

scribed in the Experimental Section (3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Supported by the National Science Foundation, Grant MPS74-20946.
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Linear Carboxylic Acid Esters from α Olefins. 2. Catalysis by Homogeneous Palladium Complexes

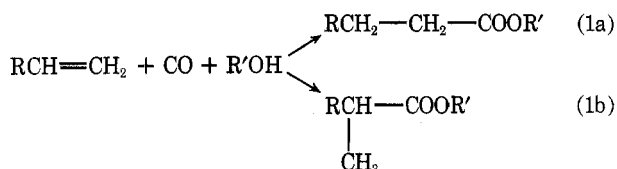
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Regioselective carbonylation of α olefins is catalyzed by a series of ligand-stabilized palladium(II)-group 4B metal halide complexes of the composition $[(p\text{-XC}_6\text{H}_4)_3\text{P}]_2\text{PdCl}_2\text{-MCl}_2$ (where X = H, CH₃, CH₃O, and Cl, and M = Sn or Ge) and by related complexes. For the synthesis of linear carboxylic acid esters the sensitivity of the carbonylation to palladium catalyst composition, the structure of the olefin substrate and that of the nucleophilic co-reactant have been examined in relation to observed kinetics and the isolation of active intermediates.

In a previous paper¹ we described the synthesis of linear carboxylic acid esters from linear α olefins in high yields (eq 1a) catalyzed by a novel class of ligand-stabilized



platinum(II)-group 4B metal halide carbonylation catalysts. These highly regioselective catalysts, typified by $[(\text{C}_6\text{H}_5)_3\text{As}]_2\text{PtCl}_2\text{-SnCl}_2$, afford up to 98 mol % selectivity to the linear ester. We report herein the extension of that work to palladium chemistry, and the development of a series of highly active ligand-stabilized palladium(II)-group 4B metal halide catalysts. These catalysts also yield linear esters in 85-89 mol % selectivity but have the intrinsic advantages of requiring lower CO pressures, greater flexibility regarding olefin feed stock, and lower cost.

Palladium salts have, in recent years, found extensive application as carbonylation catalysts.²⁻⁷ Where the addition is to an α olefin of three or more carbons, however, most catalysts, e.g., PdCl_2 ⁸ and $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$,⁵ yield a mixture of normal and iso acid derivatives and generally it is the iso ester that predominates (eq 1b).³ The use of more selective palladium bimetallic catalysts which ensure higher selectivity to linear acid derivatives has been recognized in the patent literature.⁹⁻¹²

Results

Effect of Palladium Catalyst Structure. By analogy with earlier studies¹ a broad range of palladium bimetallic complexes have been screened for carbonylation activity. Palladium bonded to group 5B and 6B tertiary donor ligands containing aryl, substituted aryl, alkyl, and aryloxy radicals in combination with group 4B metal halides has been considered.¹¹ Methyl octanoate synthesis was selected as the model reaction. Table I illustrates the importance of catalyst structure upon both activity and selectivity to linear ester. Under typical screening conditions linear ester selectivity varies from a low of 44% up to 89 mol %. Yields of methyl octanoate also vary widely, but exceed 70 mol % for at least four palladium complexes, viz., $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$, $[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$, $[(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$, and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2\text{-GeCl}_2$ (expt 1-3, 10). Total ester yields, which include 10-13% methyl 2-methylheptanoate and 1-2% methyl 2-ethylhexanoate, are in excess of 85 mol % for each of these catalysts. The remaining products are isomerized heptenes, primarily *cis*- and *trans*-2-heptenes.

No simple correlations have been found between catalyst performance and either the size or electronic character of the coordinated ligands, although both properties are clearly important. For a series of substituted arylphosphine complexes, differences in the effective size of the coordinated ligands may have a critical effect upon the degree of steric crowding and consequently upon catalyst reactivity. This is illustrated by the more than 20-fold difference in ester yield between otherwise similar ortho- and para-substituted methoxyphenylphosphine complexes, viz., $[(o\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$ and $[(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$ (expt

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Table I. 1-Heptene Carbonylation Catalyzed by Various Palladium Complexes^a

