spectrum showed major fragment ions in accord with cleavages of the C–S and S–S bonds in structure 1.

Isomerization of Methyl Oleate with Thiolsulfonate (1). A solution of 1.0 g (0.0034 mol) of methyl oleate and 0.139 g (0.00034 mol) of 1 in 40 ml of dioxane was heated to reflux for a total of 5 h. Periodic withdrawal of 5-ml aliquots, normal work-up, and GLC analysis gave the following results, with time in minutes and percent trans isomer: 61 (51), 126 (60), 178 (73), 249 (77), and 306 (77.5).

Isomerization of *cis*- and *trans*-4-Octene with 3 and *p*-Toluenesulfinic Acid. The sulfinyl sulfone 3 was prepared as previously described and gave an infrared spectrum identical with that published.[11]

For the kinetic runs, 5.0 ml of a 0.0214 M solution of 3 or the sulfinic acid in dry dioxane was added to 5.0 ml of 0.214 M *cis*-4-octene in dioxane in a round-bottom three-neck flask which had been oven dried and flushed with dry nitrogen. The octene solution was also 0.10 M in decane for use as an internal standard. The flask was immersed in an oil bath held at 70 ± 1 °C with a relay, and aliquots were withdrawn periodically via syringe through a rubber cap. After dilution with pentane and washing once with 1 N NaOH and twice with water, gas chromatographic analysis gave the amount of isomerization with an accuracy of ±0.5%. The averages of the least-squares first-order plots of three runs, taken up to 20–30% isomerization, were determined to give the initial rate constants shown in Table III. Gas chromatographically determined yields were 93% for the sulfinic acid process at equilibrium but were lower when the sulfinyl sulfone was used. A blank reaction carried out in the absence of either isomerization reagent showed no trans isomer formation after 20 h.

Registry No.—1, 3347-03-3; 3, 788-86-3; methyl oleate, 112-62-9; methyl elaidate, 1937-62-8; toluene, 108-88-3; *cis*-4-octene, 7642-15-1; *trans*-4-octene, 14850-23-8.

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Linear Carboxylic Acid Esters from α Olefins. I. Catalysis by Homogeneous Platinum Complexes

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Ligand-stabilized platinum(II)–Group 4B metal halide complexes have been found to catalyze the homogeneous carbonylation of α olefins to carboxylic acids and esters, with up to 98 mol % selectivity to the linear ester. Preferred catalysts include $[(C_6H_5)_3As]_2PtCl_2$–$SnCl_2$, $[(C_6H_5)_2ClAs]_2PtCl_2$–$SnCl_2$, and $[(C_6H_5O)_3P]_2PtCl_2$–$SnCl_2$. The activity of each of these regioselective catalysts is highly sensitive to changes in coordinated ligand structure. The effects of catalyst and olefin composition, the nature of the nucleophilic coreactant, and other experimental variables upon both the activity and selectivity of the platinum have been examined, and are discussed in relation to the mode of this catalysis.

Carbonylation, the addition of CO to unsaturated compounds to yield carboxylic acid derivatives, may be catalyzed by a variety of soluble metal carbonyl species, including those of nickel, cobalt, iron, rhodium, ruthenium, palladium, and platinum.[1–8] α-Olefin carbonylation, as catalyzed by Reppe-type nickel and cobalt catalysts, is characterized by (a) the production of large quantities of branched, as well as linear, acid derivatives (eq 1),[3,5–7] (b) the importance of competing olefin polymerization, isomerization, and reduction reactions, and (c) severe operating conditions.[2] More recently, improved palladium catalysts have been found active under milder conditions where competing side reactions are of lesser importance,[4,9] and normal esters predominate.[10,11] Linear carboxylic acid esters have also been prepared in 67–85% selectivity with the H_2PtCl_6–$SnCl_2$ couple.[12,13]

$$\mathrm{RCH{=}CH + CO + R'OH} \rightarrow \begin{cases} \mathrm{RCH_2CH_2COOR'} & \text{(1a)} \\ \mathrm{RCHCOOR'} \\ \quad\vert \\ \quad\mathrm{CH_3} & \text{(1b)} \end{cases}$$

As part of a program to develop new routes to linear carboxylic acid derivatives, we report here the use of certain ligand-stabilized platinum(II)–Group 4B metal halide complexes as catalysts for the highly selective carbonylation of α olefins to linear carboxylic acid esters.[14]

Results

Effect of Platinum Catalyst Structure. In multistep reaction sequences such as carbonylation, modification of the catalyst metal center by changes in coordinated ligand structure may dramatically affect the activity and stability of the catalyst, the selectivity to straight-chain products, and competing side reactions.[2,4,8,9,15,16] In this work, a broad range of ligand-stabilized platinum(II) complexes in combination with Group 4B metal halide cocatalysts have been screened for carbonylation activity, and methyl octanoate synthesis from 1-heptene has been selected as the model reaction (see Tables I and II).

