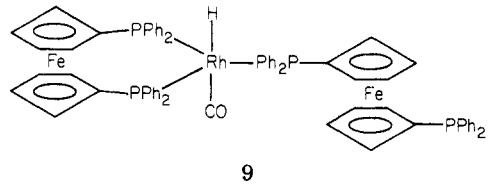
The selectivity, however, cannot be fully explained by eq 2 and 3. Increasing the CO pressure increases the production of branched product. Since an increase in CO pressure (with other variables held constant) should shift equilibrium 2 toward 5 and 6, one would expect an increase in normal product and not the observed increase in branched product. The remarkable increase in selectivity to normal product with an increase in temperature is also difficult to account for. Increasing the temperature (without any other changes) would shift equilibrium 2 toward the left because the ratio of the association constants of phosphine and CO toward rhodium (i.e., K_P/K_{CO}) increases with temperature. This, alone, would lead to an increase in branched rather than normal product. However, the rate of isomerization of alkyl complexes, 7 ⇄ 8, and the corresponding acyl complexes will increase with temperature. If the positions of these equilibria become important in determining the ultimate selectivity, then steric effects will become increasingly important. Since 8 is more stable than 7 (and the same for the corresponding acyl complexes), an increase in temperature would give higher yields of normal product if equilibrium factors become increasingly important. This explanation has been advanced in ethyl acrylate hydroformylations.[3] On this basis, one can explain the increase in branched product with an increase in temperature or in CO pressure. Increased CO pressures inhibit the isomerization of alkyl (or acyl) isomers. Also, the CO insertion rate may increase. Thus, if 7 is the kinetic product of insertion into the Rh–H bond and its isomerization to 8 is retarded as CO pressure increases, then an increase in branched product would be expected.

The use of triphos, 1, in place of PPh_3 led to moderate increases in branched selectivities. This would be expected on electronic grounds if this chelating ligand favored a tris- or bis(phosphine) intermediate species, relative to PPh_3, in the equilibria shown in eq 4 and 2. However, bis(di-



(4)

phenylphosphino)ferrocene, 2, gave a slightly lower branched selectivity compared to the selectivity obtained with PPh_3. The reasons for this are not known. However, we have found that ligand 2 promotes higher normal selectivities than PPh_3 when used in excess in allyl alcohol[11] and 1-octene hydroformylations. Furthermore, recent studies of 2 at Cellanese[16] have shown that cis-chelated species persist under "oxo" reaction conditions with a total of three phosphines coordinated to rhodium. The normal selectivity in 1-hexene hydroformylations increased when excess 2 was present.[16] Studies of this interesting ligand are continuing.



9

Experimental Section

Benzene and THF were dried over potassium/benzophenone and distilled under nitrogen. Carbon monoxide and hydrogen were obtained commercially (99+%) and used as received. $RhH(CO)(PPh_3)_3$ was prepared by the published method.[17] Methyl methacrylate was distilled through a fractionating column and stored in the cold.

Styrene–divinylbenzene resins were brominated (Br_2, $FeBr_3$, dark) and then phosphinated (excess $LiPPh_2$, THF) as previously described. $RhH(CO)(PPh_3)_3$ was attached to the phosphinated resins by thermal exchange followed by extensive benzene extraction (Soxhlet) and dried in vacuo at 80 °C for 24 h. The hydroformylations were carried out in 100-cm^3 stainless steel autoclaves which were rapidly shaken at constant temperature after careful deoxygenation. All reactions were carried out at constant pressure by using constant-pressure regulating delivery values. In each experiment, sufficient catalyst was used to give 4.67×10^{-2} mmol of Rh with methyl methacrylate (18.7 mmol; [MMA]/[Rh] = 400), *o*-xylene (internal standard, 2.5–3.0 mmol), and benzene to give a total volume of 10.0 mL. The solutions for each experiment were analyzed by analytical GLC (Varian Model 3700) on a 3 ft × $^1/_8$ in. Carbowax 20M/Chromosorb W column; electronic integration and internal standard techniques (Hewlett-Packard Model 3380A electronic integrator) were used.

The two hydroformylation products methyl α-formyl- and methyl β-formylisobutyrate were isolated by distillation under

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reduced pressure and identified by comparison of the NMR spectra with independently prepared authentic samples.[4]

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Registry No. 1, 23582-02-7; 2, 12150-46-8; 4, 17185-29-4; MMA, 80-62-6; methyl α-formylisobutyrate, 13865-20-8; methyl β-formylisobutyrate, 13865-21-9; styrene, 100-42-5; divinylbenzene, 1321-74-0.

Formation and Reactions of Ring-Substituted Derivatives of (η^5-Cyclopentadienyl)dicarbonylnitrosylchromium

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Friedel–Crafts acylation of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (1) produces the corresponding ketones and esters in good yield. Hydrolysis of [η^5-((methylthio)carbonyl)cyclopentadienyl]dicarbonylnitrosylchromium gives (η^5-carboxycyclopentadienyl)dicarbonylnitrosylchromium (pK_a = 5.1) in 50% yield. Reduction of ketone derivatives of 1 with sodium borohydride produces the corresponding secondary alcohols in high yield, whereas reduction with lithium aluminum chloride–aluminum chloride leads to products of hydrogenolysis in 55–65% yield. High yields of tertiary alcohols have been obtained by treating ketone derivatives of 1 with alkyl or aryl Grignard reagents. Dehydration of [η^5-(1-hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium produces (η^5-isopropenylcyclopentadienyl)dicarbonylnitrosylchromium in 81% yield. (η^5-Ethynylcyclopentadienyl)dicarbonylnitrosylchromium has been prepared by reaction of (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium with phosphorus oxychloride in dimethylformamide, followed by decomposition of the resulting chloro aldehyde in refluxing basic dioxane solution.

Introduction

Since the discovery that ferrocene exhibits aromatic-type reactivity analogous to that of benzene and its derivatives, there has been a steady growth in interest in metalloaromatic systems, that is, organometallic compounds in which "aromaticity" is induced by virtue of coordination of an unsaturated organic ring system to a transition metal, utilizing delocalized covalent or synergic-type bonding. This aromatic reactivity is exemplified by the ability of ferrocene to undergo electrophilic aromatic substitution reactions such as Friedel–Crafts acylation[1-3] and alkylation,[4,5] formylation,[3,6,7] mercuration,[8,9] sulfonation,[10] aminomethylation,[11,12] and arylation with diazonium salts.[8] Ferrocene will also undergo metalation with organolithium reagents.[8,13]

Several other π-bonded cyclopentadienyl organometallic compounds have also been found to exhibit aromatic-type reactivity similar to that of ferrocene. These include the sandwich compounds ruthenocene and osmocene,[14,15] the mixed (η^5-cyclopentadienyl)carbonylmetal compounds cymantrene[16-18] and its technetium and rhenium[19-21] analogues, and (η^5-cyclopentadienyl)tetracarbonylvanadium.[22,23] (η^5-Cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene)[24] (1) is the only known example of a nitrosyl-containing (η^5-cyclopentadienyl)metal compound which exhibits aromatic-type reactivity.[25] The following order of decreasing reactivity toward Friedel–Crafts acetylation has been established by Fischer et al.:[26] ferrocene > anisole > ruthenocene > cymantrene > osmocene > cynichrodene ≳ (η^5-cyclopentadienyl)tetracarbonylvanadium ≈ benzene > (η^5-cyclopentadienyl)tricarbonylrhenium.

Until the current work was undertaken, very little was known about the aromatic-type reactivity of 1 even though it was first reported in 1955.[27] In contrast, the chemistry

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