Expt	Composition of palladium complex	1-Heptene conversion, mol %	Yield of 2-, 3-heptenes, mol %	Methyl octanoate	
				Yield, mol % ^b	Selectivity, mol % ^c
1	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂ -10SnCl ₂	96	4.6	76	87
2	[(<i>p</i> -CH ₃ C ₆ H ₄) ₃ P] ₂ PdCl ₂ -10SnCl ₂	97	4.7	78	87
3	[(<i>p</i> -CH ₃ OC ₆ H ₄) ₃ P] ₂ PdCl ₂ -10SnCl ₂	88	4.6	71	85
4	[(<i>p</i> -ClC ₆ H ₄) ₃ P] ₂ PdCl ₂ -10SnCl ₂	16	<1	10	89
5	[(<i>o</i> -CH ₃ OC ₆ H ₄) ₃ P] ₂ PdCl ₂ -10SnCl ₂	5	<1	2.9	81
6	[C ₆ H ₅ (CH ₃) ₂ P] ₂ PdCl ₂ -10SnCl ₂	65	5.8	42	88
7	[(C ₆ H ₅ O) ₃ P] ₂ PdCl ₂ -10SnCl ₂	3.0	<1	2.8	89
8	[(C ₆ H ₅) ₃ As] ₂ PdCl ₂ -10SnCl ₂	2.2	<1	None	
9	[(C ₆ H ₅) ₃ As] ₂ PdCl ₂ -10GeCl ₂	42	2.3	23	76
10	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂ -10GeCl ₂	96	3.7	73	88
11	[(C ₆ H ₅) ₃ P] ₂ PdI ₂ -10SnI ₂	4.3	<1	None	
12	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂ -10PbCl ₂	87	<2	33	44
13	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂ -10SnCl(Ph) ₃	7.9	<1	3.3	89
14	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂	93	2.3	42	58

^a Run conditions: [1-heptene], 0.52 M; [Pd]:[1-C₇H₁₄]:[CH₃OH] = 1:10²:7.4 × 10²; 240 atm; 80 °C; 360 min. ^b Methyl octanoate yield based on 1-heptene charged. ^c Selectivity calculated basis: methyl octanoate yield/total methyl C₈ acid ester.

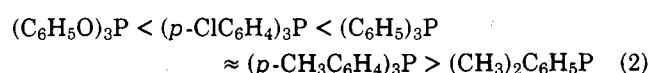
Table II. 1-Heptene Carbonylation Catalyzed by [(C₆H₅)₃P]₂PdCl₂-SnCl₂^a

Expt	Mole Ratio (C ₆ H ₅) ₃ P:Pd:SnCl ₂			Methyl octanoate	
				Selectivity, mole % ^b	Rate, M h ⁻¹ ^c
15	2	1	1	85.8	0.14
16	2	1	5	88.5	0.38
17	2	1	10	86.5	0.24
18	2	1	10 ^d	87.9	0.21
19	2	1	30	88.7	0.085
20	4	1	10	88.7	0.034

^a Run conditions: [1-heptene], 0.52 M; [Pd]:[1-C₇H₁₄]:[CH₃OH], 1:10²:7.4 × 10²; 136 atm, 70 °C, 180-360 min. ^b Selectivity calculated basis: methyl octanoate yield/total methyl C₈ acid ester. ^c Rate of methyl octanoate formation. ^d With anhydrous SnCl₂.

3 and 5). Likewise comparing arylarsine and phosphine complexes, the inactivity of [(C₆H₅)₃As]₂PdCl₂-SnCl₂ (expt 8) contrasts with that of the analogous [(C₆H₅)₃P]₂PdCl₂-SnCl₂ and [(C₆H₅)₃As]₂PdCl₂-GeCl₂ complexes (expt 1 and 9), and the 86 mol % yield of methyl octanoate realized under similar conditions with the platinum catalyst [(C₆H₅)₃As]₂-PtCl₂-SnCl₂.¹ Carbonylation is achieved in the palladium case only with the spatially smaller P vs. As atom of the tertiary donor ligands and/or Ge²⁺ vs. Sn²⁺ salts¹³ of the group 4B metal halide cocatalyst.

For a series of phosphines of similar cone angle,¹⁴ activity is maximized with arylphosphines of moderate base strength¹⁵ (eq 2). The effect of strongly electron-withdrawing para substituents (e.g., *p*-Cl, expt 4), or the replacement of aryl by the more basic alkylphosphines (expt 6), is, in both cases, to lower the yield of ester. Likewise, although both tin(II) chloride and germanium(II) chloride proved to be excellent cocatalysts, substituted tin(II) salts, tin(II) iodide and lead chloride, which form significantly weaker bonds to palladium,¹⁶ were less effective (expt 11-13). No ester was detected with PdCl₂-SnCl₂ alone, and bis(triphenylphosphine)palladium(II) without cocatalyst gave similar amounts of linear and branched ester (expt 14).⁵



In related studies (Table II) it was further established that (a) tin to palladium mole ratios of ca. 5 produce the most rapid rates of carbonylation, lower ratios leading to catalyst instability, and additional cocatalyst only suppressing the rate; (b) excess triphenylphosphine (2, mol/g-atom of Pd, expt 20) dramatically lowers the rate of methyl octanoate formation but does not influence the normal to branched isomer ratio; (c) tin(II) chloride dihydrate replacement by anhydrous tin(II) chloride (expt 17 and 18) results in ca. 12% loss in rate (cf. Pt-Sn hydrogenation catalysis^{17,18}) but overall yields of ester are within experimental error.