The first distinguishing feature of this class of catalysts is their ability to produce linear acid esters, such as methyl octanoate, in at least 90 mol % selectivity. This selectivity is consistently higher than has been reported previously,[1–10,12,13] even for related palladium bimetallic catalysts.[17] The highest selectivity to methyl octanoate achieved here (98 mol %) is with dichlorobis(triphenyl phosphite)platinum(II)–tin(II) chloride (expt 5). The highest yield of meth-

Table I. 1-Heptene Carbonylation Catalyzed by Various Platinum(II) Complexes I[a]

Expt	Composition of platinum complex	1-Heptene conversion, mol %	Yield of 2,3-heptenes, mol %	Methyl octanoate Yield, mol %[b]	Methyl octanoate Selectivity, mol %[c]
1	$[(C_6H_5)_3As]_2PtCl_2$–$10SnCl_2$	95	4.2	86	93
2	$[(C_6H_5)_2ClAs]_2PtCl_2$[d]–$10SnCl_2$	89	19	59	92
3	(DIARS)$PtCl_2$[e]–$10SnCl_2$	28	4.7	21	91
4	$[(C_6H_5)_3As]_2PtCl_2$–$10SnCl_2$–$5As(C_6H_5)_3$	91	18	61	91
5	$[(C_6H_5O)_3P]_2PtCl_2$–$10SnCl_2$	34	<2	28	98
6	$[(p\text{-}ClC_6H_4)_3P]_2PtCl_2$–$10SnCl_2$	9.3	<2	6.1	95
7	$[(C_6H_5)_3P]_2PtCl_2$–$10SnCl_2$	21	16	3.4	91
8	$[(p\text{-}CH_3OC_6H_4)_3P]_2PtCl_2$–$10SnCl_2$	15	8.7	0.8	94
9	$[C_6H_5(CH_3)_2P]_2PtCl_2$–$10SnCl_2$	3.5	<2	None	
10	$[(C_6H_5)_3Sb]_2PtCl_2$–$10SnCl_2$	12	<2	3.0	95
11	$[(C_6H_5)_2S]_2PtCl_2$–$10SnCl_2$	72	8.5	52	92
12	(1,10-PHEN)$PtCl_2$[g]–$10SnCl_2$	41	8.0	32	96
13	$[(C_6H_5)_3P]_4Pt$–$10SnCl_2$	3.5[f]	<2	2.2	90

[a] Run conditions: [1-heptene], 0.52 M; [Pt]:[1-heptene]:[methanol] 1:100:740; 240 atm, 80° C, 6 h. [b] Methyl octanoate yield based on 1-heptene charged. [c] Selectivity calculated basis: methyl octanoate yield/total methyl C_8 acid esters. [d] Prepared in situ. [e] DIARS, $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$. [f] Run at 105 °C, no reaction at 80 °C. [g] 1,10-PHEN, 1,10-phenanthroline.

Table II. 1-Heptene Carbonylation Catalyzed by Various Platinum(II) Complexes II[a]

Expt	Composition of platinum complex	1-Heptene conversion, mol %	Yield of 2,3-heptenes, mol %	Methyl octanoate Yield, mol %	Methyl octanoate Selectivity, mol %
14	$[(C_6H_5)_3As]_2PtCl_2$–$10SnCl_2$	95	4.2	86	93
15	$[(C_6H_5)_3As]_2PtCl_2$–$10GeCl_2$[b]	3.6	<2	1.0	94
16	$[(C_6H_5)_3As]_2PtCl_2$–$10PbCl_2$	2.0	<2	1.6	90
17	$[(C_6H_5)_3As]_2PtCl_2$–$10SbCl_3$	2.6	<2	None	
18	$[(C_6H_5)_3As]_2PtCl_2$–$10SnCl_4$	52	<3	44	92
19	$[(C_6H_5)_3As]_2PtI_2$–$10SnI_2$	7.0	<2	6.5	>90
20	$[(C_6H_5)_3As]_2PtCl_2$	<2	<2	None	
21	$[(C_6H_5)_3As]_2Pt(CN)_2$	<2	<2	None	
22	$[(C_6H_5)_3As]_2PtCl_2$–$30SnCl_2$	64	8.6	35	92
23	$[(C_6H_5)_3As]_2PtCl_2$–$5SnCl_2$	63	5.9	56	92
24	$[(C_6H_5)_3As]_2PtCl_2$–$1SnCl_2$	33	6.9	22	94

