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Homogeneous Olefin Hydroformylation Catalyzed by Ligand Stabilized Platinum(II)–Group IVB Metal Halide Complexes

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Ligand-stabilized platinum(II)–Group IVB metal halide complexes have been found to catalyze the homogeneous hydroformylation of olefins to aldehydes. With the preferred catalyst composition, bis(triphenylphosphine)platinum(II) chloride–tin(II) chloride, α-olefin hydroformylation proceeds under mild conditions [60–80°C, 800–1500 psig H_2/CO (1:1)], to give good yields of aldehyde (85–90 mole%), and high selectivity of the desired linear, straight-chain, aldehyde (85–93 mole%). The dependence of the yield and linear aldehyde selectivity, upon catalyst and olefin structure, temperature, H_2/CO pressures, reactant concentrations and solvent composition has been studied, and is discussed in relation to the proposed hydroformylation mechanism for this class of catalyst.

INTRODUCTION

The hydroformylation reaction has been the subject of several review articles (*1–3*) and a variety of transition metal catalysts is now known to promote this reaction (*4–14*). Following the issuance of patents (*15*, *16*), a recent paper by Hsu and Orchin (*17*) dealing with the selective hydroformylation catalyst $PtH(SnCl_3)(CO)(PPh_3)_2$, has prompted us to report in detail on a class of highly active and selective hydroformylation catalysts derived from ligand-stabilized platinum complexes in combination with Group IVB metal halide cocatalysts. The more effective compositions, exemplified by $PtCl_2(PPh_3)_2$–$SnCl_2$, have been found to hydroformylate C_3–C_{20} α-olefins yielding aldehydes in 85–90 mole%. Selectivity to straight-chain terminal aldehyde may be 85–93 mole% [Eq. (1)]. Relatively mild conditions are required (60–80°C, 800–1500 psig, H_2/CO, 1:1) and at initial olefin/platinum molar ratios ranging to 5×10^2, competing olefin isomerization and reduction to alkane are generally within the range 7 ± 2 and 4 ± 1.5 mole%, respectively. No aldehyde hydrogenation to alcohols has been detected under the stated conditions.

$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO. \quad (1)$$

Both tin(IV) chloride and germanium(II) chloride may be substituted for $SnCl_2$ as cocatalysts, and a broad range of ligands containing Group VB, VIB and VIIB donor atoms are effective in producing active $PtCl_2$–$SnCl_2$ catalysts. Among the more

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promising combinations are:

$PtCl_2[P(C_6H_5)_3]_2$–$SnCl_2$,
$PtCl_2[P(p\text{-}CH_3\cdot C_6H_4)_3]_2$–$SnCl_2$,
$PtCl_2[P(n\text{-}C_4H_9)_3]_2$–$SnCl_2$
and $PtCl_2[P(CH_3)_2C_6H_5]_2$–$SnCl_2$.

It may be noted that related homogeneous bimetallic catalysts have previously found application in the carboalkoxylation (*18–20*) and hydrogenation (*21–29*) of alkenes and alkynes.

RESULTS

Effect of platinum catalyst structure. The hydroformylation of 1-heptene to octyl aldehydes is exemplified in Tables 1 and 2 for a variety of stabilized platinum(II)–Group IVB metal halide catalyst combinations. Among $PtCl_2(PPh_3)_2$–Group IVB metal chlorides, tin(II) chloride, germanium(II) chloride, and tin(IV) chloride each afford significant yields of octanal, the highest yield of linear aldehyde being recorded with tin(II) chloride (Expt. 1). No significant olefin conversion is detected in the absence of the metal halide cocatalyst (Expt. 9), nor is hydroformylation observed in the presence of either lead chloride or silicon tetrachloride. This order of reactivity [Eq. (2)] parallels the reported order of stability of the noble metal–Group IVB metal bonds (*30, 31*) but contrasts somewhat with their performance in hydrogenation catalysis (*32*):

$$SnCl_2 > GeCl_2 \gg PbCl_2 \approx SiCl_4. \quad (2)$$

Likewie, santimony trichloride proved unsuitable as a cocatalyst (Expt. 6) even though active in $PtCl_2(PPh_3)_2$ catalyzed diene isomerization (*33*). Tin(IV) chloride (Expt. 3) is at least partially reduced to tin(II) chloride under hydroformylation conditions and likely functions in a similar manner to tin(II) chloride.

With different halogens, modifications of the bis(triphenylphosphine)platinum(II)–tin(II) halide catalyst with tin(II) chloride, bromide and iodide (Expts. 1, 7 and 8) indicates the order of effectiveness is in

TABLE 1

Hydroformylation of 1-Heptene Catalyzed by Ligand-Stabilized Platinum(II) Halide–Metal Halide Complexes; Effect of Group IVB and VB Metal Halides[a]