Effect of Olefin Structure. Palladium bimetallic catalysts, typified by [(C₆H₅)₃P]₂PdCl₂-SnCl₂, will carbonylate a variety of nonconjugated olefin types, including linear and branched α olefins, internal olefins, and cyclic olefins (see Table III). Here we chose to study the relationship between catalyst performance, as gauged by the rate and selectivity to linear ester, and the stereochemical requirements and properties of the alkene.¹⁹ Linear α olefins generally react most readily, the rate varying by a factor of 10, however, over the carbon range C₃-C₂₀ (expt 21-25), and reaching a maximum in the C₅-C₇ range. Selectivity does improve with increasing molecular weight but exceeds 90 mol % only in the case of methyl heneicosanoate synthesis from 1-eicosene.

In contrast to analogous platinum bimetallic catalysts,¹ [(C₆H₅)₃P]₂PdCl₂-SnCl₂ carbonylates at least three classes of polysubstituted olefins (expt 26-33). Sterically hindered branched α olefins in which the alkyl substituent is on the β or γ carbon provide excellent examples of regioselective carbonylation. Selectivity to linear ester exceeds 99 mol % in the case of methyl 3-methylhexanoate from 2-methyl-1-pentene (expt 28) and 98 mol % for methyl 4-methylhexanoate synthesis (expt 27). Rates of carbonylation are considerably slower, however.

Internal, disubstituted olefins also carbonylate more slowly than linear α olefins, but here the product distribution is quite different. CO addition is no longer predominantly at the terminal carbon. Some 6-10% linear methyl octanoate is formed from 2-heptenes, but the rate and selectivity are further reduced for *cis*-3-heptene, and no ester is detected with *trans*-5-decene. Of note is the significantly faster rate of *cis*- vs. *trans*-2-heptene conversion to methyl 2-methylheptanoate (the primary product in both cases).

Effect of Nucleophile Structure. Carbonylation may be effected with a range of nucleophilic coreactants having mobile hydrogen atoms, including alcohols, water, mercaptans,

Table III. Alkene Carbonylation Catalyzed by Solutions of $[(C_6H_5)_3P]_2PdCl_2-SnCl_2^a$

Expt	Alkene	Alkene conversion, mol %	Major carbonylation products		
			Identity	Selectivity, mol %	Rate, $M h^{-1}$
21	Propylene	90	Methyl butyrate	84.9	0.16
22	1-Pentene	N.D. ^b	Methyl hexanoate	89.5	0.23
23	1-Heptene	>95	Methyl octanoate	86.5	0.24
24	1-Undecene	59	Methyl dodecanoate	88.5	0.11
25	1-Eicosene	20	Methyl heneicosanoate	90.8	0.024
26	4-Methyl-1-pentene	86	Methyl 5-methylhexanoate	88.8	0.16
27	3-Methyl-1-pentene	71	Methyl 4-methylhexanoate	98.0	0.15
28	2-Methyl-1-pentene	30	Methyl 3-methylhexanoate	>99	0.021
29	Cyclooctene	36	Methyl cyclooctanecarboxylate	>99	N.D.
30	<i>trans</i> -2-Heptene	11	Methyl octanoate	10	0.004
			Methyl 2-methylheptanoate	60	0.021
			Methyl 2-ethylhexanoate ^c	30	0.012
31	<i>cis</i> -2-Heptene	54	Methyl octanoate	6.9	0.010
			Methyl 2-methylheptanoate	71	0.12
			Methyl 2-ethylhexanoate ^c	22	0.032
32	<i>cis</i> -3-Heptene	N.D.	Methyl octanoate	Trace	
			Methyl 2-methylheptanoate	22	0.018
			Methyl 2-ethylhexanoate ^c	78	0.061
33	<i>trans</i> -5-Decene	1.0	None		

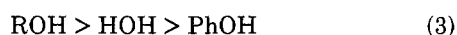
^a Run conditions: 70 °C; 136 atm; 180 min; excess CH_3OH . ^b N.D., not determined. ^c May contain some methyl 2-propylpentanoate.