[a] Run conditions: [1-heptene], 0.52 M; [Pt]:[1-heptene]:[methanol] 1:100:740, 240 atm, 80° C, 6 h. [b] Added as $CsGeCl_3$.

yl octanoate (86 mol %) is with dichlorobis(triphenylarsine)-platinum(II)–tin(II) chloride (expt 1).

The nature of the Group 5B or 6B donor ligands (Table I) and the Group 4B metal halides (Table II) generally has a marked effect upon the platinum carbonylation activity, but a far smaller effect upon the selectivity to the linear esters, and the degree of competing double bond migration. While no simple correlation has been found, or even anticipated, between the performance of the platinum(II)–tin(II) chloride complexes and either the steric[18] or electron donor-acceptor properties[19] of the coordinated Group 5B and 6B ligands, generally improved yields of linear ester have been obtained with strong π-acceptor ligands of low basicity such as triphenylarsine and triphenyl phosphite. In a homologous series of platinum–phosphine complexes (expt 5–9), decreasing basicity of the coordinated ligands[19] leads to increasing yields of ester in the order

$$P(CH_3)_2C_6H_5 < P(p\text{-}CH_3OC_6H_4)_3 < P(C_6H_5)_3 < P(p\text{-}ClC_6H_4)_3 < P(OC_6H_5)_3 \quad (2)$$

with complexes of strongly basic ligands, such as $P(n\text{-}C_4H_9)_3$ and $P(CH_3)_2(C_6H_5)$, being inactive under these conditions. For ligands of different donor atoms, however, the observed trends (e.g., eq 3) may best be rationalized in terms of competing steric and electronic factors.[20,21]

$$P(C_6H_5)_3 \approx Sb(C_6H_5)_3 < S(C_6H_5)_2 < AsCl(C_6H_5)_2 < As(C_6H_5)_3 \quad (3)$$

Analogous platinum(0) complexes, e.g., $(Ph_3P)_4Pt$–$SnCl_2$, expt 13, provide poor catalyst precursors. Complexes of bidentate ligands such as bis(diphenylarsino)ethane and 1,10-phenanthroline show improved thermal stability, but this is accompanied by a marked reduction in activity that may be attributed either to the limited solubility of these complexes, or the increased difficulty in ligand substitution.

Dichlorobis(triphenylarsine)platinum(II), in the absence of a Group 4B metal halide cocatalyst, fails to carbonylate α olefins (Table II, expt 20). Significant yields of methyl octanoate are afforded, however, with metal chloride cocatalysts such as tin(II) chloride, tin(IV) chloride, and lead(II) chloride; the highest yields of linear ester are obtained with tin(II) chloride (expt 14) at Sn:Pt mole ratios of around 10 (expt 14, 22–24). Similarly, among different tin(II) halides, $SnCl_2$ is more effective than SnI_2. This order of effectiveness (eq 4 and 5) parallels that found for the bimetallic hydroformylation catalysts $(R_3P)_2PtX_2$-MX_2[22], and the order of stability of platinum–Group 4B metal bonds.[23,24] It should be noted, nevertheless, that no carbonylation is evident when $SnCl_3^-$ is replaced by other powerful π-acceptor ligands[25,26] such as antimony trichloride, cyanide ion, and CO itself.

$$GeCl_2 < SnCl_2 > PbCl_2 \quad (4)$$

$$SnCl_2 > SnI_2 \quad (5)$$

Table III. Olefin Carbonylation Catalyzed by Solutions of $[(C_6H_5)_3As)]_2PtCl_2$–$SnCl_2$[a]