Expt.	Catalyst composition	1-Heptene conversion (%)[b]	Total octyl aldehyde yield (mole%)	Selectivity to octanal (mole%)	Isomerization to 2,3-heptenes (mole%)	Reduction to *n*-heptane (mole%)
1	$PtCl_2(P(C_6H_5)_3)_2$–$SnCl_2$	100	85	90	3.6	2.7
2	$PtCl_2(P(C_6H_5)_3)_2$–$GeCl_2$[c]	14	14	98	—	—
3	$PtCl_2(P(C_6H_5)_3)_2$–$SnCl_4$	100	50	84	6.5	8.5
4	$PtCl_2(P(C_6H_5)_3)_2$–$PbCl_2$	0	—	—	—	—
5	$PtCl_2(P(C_6H_5)_3)_2$–$SiCl_4$	0	—	—	—	—
6	$PtCl_2(P(C_6H_5)_3)_2$–$SbCl_3$	0	—	—	—	—
7	$PtBr_2(P(C_6H_5)_3)_2$–$SnBr_2$	100	64	85	6.2	2.6
8	$PtI_2(P(C_6H_5)_3)_2$–SnI_2[c]	<2	0.6	—	—	—
9	$PtCl_2(P(C_6H_5)_3)_2$	0	—	—	—	—
10	$Pt(CN)_2(P(C_6H_5)_3)_2$	0	—	—	—	—

[a] Runs carried out according to Procedure 1, Experimental Section. Run conditions: solvent, methyl isobutyl ketone; [1-heptene], 0.88 *M*; [1-heptene]/[SnX_2]/[$PtX_2(P(C_6H_5)_3)_2$], 200:5:1; H_2/CO (v/v), 1:1; 1500 psig, 66°C, 3 hr.

[b] The formation of some high boiling material was also evident in these screening experiments (see also Experimental Section).

[c] Catalyst appears to remain incompletely soluble throughout reaction.

TABLE 2

Hydroformylation of 1-Heptene Catalyzed by Ligand-Stabilized Platinum(II) Chloride–Tin(II) Chloride Complexes; Effect of Group VB, VIB and VIIB Donor Ligands[a]

Expt.	Catalyst composition	1-Heptene conversion (%)[b]	Total octyl aldehyde yield (mole%)	Selectivity to octanal (mole%)	Isomerization to 2,3-heptenes (mole%)	Reduction to *n*-heptane (mole%)
11	$PtCl_2(P(C_6H_5)_3)_2$–$SnCl_2$	100	85	90	3.6	2.7
12	$PtCl_2(As(C_6H_5)_3)_2$–$SnCl_2$	100	46	75	10	9
13	$PtCl((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)$–$SnCl_2$[c]	100	60	81	7	27
14	$PtCl_2(Sb(C_6H_5)_3)_2$–$SnCl_2$	94	61	75	12	8
15	$PtCl_2(C_{12}H_8N_2)$–$SnCl_2$[c,d,e]	96	56	71	15	8
16	$PtCl_2(S(C_6H_5)_2)_2$–$SnCl_2$[c,d]	91	52	72	9	8.0
17	$PtCl_2(P(p\text{-}CH_3\cdot C_6H_4)_3)_2$–$SnCl_2$	90	78	93	8.9	1.9
18	$PtCl_2(P(CH_3)_2C_6H_5)_2$–$SnCl_2$	78	59	87	9.7	6.3
19	$PtCl_2(P(n\text{-}C_4H_9)_3)_2$–$SnCl_2$	100	83	89	7.9	2.5
20	$PtCl_2(P(C_6H_5)_2Cl)_2$–$SnCl_2$	100	72	89	13.6	5.4
21	$PtCl_2((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)$–$SnCl_2$[c]	42	31	78	5.8	4.1
22	$PtCl_2(P(OC_6H_5)_3)_2$–$SnCl_2$	100	45	73	19	16
23	K_2PtCl_4–$SnCl_2$	99	60	73	13	10

[a] Runs carried out according to Procedure 1, Experimental Section. Run conditions: solvent, methyl isobutyl ketone; [1-heptene], 0.88 *M*; [1-heptene]/[Sn]/[Pt], 200:5:1; H_2/CO (v/v), 1:1; 1500 psig, 66°C, 3 hr.

[b] The formation of some high boiling materials was also evident in these screening experiments (see also Experimental Section).

[c] Catalyst appears to remain incompletely soluble throughout reaction.

[d] Catalyst partially decomposed to fine black solids.

[e] $C_{12}H_8N_2$, 1,10-Phenanthroline.

the direction [Eq. (3)]:

$$SnCl_2 > SnBr_2 \gg SnI_2. \qquad (3)$$

The pseudo-halogen, CN^-, is not effective in promoting hydroformylation under the selected conditions (Expt. 10), even though, like $SnCl_3^-$, it too is a powerful π-acceptor ligand (*22*).

Modification of the platinum(II)–tin(II) chloride catalyst with various Group VB, VIB and VIIB donor ligands is summarized in Table 2. While all selected catalyst compositions gave octyl aldehyde in fair yields, with good selectivity to the 1-octanal, organophosphines appear distinctly superior to all others. A number of trivalent phosphorus compounds have been shown to produce active $PtCl_2(PR_3)_2$–$SnCl_2$ hydroformylation catalysts (Expts. 11, 17–22), each with selectivity to the linear 1-octanal that is consistently higher than that for Pt(II)–Sn(II) alone (Expt. 23). Suitable PR_3 groups include both monodentate and bidentate, alkyl, aryl, mixed alkyl-aryl, and halo-aryl phosphines, the highest yields of 1-octanal being obtained with: $PtCl_2[P(C_6H_5)_3]_2$–$SnCl_2$, $PtCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$–$SnCl_2$, and $PtCl_2[P(n\text{-}C_4H_9)_3]_2$–$SnCl_2$.