Table IV. 1-Heptene Carbonylation Catalyzed by Solutions of $[(C_6H_5)_3P]_2PdCl_2-SnCl_2$. The Effect of Changes in Nucleophilic Coreactant^a

Expt	Nucleophilic coreactant	Heptene conversion, mol %	Major carbonylation products		
			Identity	Selectivity, mol %	Rate, $M h^{-1}$
34	Methanol	>95	Methyl octanoate	87.8	0.26
35	1-Hexanol	>95	<i>n</i> -Hexyl octanoate	88.6	0.26
36	2-Propanol	30	Isopropyl octanoate	89.4	0.084
37	2-Chloroethanol	95	2-Chloroethyl octanoate	87	N.D. ^b
38	Phenol	59	Phenyl octanoate	84	0.022 ^c
39	Water	>95	Octanoic acid ^d	86	0.21
40	Ethanethiol	25	Ethyl thioloctanoate	88	0.065 ^e

^a Run conditions: [1-heptene] = 0.49–0.59 M; [Pd]:[1-C₇H₁₄]:[ROH] = 1:10²:3 × 10²; 136 atm; 70 °C. ^b N.D., not determined. ^c 1-Heptene conversion faster by a factor ≈ 3; final product contains 0.04 M octanoic acid. ^d Identified as methyl octanoate by treating crude product with methanol/BF₃ reagent. ^e Thiol addition reactions predominate.

and hydrogen halides. The trends parallel those for nickel carbonyl²⁰ and platinum bimetallic catalysts.¹ Here the nucleophile structure has only a small effect upon 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 10. Where oxygen is the attacking atom of the nucleophile, increasing nucleophilicity²¹ leads to improved rates of product formation (eq 3). Competing addition reactions are prevalent with thiols (expt 40).



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 in moderate yields using HCl treated solutions of the palladium salts in halogenated solvents such as methylene chloride.²²

Kinetic Studies. As a means of establishing general trends, carbonylation activity was surveyed over a broad range of temperatures (ambient to 120 °C) and superatmospheric pressures of CO (up to 300 atm).¹¹ Selectivity to linear ester is not seriously affected by these changes except at low CO pressures (Table V, expt 59), where 1-heptene isomerization

becomes the predominant reaction and the rates of *cis*- and *trans*-2-heptene carbonylation rival that of the 1 isomer.

Kinetic measurements, made under more selective conditions, were set to avoid induction periods prior to carbonylation by heating the catalyst solution under CO pressure before the injection of olefin (see Experimental Section). The effects of varying the tin to palladium mole ratio have already been summarized in Table II; for a constant Sn/Pd ratio of 10, the dependence of carbonylation rate upon catalyst concentration has been examined up to ca. 50 mM (data exemplified in Table V). Reproducibility is poor below 1 mM [Pd], but the rate obeys pseudo-first-order kinetics up to about 6 mM, and then reaches an asymptotic value. Similar rates at [Pd] > 6 mM might be due to the limited solubility of the active catalyst, but we see no evidence for insoluble material under these conditions. More likely it may be ascribed, as in related Pt-Sn catalysis,¹⁸ to association of the effective catalyst, and/or inhibition of the associated complex, the palladium existing as a cluster²³ or halogen-bridged²⁴ species. The observed rate is also first order in CO pressure (expt 44, 45, 56–62), but independent of alcohol concentration provided at least a stoichiometric excess is present to satisfy eq 1. A zero-order de-

Table V. 1-Heptene Carbonylation Catalyzed by Solutions of [(C₆H₅)₃P]₂PdCl₂-SnCl₂. Rate Studies^a

Expt	[Pd], mM	[C ₇ H ₁₄], M	C ₇ H ₁₅ COOCH ₃		
			CO, atm	Selectivity, mol % ^b	Rate, M h ⁻¹ c
41	25.8	0.52	136	84.4	0.32
42	20.6	0.52	136	84.6	0.30
43	10.3	0.52	136	85.6	0.29
44	5.15	0.52	136	86.5	0.25
45	3.61	0.52	136	87.6	0.17
46	2.58	0.52	136	87.5	0.13
47	2.06	0.52	136	87.5	0.095
48	1.55	0.52	136	87.3	0.078
49	5.15	1.72	136	87.8	0.23
50	5.15	0.96	136	90.9	0.24
51	5.15	0.78	136	88.1	0.22
52	5.15	0.36	136	88.1	0.23
53	5.15	0.11	136	88.9	0.12
54	5.68	0.57 ^d	136	86.5	0.23
55	5.95	0.60 ^e	136	88.6	0.13
56	5.15	0.52	102	87.8	0.17
57	5.15	0.52	68	87.0	0.13
58	5.15	0.52	34	88.0	0.060
59	5.15	0.52	8	76	<0.02
60	3.61	0.52	102	88.8	0.11
61	3.61	0.52	68	88.2	0.075
62	3.61	0.52	34	86.7	0.049

^a Run conditions: [Sn]/[Pd] = 10; [CH₃OH] = 3.82 M; 70 °C.