Expt	Alkene	Registry no.	Initial mole ratio alkene/Pt	Reaction time, min	Alkene conversion, %	Major carbonylation products: Identity	Major carbonylation products: Selectivity, mol %
25	Propylene	115-07-1	100	360	30	Methyl butyrate	76
26	1-Heptene	592-76-7	100	360	51	Methyl octanoate	95
27	1-Tetradecene	1120-36-1	100	360	34	Methyl pentadecanoate	88
28	1-Eicosene	3452-07-1	50	300	29	Methyl heneicosanoate	>95
29	3-Methyl-1-pentene	760-20-3	50	480	74	Methyl 4-methylhexanoate	>99
30	4-Methyl-1-pentene	691-37-2	50	360	50	Methyl 5-methylhexanoate	97
31	2,4,4-Trimethyl-1-pentene	107-39-1	50	360	No reaction		
32	Cyclohexene	110-83-8	50	360	No reaction		
33	2-Decene	6816-17-7	100	180	No reaction		
34	1-Heptene		100	180	41	Methyl octanoate	92
	trans-2-Heptene	14686-13-6	100	180	<1	None	—
	trans-5-Decene	7433-56-9	50	180	<1	None	—

[a] Run conditions: 80° C, 140 atm, excess methanol.

Table IV. 1-Heptene Carbonylation Catalyzed by Solutions of $[(C_6H_5)_3)As]_2PtCl_2$–$SnCl_2$. Effect of Changes in Nucleophilic Coreactant

Expt	Nucleophilic coreactant	Heptene conversion, mol %	Major carbonylation product: Identity	Major carbonylation product: Selectivity, mol %	Major carbonylation product: Yield, mol %
35	Ethanethiol	5.1	Ethyl thioloctanoate	95	2.8
36	Water	43	Octanoic acid[b]	91	30
37	2-Chloroethanol	79	2-Chloroethyl octanoate	90	65
38	2-Propanol	15	Isopropyl octanoate	94	12
39	1-Octanol	67	Octyl octanoate	94	60
40	Methanol	91	Methyl octanoate	93	86
41	Phenol	52	Phenyl octanoate	93	25

[a] Run conditions: [1-heptene], 0.47 → 0.59 M, [Pt]:[1-heptene]:[ROH] 1:100:300, 240 atm, 80° C, 6 h. [b] Identified as methyl octanoate by treating crude product solution with methanol–BF_3 reagent.

For the more active platinum catalysts, the principal side reactions are (a) the formation of small quantities of branched (α-methyl) acid esters, in this case methyl 2-methylheptanoate, and (b) isomerization of the 1-heptene to internal isomers, notably *cis*- and *trans*-2-heptene. Normally less than 10% of the 2-heptene is isomerized further to *cis*- and *trans*-3-heptene, and there is negligible *n*-heptane formation.

Effect of Olefin Structure. The sensitivity of the $(Ph_3P)_2PtCl_2$–$SnCl_2$ catalyst to substrate structure has been noted previously for both olefin hydrogenation[27] and hydroformylation;[22] here the preferred carbonylation catalyst, $(Ph_3As)_2PtCl_2$–$SnCl_2$, shows even greater sensitivity to the stereochemical requirements of the alkene (see Table III). Generally, monoalkenes are found to carbonylate readily only where the double bond is terminal. In the case of typical C_3–C_{20} linear 1-alkenes, the selectivity to desired linear carboxylic acid ester improves with increasing chain length (eq 6, mole selectivity in parenthesis), whereas the rate appears to reach a maximum around C_7.

$$C_3\ (76\%) < C_7\text{–}C_{14}\ (88\text{–}95\%) < C_{20}\ (95\%) \qquad (6)$$

The substitution of alkyl groups into the 1-alkene molecule acts to change both the activity and selectivity of the $(Ph_2As)_2PtCl_2$–$SnCl_2$. The observed pattern of behavior reflects primarily the steric effect of the alkyl substituent.[27] No carbonylation has been detected, for example, when the double bond is hindered by substituent groups on the α or β carbons (expt 31–33); this includes 2- and 5-decenes, cyclic olefins like cyclohexene, and β-substituted alkenes such as 2,4,4-trimethyl-1-pentene. On the other hand, where the substitution is one carbon removed from the double bond, as in the case of 3-methyl-1-pentene, carbonylation proceeds smoothly in high selectivity to give almost 100% methyl 4-methylhexanoate (expt 29). Even for δ-substituted materials, such as 4-methyl-1-pentene, selectivity for anti-Markownikoff addition remains close to 97 mol %.