There appears to be no significant trend in the hydroformylation selectivity to 1-octanal as a function of either the size (*34*) or basicity (*35*) of the phosphine donor ligands, provided the phosphine is at least moderately basic. For platinum(II)–tin(II) complexes with the coordinated phosphine donor ligands exemplified in Expts. 11, 17–20, the selectivity to 1-octanal remains within the range of $90 \pm 3\%$. Only with the extremely weak base, triphenylphosphite ($pK_a \approx 0.0$), does the selectivity drop to 73 mole% (Expt. 22), a value similar to that obtained for the base case, K_2PtCl_4–$SnCl_2$ alone (Expt. 23). Similarly, a selectivity to 1-octanal of less than 82 mole% was recorded with each of the Pt(II)–Sn(II) complexes coordinated to other Group VB (N, As, Sb) and Group VIB donor ligands (Expts. 12–16). The complexes screened show varying degrees of activity, but there is apparently no simple relationship linking hydroformylation rate with ligand basicity (*2*).

TABLE 3

Hydroformylation of Various Olefins Catalyzed by Bis(triphenylphosphine)platinum(II) Chloride–Tin(II) Chloride Complex[a]

Expt.	Olefin structure	Procedure[a]	Olefin conversion (%)	Total aldehyde yield (mole%)	Selectivity to 1-aldehyde (mole%)	Olefin isomerization (mole%)	Olefin reduction (mole%)
24	Propylene	2	95	92	85	—	—
25	1-Heptene	1	100	85	90	3.6	2.7
26	1-Undecene	2	100	86	96	10.8	3.2
27	1-Eicosene	1	100	57	89	12.3	6.5
28	2-Methyl-1-pentene	1	27	18	100	—	—
29	2-Heptene	1	6.5	6.5	3	—	—
30	Cyclohexene	2[b]	26	25	—	—	—
		1	0	—	—	—	—

[a] For details of experimental procedures see Experimental Section. General run conditions; solvent, methyl isobutyl ketone; [olefin], 0.88 *M*; [olefin]/[Sn]/[Pt] = 200:5:1, H_2/CO (v/v), 1:1, 1260–1500 psig; 66–78°C, 3–5 hr.

[b] Reaction temperature 108°C.

Effect of olefin structure. The performance of the preferred catalyst, $PtCl_2(PPh_3)_2$–$SnCl_2$, is very much a function of the structure of the substrate olefin. It can be seen from the data in Table 3 that while straight-chain α-olefins, such as propylene, 1-heptene, and 1-eicosene, are readily hydroformylated to the corresponding linear aldehyde, under standard experimental conditions, branched α-olefins, like 2-methyl-1-pentene are less easily hydroformylated (Expt. 28), and internal and cyclic olefins may require more stringent conditions (Expt. 29, 30). This order of reactivity with change in olefin structure [Eq. (4)] is similar to that observed, under nonisomerizing conditions, for olefin hydroformylation catalyzed by dicobalt octacarbonyl (*36*), and by $RhHCO(PPh_3)_3$ (*10*):

$$RCH{=}CH_2 > RR'C{=}CH_2 > RCH{=}CHR'. \quad (4)$$

A parallel order of reactivity has also been

TABLE 4

Hydroformylation of 1-Heptene Catalyzed by Bis(triphenylphosphine)platinum(II) Chloride–Tin(II) Chloride; Effect of Reactant Concentrations[a]

Expt.	Reactant conc [1-Heptene]:[Sn]:[Pt]:[PPh_3]				H_2/CO (v/v)	Reaction time (hr)	1-Heptene conversion (%)	Total octyl aldehyde yield (mole%)	Selectivity to octanal (mole%)	Isomerization to 2,3-heptenes (mole%)	Reduction to *n*-heptane (mole%)
31	200	5	1	2	1/1	3	98	85	91	9.5	3.5
32	400	5	1	2	1/1	3	98	84	93	9.2	4.8
33	200	1	1	2	1/1	8	99	88	93	7.5	2.5
34	800	10	1	2	1/1	20	90	73	93	11.2	5.4
35	200	5	1	4	1/1	6	21	18	99	3	—
36	200	5	1	2	30/1	1	100	56	93	26	18
37	200	5	1	2	2/1	2	98	81	91	12	5
38	200	5	1	2	1/2	4	98	83	92	12	3
39	200	5	1	2	1/5	10	100	78	93	18	2

[a] Runs carried out according to Procedure 2, Experimental Section. Run conditions: solvent, methyl isobutyl ketone; [1-heptene] 0.88 *M*; 1260 psig; 78°C.