^b Selectivity basis: methyl octanoate/total methyl C₈ acid ester.

^c Rate of methyl octanoate formation. ^d [CH₃OH] = 1.73 M.

^e [CH₃OH] = 0.59 M.

pendence on olefin concentration has been confirmed at different palladium concentrations (e.g., expt 49–52) but some dropoff in rate is evident at low olefin/Pd mole ratios. Under normal operating conditions linear ester formation may be expressed in the form

$$\frac{d(\text{ester})}{dt} = \frac{k[\text{Pd}]p_{\text{CO}}}{(1 + K[\text{Pd}])} \quad (4)$$

for which the constant k has been calculated at 0.34 M⁻¹ h⁻¹. An activation energy for this reaction of 31 kcal mol⁻¹ was determined from Arrhenius plots over the temperature range 38–70 °C.

Nature of Palladium Catalyst. Beyond the analysis of recovered catalyst samples, other experiments were designed to isolate labile intermediates more akin to those truly responsible for carbonylation. The heating of an equimolar mixture of bis(triphenylphosphine)palladium(II) chloride (5 mmol) and tin(II) chloride dihydrate in benzene-ethanol under CO (100 atm) yielded a clear-red solution from which was isolated a green, crystalline solid (2.0 g) of the approximate composition PdH(SnCl₃)(P(C₆H₅)₃)₂. Anal. Calcd: Pd, 12.4; Cl, 12.4; P, 7.23. Found: Pd, 12.5; Cl, 13.0; P, 7.5; $\nu_{\text{Pd-H}}$ 2040 cm⁻¹, $\nu_{\text{Sn-Cl}}$ 315 cm⁻¹. Recycle of this material (1 mmol) in benzene with 1-octene (50 mmol) and excess ethanol gave ethyl nonanoate in 85.7 mol % selectivity. Total yield of ethyl C₉ acid ester was 92 mol %, octene conversion 94 mol %.

Palladium-trichlorotin complexes related to PdH(SnCl₃)[P(C₆H₅)₃]₂ have been reported previously;²⁵ the platinum analogue, PtH(SnCl₃)[P(C₆H₅)₃]₂, containing coordinated olefin, was isolated by Tayim and Bailar²⁶ during polyene hydrogenation catalyzed by [(C₆H₅)₃P]₂PtCl₂-SnCl₂ solutions.

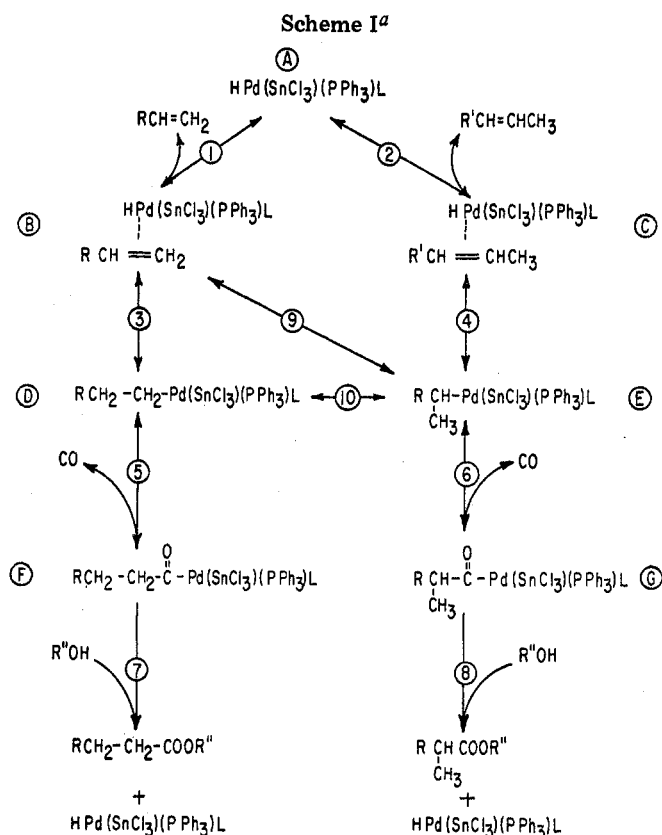
The heating of bis(triphenylphosphine)palladium(II) chloride (0.5 mmol) with additional quantities of tin(II) chloride (5.0 mmol) under CO led to the isolation of reddish-

brown solids of the approximate composition Pd(SnCl₃)₂-[P(C₆H₅)₃]₂. Similar materials were recovered from product solutions after carbonylation, but repeated studies failed to yield unequivocal evidence either for palladium carbonyl or for palladium-olefin adducts.