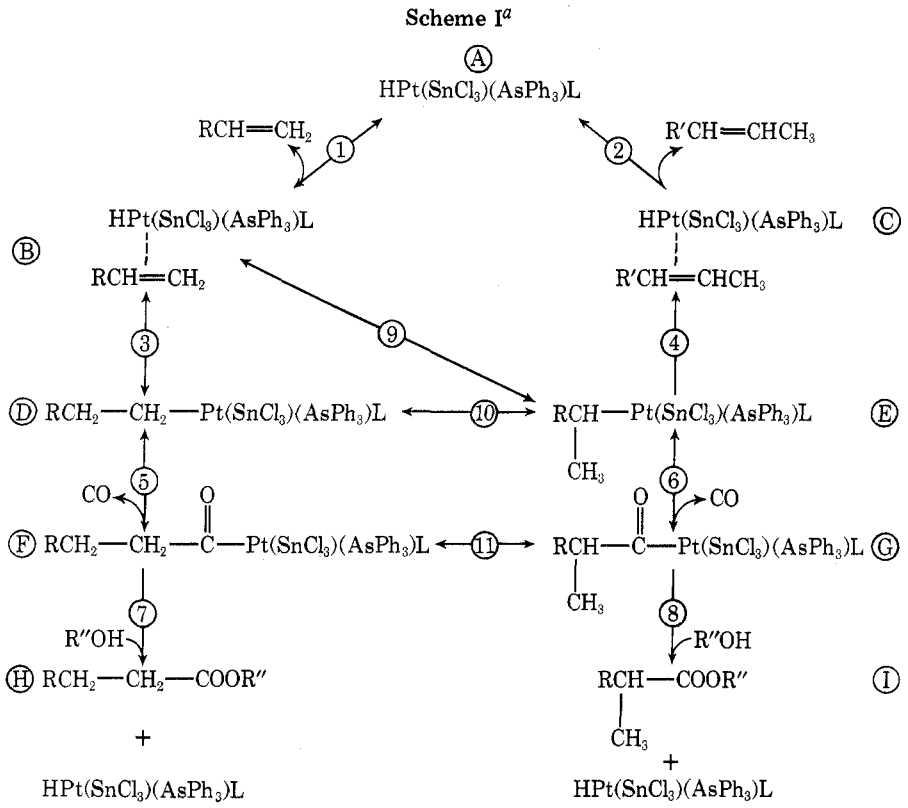
Effect of Nucleophile Structure. Carbonylation has been effected with a range of nucleophilic coreactants having mobile hydrogen atoms, including alcohols, water, mercaptans, and hydrogen halides. The trends parallel those for nickel and cobalt carbonyl catalysts.[2] Here the nucleophile structure has very little effect upon the catalyst selectivity, be it primary, secondary, or substituted alcohol, water, or thiol (Table IV), but the catalytic effectiveness varies by a factor of at least 20. Where oxygen is the attacking atom of the nucleophile, increased nucleophilicity[28] leads to improved yields of ester (eq 7). Competing addition reactions are prevalent with thiol (expt 35), but complexation with the platinum catalyst may account for the low conversion in this case. For methanol, at least, the rate of carbonylation is independent of the initial alkanol concentration provided that sufficient is present to satisfy the stoichiometry of eq 1.

$$ROH > HOH > PhOH \qquad (7)$$

Attempts to prepare fatty acid amides and anilides led to the formation of intractable tars. Carboxylic acid halogenides, such as octanoyl chloride, may be synthesized using HCl-treated solutions of the platinum salts in halogenated solvents such as methylene chloride.[29]

Temperature–Pressure Effects. While methyl octanoate synthesis may be carried out at temperatures of 25 °C or higher, and CO pressures up to 300 atm or more, a narrower range of conditions is necessary for preparative yields of ester with the $(Ph_3As)_2PtCl_2$–$SnCl_2$ catalyst.[14] The rate of carbonylation is slow below 60 °C and, as with related CO insertion reactions catalyzed by platinum,[30] ester preparations normally required pressures of about 70 atm.

Scheme I[a]



[a] Where L = $SnCl_3^-$, CO, chloride ion, or a solvent species.