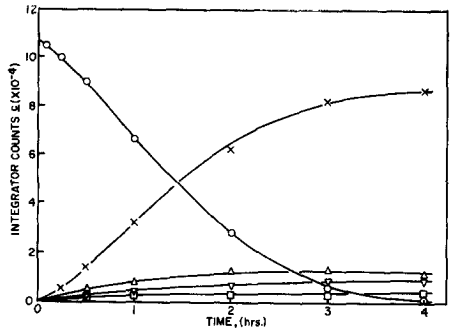

FIG. 1. Typical rate profile for $PtCl_2(PPh_3)_2$–$SnCl_2$ catalyzed 1-heptene hydroformylation. (○) 1-Heptene; (×) octanal; (△) 2-methylheptanal; (▽) 2- and 3-heptenes; (□) heptane.

found for olefin hydrogenation catalyzed by $PtCl_2(PPh_3)_2$–$SnCl_2$, even though there, hydrogenation reaction conditions in many cases favored isomerization to internal olefins as the major reaction (*37*).

Effect of reactant concentrations. 1-Heptene hydroformylation catalyzed by $PtCl_2(PPh_3)_2$–$SnCl_2$ has been demonstrated over a wide range of olefin and platinum concentrations (*15*) (see Table 4), although rate and aldehyde yields fall off somewhat where initial [1-heptene]/[Pt] mole ratios exceed 400 (Expt. 34). Selectivity to straight-chain aldehyde, 1-octanal, remains essentially constant at 91 and 93 mole%.

Tin(II) chloride to platinum mole ratios of greater than one are needed to ensure rapid hydroformylation rates, and a stable catalyst. A [Sn]/[Pt] ratio of 5:1 was used throughout most of this work, and increasing the ratio to 10:1 (Expt. 34) did not significantly improve the rate at higher initial [1-heptene]/[Pt] ratios.

Expts. 36–39 serve to demonstrate that $PtCl_2(PPh_3)_2$–$SnCl_2$ remains active even with wide variations in the hydrogen to carbon monoxide ratio. Yields of octyl aldehyde tend toward a maxima of ca. 85 mole%, at H_2/CO ratios of 1:1 (Expt.31), and where H_2/CO ratios diverge widely from this ratio, reduction and/or isomerization of the 1-heptene become increasingly important.

It should be noted that in Expt. 35, the addition of excess triphenylphosphine (2 moles/mole Pt) to a solution of $PtCl_2(PPh_3)_2$–$SnCl_2$ in MIBK markedly decreases the rate of 1-heptene hydroformylation. Here only an 18 mole% octyl aldehyde yield was produced after 6 hrs, with 99 mole% selectivity to 1-octanal. This inhibition by excess PPh_3 could be the result of $SnCl_3^-$ displacement from the active complex, or due to PPh_3 association to form a less reactive, but more sterically restricted, catalyst (*10*).

A typical rate profile for the hydroformylation of 1-heptene via Procedure 2 (described in detail in the Experimental

TABLE 5

Hydroformylation of 1-Heptene Catalyzed by Bis(triphenylphosphine)platinum(II) Chloride–Tin(II) Chloride; Effect of Pressure and Temperature[a]

Expt.	CO/H_2 pressure (psig)	Temperature (°C)	Rx. time (hr)	1-Heptene conversion (%)	Total octyl aldehyde yield (mole%)	Selectivity to octanal (mole%)	Isomerization to 2,3-heptenes (mole%)	Reduction to *n*-heptane (mole%)
40	100	78	3	100	25	95	70	5
41	500	125	0.5	100	18	92	75	7
42	1000	66	6	100	90	91	7.3	2.7
43	1260	78	3	98	85	91	9.5	3.5
44	1260	95	1	100	74	91	18.5	5.6
45	1500	24	20	58	57	91	1.1	0.3
46	1500	66	3	100	85	90	3.6	2.7
47	1500	93	3	100	66	77	5.6	3.2
48	3000	66	3	100	88	89	5.0	3.8

[a] Experimental conditions: solvent, methyl isobutyl ketone; [1-heptene], 0.88 *M*; [1-heptene]/[Sn]/[Pt] = 200:5:1; H_2/CO (v/v), 1:1.

Section) is reproduced in Fig. 1. The rate of disappearance of 1-heptene is equal to the sum of the rates of appearance of octanal, 2-methylheptanal, 2- and 3-heptenes and *n*-heptane under the specified run conditions.

Effect of pressure and temperature. The data of Table 5 indicate that meaningful hydroformylation to octyl aldehydes can be obtained between 24 and 125°C at pressures ranging from 100 to 3000 psig. The preferred temperature and pressure ranges, which afford the best balance between rate, catalyst stability, aldehyde yield, and selectivity to straight-chain aldehyde, appear to be between 66 and 80°C, and between 1000 and 1500 psig. Reaction rates are low at temperatures below 66°C (Expt. 45), while at reaction temperatures above 100°C, isomerization of olefin, and other undesirable side reactions, become serious (Expt. 41); catalyst decomposition is also observed. Low pressures also afford slow reactions, and the same undesirable side reactions (Expt. 40). Increasing the pressure from 1500 to 3000 psig does not have a significant effect on conversion, aldehyde yield, or selectivity to 1-aldehyde (cf. Expts. 46 and 48).