Discussion

The facile conversion of terminal olefins to linear, straight-chain acid esters in better than 85 mol % selectivity is the most significant feature of the stabilized palladium(II)-tin(II) chloride catalysts exemplified in Table I. This high regioselectivity is relatively insensitive to parameters such as temperature, CO pressure, solvent, and the nature of the coreactant, but is significantly influenced by the structure of the alkene and the composition of the active palladium catalyst.

The observed trends, summarized in Tables I and IV, may be rationalized in terms of the proposed reaction Scheme I.

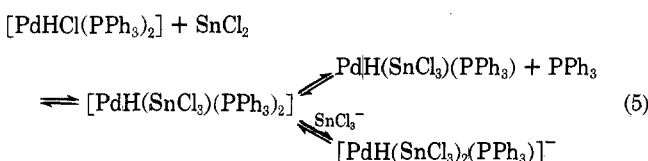


This scheme, similar to those for related catalyses,^{1,3,27} is consistent with observed rate data, identified intermediate species, and prior studies of the integral steps of carbonylation, particularly the formation of labile palladium alkyls via olefin migration^{3,6} and acyl-palladium species via CO insertion.^{28–30}

The purpose of initially screening a large number of stabilized palladium-group 4B metal halide complexes was to identify ligand combinations which, through modification of the metal center, might (a) increase the selectivity to linear acid isomer, (b) accelerate the rate of carbonylation, and (c) suppress competing olefin isomerization. Although no simple correlations have been recognized between catalyst structure vs. effectiveness, a series of preferred catalysts of the composition [(*p*-XC₆H₄)₃P]₂PdCl₂-MCl₂ (where X = H, Cl, CH₃O, and CH₃ and M = Sn or Ge) has been identified (Table I). The moderately basic arylphosphines would be expected

to raise the hydridic nature of intermediate A, Scheme I, and thereby to promote both anti-Markownikoff Pd-H addition to the olefin substrate (step 3) and the formation of straight-chain palladium alkyls, such as D. Although this would be partly offset by the strong π -acceptor ability of coordinated SnCl_3^- ,¹⁶ the combined steric bulk of the phosphine and SnCl_3^- ligands should provide a particularly sterically hindered catalyst in which steric constraints would act to favor both anti-Markownikoff Pd-H addition and high equilibrium concentrations of the less sterically hindered σ -alkyl and σ -acyl-Pd isomers such as D and F. Additional steric bulk serves only to block one or more of these rearrangements, as in the replacement of (*p*- $\text{CH}_3\text{OC}_6\text{H}_4$)₃P by (*o*- $\text{CH}_3\text{OC}_6\text{H}_4$)₃P and (C_6H_5)₃P by (C_6H_5)₃As (Table I).

The maximum catalytic activity realized at Sn:Pd mole ratios of ca. 5 (Table II) is in contrast to the isolation of the reactive intermediate $\text{PdH}(\text{SnCl}_3)(\text{PPh}_3)_2$, analogous to A in Scheme I, and to the fact that no palladium-tin(II) chloride complexes with group 5B donor ligands have been reported containing more than two SnCl_3^- coordinated to each palladium.³¹ Although unequivocal identification of the active catalyst has not been possible, evidence, such as the suppression of the rate by excess triphenylphosphine, and additional tin(II) chloride, suggests several interdependent equilibria existing in these tin-rich solutions (eq 5) prior to car-



bonylation, and the formation of inactive species with excess ligand. A platinum hydrocarbonyl species analogous possibly to the known³² hydroformylation catalyst $[\text{PtH}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2]$ has been isolated³³ from solutions of the related platinum carbonylation catalyst $[(\text{C}_6\text{H}_5)_3\text{As}]\text{PtCl}_2\text{-SnCl}_2$.¹ However, in line with the well-recognized lability of palladium carbonyls bonded to arylphosphines²⁹ no palladium hydrocarbonyl could be detected in this work.

Olefin structure plays a critical role in carbonylations catalyzed by $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$. Of particular note (Table III) is (a) the reduced rate of carbonylation with increase in polysubstitution about the double bond, in the order linear α olefin > branched α olefin > internal olefin, (b) the variation in regioselectivity with α olefin structure, from a low of 84.9% for the least hindered homologue, propylene, to near 100% for certain β -substituted isomers such as 2-methyl-1-pentene, and (c) the markedly different product distributions for terminal and nonterminal olefins.