No attempt has been made to correlate carbonylation activity with the nature of the solvent media,[2] but a range of moderately polar and nonpolar solvents has been found suitable for this synthesis. Methyl isobutyl ketone and dimethoxyethane were the standard solvents; *p*-dioxane, methylene chloride, and benzene also proved satisfactory.[14] *N,N*-Dimethylformamide inhibits carbonylation by forming stable adducts with the platinum complex.[31]

Discussion

The addition of tin(II) chloride to solutions of the complex $(Ph_3As)_2PtCl_2$ in non- or moderately polar solvents generates an active and very regiospecific carbonylation catalyst. This high regioselectivity is relatively insensitive to reaction parameters such as temperature, CO pressure, and solvent,[14] and the nature of the nucleophllic coreactant, but is significantly influenced by the structure of the alkene and the composition of the active catalysts. The observed trends, summarized in Tables I–IV, may be rationalized in terms of Scheme I, similar to that proposed for related catalysis.[4,32] Among stabilized Pt(II)–$SnCl_3$ catalysts the highest yields of linear carboxylic acid esters have been obtained with ligands of low basicity and high π-acceptor strength, such as $AsPh_3$, $AsClPh_2$, and $P(OPh)_3$ (eq 2 and 3). Likewise there appears to be a close parallel between catalyst activity and the π-acceptor strength of the MX_3^- cocatalyst (eq 4 and 5). For the preferred composition then, $(Ph_3As)_2PtCl_2$–$SnCl_2$, this combination of ligands, by lowering the electron density of the platinum, should favor both initial platinum hydride formation[20,21] and subsequent attack by nucleophiles such as CO and the multiple bonds of the olefin.[33]

With regard to the regioselectivity of the carbonylation, removal of electron density from the platinum metal center may also be expected to lower the hydridic character of the catalyst,[15] thereby favoring Markownikoff addition of Pt–H to the olefin (step 9) and branched acid ester formation via intermediates such as E and G. This increased acidity of the hydride is generally small,[15] however, and for $AsPh_3$ and $SnCl_3^-$ more than offset by the combined steric effects of these bulky ligands. Molecular models show that a combination of such ligands provides a particularly sterically hindered Pt complex, A, in which steric constraints should act to favor both anti-Markownikoff Pt–H addition (step 3) and high equilibrium concentrations of the less sterically hindered straight-chain σ-alkyl and σ-acyl Pt complexes such as D and F.

Similar reasoning based on the steric requirements of these highly crowded platinum catalysts may account for the observed selective carbonylation of only terminal olefins and the changes in product linearity with α-olefin structure (Table III), for example, the improvement in ester linearity from a low of 76 mol % for the least hindered homologue, propylene (expt 25), to near 100% for certain partially hindered α olefins such as 3-methyl-1-pentene (expt 29). Since internal, cyclic, and β-substituted α olefins are not carbonylated under these conditions, branched acid ester products likely originate not from 1-alkene isomerization and carbonylation of free internal isomer, but rather via Markownikoff Pt–H addition to the olefin (step 9) and/or isomerization of the σ-alkyl and σ-acyl intermediates to less favored forms (e.g., D → E and F → G). Preferential complexation of the platinum catalyst with 1-alkenes is consistent also with the observed selective carbonylation of internal–terminal olefin mixtures[34] (expt 34).

It may be noted that analogues of the hydridoplatinum species A and B have been prepared previously,[20,35] as have phosphine-stabilized platinum–alkyl complexes[36,37] and platinum–acyl species analogous to F, under more forcing conditions.[30] Intermediate platinum carbonyls such as $Pt(CO)(EtOH)(PPh_3)_2(SnCl_3)_2$ have also been isolated by the carbonylation of phosphine treated platinum–tin solutions.[38] However, while maximum catalyst activity is realized in this work at Sn:Pt mole ratios of about 10 (expt 14, 22–24), no Pt–Sn complexes with Group 5B ligands have been isolated having more than two $SnCl_3^-$ ions per plati-

num.[24] As in related catalysis,[33] it is likely that several interdependent equilibria exist prior to carbonylation, with at least partial displacement of the organoarsine ligand being consistent with (a) the relatively low sensitivity of the isomer distribution (selectivity 90–98 mol %) to significant changes in Group 5B ligand structure (Table I) and (b) the slower carbonylation rate in the presence of excess organoarsine (expt 4). Mixed complexes such as $(Ph_3As)_2PtCl(SnCl_3)$ are known,[39] although $SnCl_2$ may be readily displaced by other strong back-bonding ligands[24] such as CO.