Solvent effect. Bis(triphenylphosphine)-platinum(II) chloride–tin(II) chloride catalyzes α-olefin hydroformylation in a variety of polar and nonpolar solvent media (see Table 6). In nonpolar solvents such as methylene chloride, toluene and isooctane (Expts. 57–60) the catalyst is only moderately soluble, and long induction periods are usually observed. Higher temperatures are required to effect rapid hydroformylation. In highly polar solvents like dimethylformamide, tetrahydrofuran and acetonitrile (Expts. 53–55) the catalyst dissolves readily, but the hydroformylation reaction is inhibited. It is likely that such solvents complex too strongly with the catalyst and prevent coordination and/or activation of the substrate (*22*). An alternative possiblity is that a strongly coordinating solvent could displace $SnCl_3^-$ from the active catalyst. A measurement of the conductivity of the platinum complex $Pt(CO)(PPh_3)_2(SnCl_3)_2$ in DMF indicated the presence of a bi-univalent electrolyte. The following dissociation was postulated (*38*):

$$Pt(CO)(PPh_3)_2(SnCl_3)_2 \overset{DMF}{\rightleftharpoons} [Pt(CO)(PPh_3)_2(DMF)_x]^{2+} + 2SnCl_3^- \quad (5)$$

The preferred solvents appear to be those of intermediate polarity and coordinating ability such as the ketones, acetophenone, acetone, and methyl isobutyl ketone. Such solvents will dissolve the catalyst, but do not interfere with its catalytic activity.

DISCUSSION

The effectiveness of platinum–Group IVB metal halide complexes in catalyzing the hydroformylation reaction is believed to be related to the ability of the Group IVB ligands, such as $SnCl_3^-$, which are strong π-acceptors and weak σ-donors, to accept electrons from filled 5*d* orbitals of platinum. This lowering of the electron density on the platinum (*39*) should favor both initial platinum hydride formation (*32*), and subsequent attack by nucleophiles such as CO and the multiple bonds of the olefin (*33*). Furthermore, the π-acceptor capability of the $SnCl_3^-$ ion should also stabilize such complexes against reduction of the platinum to the metal (*33*).

In this work, solutions of $PtCl_2(PPh_3)_2$–$SnCl_2$, and related catalysts, have been found to exhibit excellent olefin hydroformylation activities, under relatively mild conditions, at [Sn]/[Pt] ratios of ca. five (*15*). Mixed complexes, such as $(Ph_3P)_2PtCl(SnCl_3)$ (*31*) [Eq. (6)], together with related platinum carbonyl and hydrocarbonyl analogues, such as $Pt(CO)(EtOH)(PPh_3)_2(SnCl_3)_2$ (*38*) and $PtH(CO)(SnCl_3)(PPh_3)_2$ (*17*, *40*), have been isolated from these solutions prior to, and

TABLE 6

Hydroformylation of 1-Alkenes Catalyzed by $PtCl_2(PPh_3)_2$–$SnCl_2$; Effect of Solvent[a]

Expt.	Solvent	Procedure	Olefin	Rx, time (hr)	Olefin conversion	Total yield aldehyde	Selectivity 1-aldehyde	Isomerization to internal olefins	Reduction to alkane
49	Methyl isobutyl ketone	1	1-Heptene	3	100	85	90	3.6	2.7
50	Acetone	1	1-Nonene	3	100	87	92	9.7	1.3
51	Acetophenone	2	1-Heptene	2	100	85	93	12.5	2.5
52	Cyclohexanone	2[b]	Propylene	5	ND[c]	52	87	—	ND[c]
53	Acetonitrile	1	1-Nonene	3	16	16	89	0	0
54	Tetrahydrofuran	2	1-Heptene	5	6.5	6.5	97	0	0
55	Dimethylformamide	2[b]	Propylene	2	0	0	0	0	0
56	*o*-Dichlorobenzene	2	1-Heptene	4	100	80	94	17.4	2.6
57	Methylene chloride	2	1-Heptene	4	100	68	92	27.5	4.5
58	Toluene	2	1-Heptene	6	100	82	95	15.7	2.3
59	Isooctane	2	1-Heptene	6	9	9	97	Tr	0
60	Isooctane	1[d]	1-Nonene	6	100	36	87	18	11

[a] Experimental conditions Procedure 1: [olefin], 0.88 *M*, [olefin]/[Sn]/[Pt] = 200:5:1, H_2/CO = 1:1, 1500 psig, 66°C. Experimental conditions Procedure 2: [olefin], 0.88 *M*, [olefin]/[Sn]/[Pt] = 200:5:1, H_2/CO = 1:1, 1260 psig, 78°C.

[b] [Olefin], 1.76 *M*, [olefin]/[Sn]/[Pt] = 400:5:1.

[c] Not determined.