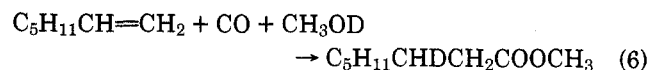
The selectivity trends outlined above will depend primarily upon how olefin structure influences initial Pd-H addition, subsequent skeletal rearrangement of the σ -alkyl- and, to a lesser extent, σ -acylpalladium transition states, and the relative rates of CO insertion.³⁴ The latter is most likely to be product controlling in view of the derived rate expression (eq 4). Regioselective carbonylation will be maximized where steric factors dictate an equilibrium dominance of least hindered palladium-alkyl (e.g., D vs. E) and comparatively faster rates of CO insertion for the least hindered isomer ($k_5 > k_6$). This condition is realized in the case of 2-methyl-1-pentene conversion to methyl 3-methylhexanoate (expt 28). Differences in the ease of carbonylation of *cis*- and *trans*-2-heptenes (expt 30 and 31) are consistent with the well-established³⁴ initial *cis* addition of olefin to the $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$ catalyst, but suggest, at least for internal monoene carbonylation, that initial π complexation is a slow step.³⁵

Competing double bond migration, which likely proceeds via $\pi \rightleftharpoons \sigma$ interconversions similar to those depicted in Scheme

I, competes successfully with olefin carbonylation only at low CO pressures (Table V). A relatively slow rate of alkylpalladium isomerization vs. CO insertion at higher CO pressures (>30 atm) is consistent with the relative yield data in Table I, the low selectivity to methyl octanoate realized with 2- and 3-heptenes, and the negligible changes in isomer distribution when carbonylating 1-heptene over the pressure range 34–240 atm. This latter result also implies no change in active catalyst composition at higher CO pressures, i.e., coordinated organophosphine is not displaced by additional CO.³⁴

The observed minimal variation in linear ester selectivity with change in alkanol structure (Table IV), be it primary, secondary, or substituted alcohol, water, or phenol, militates against their involvement in the regioselective steps of the carbonylation (Scheme I). Rates of ester formation are affected by coreactant structure, but such variations are pronounced only where the coreactant is a poor nucleophile (e.g., phenol) or competing reactions become important as in the case of thiols. There is little evidence for the intermediate formation of palladium alkoxy carbonyl species,⁶ similar to those recently synthesized in the presence of tertiary amine,³⁶ being of importance here.

Finally, regarding the source of hydrogen in Scheme I, the carbonylation of 1-heptene in the presence of methanol-*d*₁ yields linear ester of which >80% is methyl octanoate-3-*d*₁ (eq 6). These syntheses were run in carbon tetrachloride solutions of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$ (experimental conditions specified in Table II). Similar studies in methyl isobutyl ketone were less definitive, but for carbonylations in ³H₂-treated MIBK both the methyl octanoate product and unreacted heptene showed only a low level of tritium incorporation (see Table VI³⁷). Furthermore, there were insignificant concentrations of ³H in samples of recovered palladium catalyst. It would appear that solvent exchange is not important to the carbonylation sequence (Scheme I). Equation 6 is in agreement, however, with the work of Itatani and Bailar,³⁵ who found $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2\text{-SnCl}_2$ to be an adequate hydrogen transfer catalyst where methanol is the hydrogen donor.



Experimental Section

Materials. Carbon monoxide was CP grade. Reagents and solvents were commercial grade; olefins were generally of high purity, and were freed of peroxide prior to use by passage through a column of neutral alumina. The palladium complexes $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ³⁵ and $\text{PdCl}_2[\text{As}(\text{C}_6\text{H}_5)_3]_2$ ³⁵ were prepared by published methods. Similar techniques were used to prepare $\text{PdCl}_2[\text{P}(\text{p-CH}_3\text{C}_6\text{H}_4)_3]_2$, $\text{PdCl}_2[\text{P}(\text{o-CH}_3\text{OC}_6\text{H}_4)_3]_2$, $\text{PdCl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$, and $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$. Hydrated tin(II) chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, was used throughout as the 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–IV. Rates of carbonylation were measured using a 300-ml capacity, glass-lined autoclave equipped with Magnadrive stirrer and sampling valve.

Synthesis of Methyl Octanoate. Bis(triphenylphosphine)palladium(II) chloride (0.5–20 mmol) and tin(II) chloride dihydrate (2.5–20 mmol) were added to a N₂-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 partially 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 N₂, and heated to 80 °C under 240 atm of carbon monoxide. After rocking the reactor at temperature for 3–6 h, the apparatus was allowed to cool, and the clear reddish-brown, liquid product recovered. Typical analyses data are as follows: 1-heptene conversion 95%, yield of methyl C₈ acid ester 88 mol %, selectivity to linear methyl octanoate 88 mol %, material balance, 97%.