Experimental Section

Materials. Carbon monoxide was CP grade. Reagents and solvents were commercial samples, and olefins were generally of high purity, and were freed of peroxides prior to use by passage through a column of neutral alumina. The platinum halide complexes, $PtCl_2(AsPh_3)_2$,[40] $PtCl_2(PPh_3)_2$,[40] $PtCl_2(SbPh_3)_2$,[40] $PtCl_2[P(OPh)_3]_2$,[21] $PtCl_2(SPh_2)_2$,[20] $PtCl_2$(*o*-phenanthroline),[41] and $Pt(CN)_2(PPh_3)_2$[21] were prepared by the published methods. Similar techniques were used to prepare $PtCl_2[PPh(CH_3)_2]_2$, $PtCl_2(Ph_2AsCH_2CH_2AsPh_2)$, $PtCl_2(AsPh_2Cl)_2$, and $PtI_2(AsPh_3)_2$. Hydrated tin(II) chloride, $SnCl_2 \cdot 2H_2O$, was used throughout as cocatalyst, except where specified.

General Procedures. The extent of carbonylation and the distribution of products were estimated by GLC. Olefin and ester analyses were both carried out with 4–10-ft columns of 10–20% polyphenyl ether (five rings, Analabs Inc. GP77) on 60/80 mesh Chromosorb G. High molecular weight fractions were also analyzed with the aid of a 4-ft column of 7% SE-30 on Chromosorb G. The esters were isolated by preparative GLC and by distillation, and identified by a combination of GLC, ir, NMR, mass spectrometric, and elemental analyses techniques.

After some preliminary experiments to establish suitable carbonylation conditions, most catalyst screening was carried out in a 600-ml glass-lined rocking autoclave under the conditions specified in Tables I and II. Rates of carbonylation were measured using a 300-ml capacity, glass-lined autoclave equipped with Magnadrive stirrer and sampling valve.

Synthesis of Methyl Octanoate. Dichlorobis(triphenylarsine)platinum(II) (0.5–20 mmol) and tin(II) chloride dihydrate (2.5–20 mmol) were added to a N_2-saturated mixture of methyl isobutyl ketone (75 ml), methanol (5–15 ml) and 1-heptene (50–200 mmol). The mixture was stirred for 2–5 min to dissolve the solid catalyst, and the loaded liner containing the deep red liquid charge was transferred to the autoclave. The autoclave was sealed, deoxygenated with a purge of N_2, and heated to 80 °C under 200 atm of carbon monoxide. After the reactor was rocked at this temperature for 3–6 h, the apparatus was allowed to cool, and the clear reddish-brown, liquid product recovered. Typical analyses data were as follows: 1-heptene conversion 95%, yield of methyl C_8 acid ester 92%, selectivity to linear methyl octanoate 93 mol %, material balance 97%.

The methyl C_8 acid ester may be recovered from the crude product liquid by fractional distillation in vacuo. Anal. Calcd for $C_7H_{15}COOCH_3$: C, 68.3; H, 11.4. Found: C, 68.4; H, 11.6.

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Registry No.—$((C_6H_5)_3As)_2PtCl_2$, 16242-55-0; (DIARS)$PtCl_2$, 14647-20-2; $[(C_6H_5O)_3P]_2PtCl_2$, 16337-54-5; $[(p\text{-}ClC_6H_4)_3P]_2PtCl_2$, 57606-46-9; $[(C_6H_5)_3P]_2PtCl_2$, 10199-34-5; $[(p\text{-}MeOC_6H_4)_3P]_2PtCl_2$, 57606-47-0; $[C_6H_5(CH_3)_2P]_2PtCl_2$, 30759-88-7; $[(C_6H_5)_3Sb]_2PtCl_2$, 16337-53-4; $[(C_6H_5)_2S]_2PtCl_2$, 50525-38-7; (1,10-PHEN)$PtCl_2$, 18432-95-6; $[(C_6H_5)_3P]_4Pt$, 14221-02-4; $[(C_6H_5)_2ClAs]_2PtCl_2$, 57606-48-1; $SnCl_2$, 7772-99-8; $As(C_6H_5)_3$, 603-32-7; $[(C_6H_5)_3As]_2PtI_2$, 24151-00-6; $[(C_6H_5)_3As]_2Pt(CN)_2$, 16242-57-2; SnI_2, 10294-70-9; $GeCl_2$, 10060-11-4; $PbCl_2$, 7758-95-4; $SbCl_3$, 10025-91-9; $SnCl_4$, 7646-78-8; methyl octanoate, 111-11-5; methyl isobutyl ketone, 108-10-1.

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