[d] Temperature 125°C.

during, carbonylation (*18*). An excess of $SnCl_3^-$ and/or the presence of certain strongly coordinating solvents, generally results in inhibition of the hydroformylation reaction (Tables 4 and 6), due either to the formation of coordinatively saturated species (*33*) [Eq. (7)] or the displacement of $SnCl_3^-$ from the active catalyst [Eq. (5)].

$$PtCl_2(PPh_3)_2 + SnCl_2 \rightleftharpoons Pt(SnCl_3)Cl(PPh_3)_2, \quad (6)$$

$$Pt(SnCl_3)Cl(PPh_3)_2 + SnCl_2 \rightleftharpoons Pt(SnCl_3)_2(PPh_3)_2. \quad (7)$$

At least partial displacement of the organophosphine from the $PtCl_2(PR_3)_2$ complexes, during hydroformylation is also considered likely in view of (a) the loss of reaction rate in the presence of excess phosphine (Expt. 35), and (b) the relative insensitivity of the platinum catalyst selectivity to changes in the nature of the bulky organophosphine ligands (Expts. 17–20).

In accord with the results of this work, and related catalysis by platinum–Group IVB metal halide complexes (*19*, *25*, *28*, *33*), we believe the active platinum(II)–tin(II) chloride hydroformylation catalyst to have the following minimum composition:

$$Pt(H)(CO)(SnCl_3)_2.$$

Although there have been numerous examples of both four and five coordinated Pt(II)–$SnCl_2$ stabilized complexes reported in the literature (*33*, *38*, *41*), it appears likely that a four coordinated complex would prove more favorable for initial formation of a π-complex with an unsaturated moiety such as a 1-alkene. When other Group VB donor ligands, in addition to $SnCl_3^-$, are present, the active platinum catalyst will contain at least one molecule of the additional ligand and may be represented, for a phosphine, as:

$$Pt(H)(CO)(SnCl_3)(PR_3).$$

Again, related phosphine-stabilized hydrido-platinum species have been isolated (*vide supra*) both from homogeneous reactions (*42*), and by independent synthesis (*17*, *22*).

The mechanism of olefin hydroformylation catalyzed by typical stabilized platinum(II)–tin(II) halide complexes

likely has several points in common with mechanisms proposed earlier for both cobalt (*1–3*), and rhodium (*9, 10*) catalysis. In particular, preliminary kinetic studies (*40*) of 1-heptene hydroformylation to octanal, using solutions of $PtCl_2(PPh_3)_2$–$SnCl_2$ in methyl isobutyl ketone, have led to the following general rate expression:

$$\frac{d(\text{1-octanal})}{dt} = \frac{K \cdot (\text{Pt})^{1.5}(\text{1-heptene})P_{H_2}}{P_{CO}^{0.5}}.$$

This is similar to kinetic expressions for other transition metal catalyzed hydroformylations.

Generally the yield of aldehyde produced by hydroformylation, and the selectivity to straight-chain terminal aldehyde, are both intimately connected with the nature of the active catalyst, the structure of the olefin substrate and the reaction conditions. This can be understood from a consideration of Scheme I, Fig. 2 (where X and Y represent $SnCl_3^-$ and PR_3). The first step in the reaction involves platinum–π-olefin complexation (*33*) to yield a π-complex similar to **II** of Scheme I. Species **II** may then follow any of Pathways A through F depending upon the regioselectivity of the active Pt complex, the olefin used, the solvent, the reaction parameters, P_{H_2}, P_{CO}, temperature, and the values of the various k's.

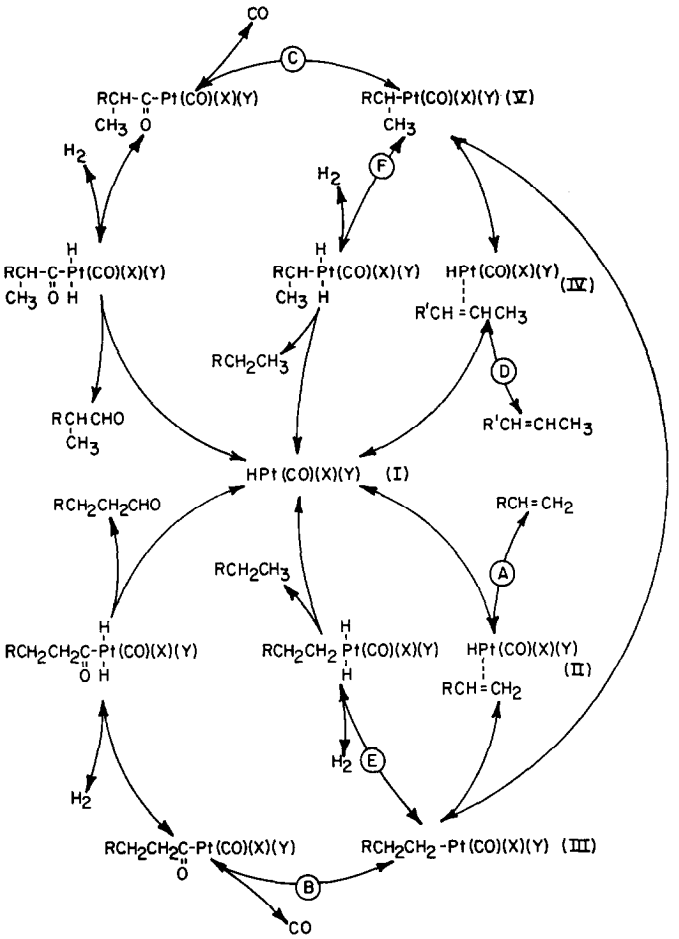

FIG. 2. Scheme I, mechanism of olefin hydroformylation, and competing isomerization and reduction.