The methyl C₈ acid esters may be recovered from the crude product liquid by fractional distillation in vacuo. Anal. Calcd for C₇H₁₅COOCH₃: C, 68.3; H, 11.4. Found: C, 68.4; H, 11.6.

Kinetic Measurements. Degassed solvent (70 ml) and methanol (15 ml) containing a weighed quantity of palladium complex (0.5–1.0 mmol) and tin(II) chloride dihydrate (2.5–20 mmol) were introduced into the glass-lined autoclave, and flushed with N₂. The clear, red solution was heated to temperature under a small pressure of carbon monoxide (5–10 atm), a mixture of olefin (50–200 mmol) and solvent (5 ml) injected from a side ampule, and the pressure adjusted with CO. The rate of carbonylation was monitored by withdrawing liquid samples (0.5 ml) at regular time periods. The samples were rapidly cooled and analyzed by GLC for olefin and methyl ester content with the aid of standard calibration curves.

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Supplementary Material Available. Table VI describing 1-heptene carbonylation in tritiated methyl isobutyl ketone (1 page). Ordering information is given on any current masthead page.

Registry No.—[(C₆H₅)₃P]₂PdCl₂, 13965-03-2; [(*p*-CH₃C₆H₄)₃P]₂PdCl₂, 31173-63-4; [(*p*-CH₃OC₆H₄)₃P]₂PdCl₂, 56781-20-5; [(*p*-ClC₆H₄)₃P]₂PdCl₂, 57457-62-2; [(*o*-CH₃OC₆H₄)₃P]₂PdCl₂, 57512-77-3; [C₆H₅(CH₃)₂P]₂PdCl₂, 15616-85-0; [(C₆H₅O)₃P]₂PdCl₂, 29891-44-9; [(C₆H₅)₃As]₂PdCl₂, 14126-26-2; [(C₆H₅)₃P]₂PdI₂, 23523-32-2; SnCl₂, 7772-99-8; GeCl₂, 10060-11-4; SnI₂, 10294-70-9; PbCl₂, 7758-95-4; SnCl(Ph)₃, 639-58-7; propylene, 115-07-1; 1-pentene, 109-67-1; 1-heptene, 592-76-7; 1-undecene, 821-95-4; 1-eicosene, 3452-07-1; 4-methyl-1-pentene, 691-37-2; 3-methyl-1-pentene, 760-20-3; 2-methyl-1-pentene, 763-29-1; cyclooctene, 931-88-4; *trans*-2-heptene, 14686-13-6; *cis*-2-heptene, 6443-92-1; *cis*-3-heptene, 7642-10-6; *trans*-5-decene, 14686-14-7; methanol, 67-56-1; 1-hexanol,

111-27-3; 2-propanol, 67-63-0; 2-chloroethanol, 107-07-3; phenol, 108-95-2; ethanethiol, 75-08-1.

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Stereochemistry of Reduction of Ketones by Simple and Complex Metal Hydrides of the Main Group Elements

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The stereochemistry of reduction of selected ketones by a variety of simple and complex main group metal hydrides, both old and new, has been investigated under identical conditions of solvent, concentration, stoichiometry, temperature, and reaction time for comparison purposes. The stereochemical results of these studies are discussed in terms of steric approach control, torsional strain, compression effect, change in conformation of the ketone, and orbital distortion theory. The stereochemistry of reduction of complex aluminohydrides is shown to be dependent on the nature of the cation. Comparison of LiAlH₄ and LiBH₄ as reducing agents toward ketones shows LiBH₄ to be less sensitive to steric interactions. Reduction of 2-methylcyclohexanone with ClMgAlH₄ and Mg(AlH₄)₂ gave results best explained by assuming complexation of the carbonyl oxygen by magnesium followed by a change in the conformation of the ketone (methyl group equatorial to axial). Results obtained from reduction studies of substituted cyclopentanones and *cis*-2-methyl-4-*tert*-butylcyclohexanone do not suggest the presence of a compression effect in metal hydride reductions. A study of the reduction of ketones by LiAl(OR)₃H compounds shows the stereochemistry to be independent of concentration. The stereochemistry of reduction of ketones by LiAlH₄ and LiAlD₄ is similar.

In recent years the area of stereoselective reduction of ketones by AlH₃, LiAlH₄, and their alkoxy derivatives has been investigated by several workers.^{1,2}

Stereochemical results were first explained by Dauben, who suggested the concepts of "product development and steric approach control".³ While "steric approach control" appears