Pathway A leads back to starting α-olefin. Pathways B and C result in straight and branched chain aldehyde products. Pathway D leads to isomerized internal olefin. Pathways E and F lead to alkane. The extent of aldehyde, isomerized olefin, and alkane formation, although primarily dependent upon catalyst and olefin structure, is also sensitive to reaction conditions. The regioselectivity of the reaction, i.e., the ratio of normal to branched chain aldehyde, is on the other hand, almost independent of the reaction parameters. These statements are supported by the results shown in Tables 4 and 5. They indicate that competing olefin isomerization is strongly favored by high temperature (75 mole% at 125°C, Expt. 41), and low total pressure (70 mole% at 100 psig, Expt. 40), as well as by H_2/CO ratios widely divergent from unity (Expts. 36 and 39). Reduction to alkane is at a maximum in our work at the maximum partial pressure of hydrogen (18 mole% at $H_2/CO = 30:1$, Expt. 36). However, the selectivity to normal aldehyde over this wide range of temperatures, pressures, and H_2/CO ratios, remains almost constant, at 92 ± 1 mole%, as long as the catalyst, $PtCl_2(PPh_3)_2$–$SnCl_2$ (1:5), the olefin, 1-heptene, and the solvent, methyl isobutyl ketone, are maintained constant. The factors which do affect the regioselectivity of the addition step are those relating to the structure of the alkene (see Table 3), and the composition of the active catalyst (Table 1 and 2). The relatively large bulk of the $SnCl_3^-$ ligand would tend to favor addition which leads to the sterically less hindered, straight-chain, σ-alkyl-Pt complex, **III**, of Scheme I. However, the high π-acidity of such ligands, by increasing the polarity of the Pt–H bond (*9*), should favor Markovnikov addition, and the formation of the branched-chain σ-alkyl-Pt complex, **V**, of Scheme I. These opposing steric and electronic effects result in only fair selectivity (73 mole% normal aldehyde) when K_2PtCl_4–$SnCl_2$ is used alone (Expt. 23).

Introduction of moderately basic ligands, such as organophosphines, to the Pt–Group IVB complexes should once again favor the formation of straight-chain sigma-alkyl-Pt complex, **III**, since the increased hydridic nature would lead to H-addition to the more electropositive nonterminal carbon atom. Any steric argument would depend on the relative bulk of phosphine *vis-a-vis* the Group IVB metal halide. The results in Table 2 show that addition of moderately basic phosphines does improve the selectivity of the hydroformylation reaction to normal aldehyde from 73 to 90 ± 3 mole%. The trends, however, are not clearly enough defined to allow for detailed arguments concerning the relative importance of steric vs electronic effects within a series of phosphines.

Both the rate and regioselectivity of the hydroformylation reaction are also sensitive to the nature of the alkene substrate. Terminal olefins afford similar reaction rates with $t_{\frac{1}{2}}$ values of about 1.4, 1.4, and 1.6 hr for propylene, 1-heptene, and 1-undecene, respectively. However, selectivity to 1-aldehyde (Table 3) increases from 85 to 90 to 96%, respectively, for this series (Expts. 24–26). These results may be rationalized by assuming that the overall rate of hydroformylation is not dependent upon the initial olefin addition steps, which are fast with respect to later steps, but that the overall selectivity, involving as it does initial σ-alkylplatinum formation, subsequent σ-alkylplatinum and σ-acylplatinum isomerization, and the relative rates of CO insertion, is significantly influenced by the stereo requirements of the alkyl group. Thus in the extreme case of the sterically hindered 2-methyl-1-pentene, the corresponding 1-aldehyde, 3-methylhexanal, is obtained in near 100% selectivity (Expt. 28). As with internal and cyclic olefins (Expts. 29, 30), the formation of less stable π-complexes with this catalyst (*2*) generally leads to slower hydroformylation rates. The specific effect of solvent on regioselectivity, summarized

in Table 6, does not indicate any significant trends in selectivity with respect to either solvent coordinating ability or polarity and it appears unlikely that the solvent participates strongly in the transition states leading to the Pt-alkyl and acyl isomers.

Olefin isomerization and hydrogenation, which compete with the hydroformylation reaction, are represented in Scheme I as proceeding via the same σ–π–σ interconversions and σ-alkylplatinum complexes **III** and **V**, although alternative mechanistic paths may be important (*3*). At low CO pressures, considerable olefin isomerization occurs (Expt. 40) as the rates of σ–π interconversions compete favorably with the rates of alkyl-acyl migration. Only at higher CO pressures, where the CO insertion step is essentially irreversible, is the rate of olefin displacement no longer able to compete successfully with the rate of the alkyl to acyl conversion.

EXPERIMENTAL SECTION

Materials. Hydrogen (Airco, prepurified grade) and carbon monoxide (Matheson, CP grade) were used directly or were preblended in a suitable steel mixing cylinder. Reagents and solvents were commerical samples. Olefins were generally of high purity, and were freed of peroxides, just prior to use, by passage through a column of neutral alumina. The platinum halide complexes, $PtCl_2(PPh_3)_2$ (*43*), $PtCl_2(AsPh_3)_2$ (*43*), $PtCl_2(SbPh_3)_2$ (*43*), $PtCl_2[P(OPh)_3]_2$ (*32*), $Pt(CN)_2(PPh_3)_2$ (*32*), $PtCl_2[P(n\text{-}Bu)_3]_2$ (*44*), $PtCl_2$(*o*-phenanthroline) (*45*), and $PtCl_2(SPh_2)_2$ (*42*), were prepared by published methods. Similar techniques were used to prepare: $PtCl_2[PPh(CH_3)_2]_2$, $PtCl_2[P(p\text{-}CH_3Ph)_3]_2$, $PtCl_2(Ph_2AsCH_2CH_2AsPh_2)$, $PtCl_2(Ph_2PCH_2CH_2PPh_2)$, $PtBr_2(PPh_3)_2$, $PtI_2(PPh_3)_2$, and $PtI_2(AsPh_3)_2$.

General procedures. The extent of reactions, and the distribution of reaction products were determined by glc. The identity of all products was confirmed by one or more of the following analytical procedures: glc, ir, nmr, mass spectroscopic, or elemental analyses.

After initial screening, it was decided to carry out all catalyst evaluations by Procedure 1, described *infra*. The majority of reaction parameter studies were carried out in the stirred autoclave in accordance with Procedure 2.

Procedure 1. These high pressure runs were made at constant volume using a 600 ml, glass-liner equipped, rocking autoclave. To the 350 ml glass liner of the rocking autoclave was added 58 ml of methyl isobutyl ketone and 7.9 ml (0.058 mole) of 1-heptene. The solution was deoxygenated with nitrogen and 0.235 g (1.45×10^{-3} mole) of $SnCl_2 \cdot 2H_2O$ was added and magnetically stirred 2–3 min until dissolved. The $PtCl_2(PPh_3)_2$, 0.229 g (2.9×10^{-4} mole) was added, and the mixture was stirred for a further 2–3 min under a nitrogen purge. The catalyst solution turned to a light yellow-green color, but some of the $PtCl_2(PPh_3)_2$ remained undissolved (the solution becomes completely homogeneous after warming briefly under CO/H_2). The loaded liner was then added to the autoclave and the apparatus was deoxygenated with nitrogen. Carbon monoxide, 750 psig, and hydrogen, 750 psig, were then charged to the bomb, and the bomb was heated to 66°C. The reactor was rocked for 3 hr, and the heat was turned off.

After the apparatus cooled, 62 ml of a greenish-red solution containing a small amount of dark solids was recovered. Gas–liquid chromatography analysis revealed the following results:

	Mole%
Conversion	100
Yield C_8 aldehydes	85.0
Isomerization to 2- and 3-heptenes	3.6
Hydrogenation to *n*-heptane	2.7
Total yield	91.3
Selectivity to 1-octanal	90.0

Gas chromatographic analysis of the C_7 hydrocarbon fraction revealed:

	Mole%
1-Heptene	0.0
trans-3-Heptene	9.2
n-Heptane + *cis*-3-heptene	35.5
trans-2-Heptene	44.0
cis-2-Heptene	11.3
Total	100.0

Procedure 2. Low and medium pressure runs, made at constant pressure (100–1500 psig), were carried out with, or without, a glass liner, in a 300 ml autoclave equipped with a magnedrive stirrer and sampling valve. The 300 ml autoclave was connected to a $H_2/CO/N_2$ reservoir through a septum-equipped loading ampoule system which could be used for introducing charges to the reactor while it was at operating temperatures and pressures. Samples could be removed during the course of the reaction under study without disturbing the reaction conditions.

Example of procedure. To deoxygenated methyl isobutyl ketone, 100 ml which had been placed in the 300 ml stirred autoclave, was added under a nitrogen purge, 0.561 g of $SnCl_2 \cdot 2H_2O$ (2.5×10^{-3} mole), and 0.395 g of $PtCl_2(PPh_3)_2$, (5×10^{-4} mole), as described in Procedure 1. The autoclave was then sealed, deoxygenated, and pressure tested with nitrogen. The system was then flushed out with H_2/CO (1:1), pressured to 500 psig with H_2/CO, and heated to 78°C. While the reactor was being heated to temperature, 13.7 ml (0.1 mole) of deoxygenated 1-heptene was introduced into the loading ampoule by syringe. After the reaction temperature reached a constant value, the 1-heptene was forced into the reactor at a total pressure of 1260 psig. The H_2/CO pressure was maintained constant at 1260 psig throughout the course of the reaction by means of a pressure regulator. Reaction aliquots were taken periodically via the sampling valve, all reaction aliquots were clear yellow-green solutions with no solids present. After 4 hr the reaction was terminated by rapidly cooling in an ice-water bath. After venting, 98 ml of a clear, light yellow-green solution with no solids present was recovered. The solution turned yellow-brown after exposure to air, but no solids precipitated. Figure 1 shows the complete rate profile for the hydroformylation reaction. The material balance is essentially 100%.

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