Regiochemical Control in Palladium(0) and Palladium(II) Catalysed Alkene–Formate Ester Carbonylation Reactions

Ivan J. B. Lin and Howard Alper*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ontario, Canada K1N 9B4

Palladium(0) complexes [Pd(PPh₃)₄ or Pd(dba)₂], (dba = dibenzylideneacetone) in the presence of 1,4-bis(diphenylphosphino)butane, can catalyse the reaction of alkenes and formate esters to give linear carboxylic esters as the major product, while the branched chain isomer was the principal ester obtained by use of a palladium(II) complex [bis(triphenylphosphine)palladium dichloride] as the catalyst.

One of the most thoroughly investigated homogeneous, metal catalysed reactions, is the conversion of alkenes to carboxylic esters,[1—5] Almost all of these processes are carried out using carbon monoxide and an alcohol. Although the chemistry of formate esters has attracted much interest,[6] little is known concerning alkene–formate reactions as a route to carboxylic esters. One example is the formation of methyl propionate in low yield by ruthenium-(II) or -(III) catalysed interaction of ethylene and methyl formate. However little, if any, reaction occurs f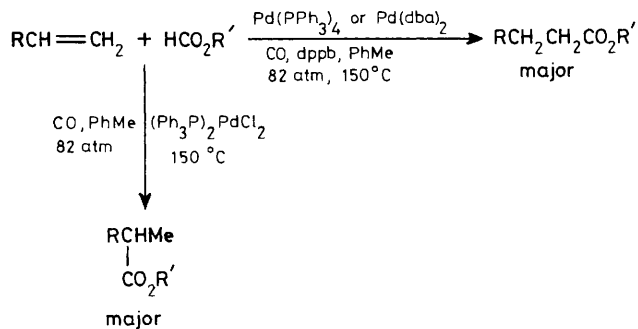or other formate esters and the process is not regioselective using propene as the reactant.[7] Very low yields of mostly linear esters result from RuH₂(PPh₃)₄ catalysed reaction of monosubstituted alkenes with methyl formate.[8]

A recent report describes the synthesis of branched chain carboxylic esters by the palladium catalysed reaction of an alkene with a formate ester, carbon monoxide, oxygen, copper(II) chloride, and hydrochloric acid in dioxane.[9] It was of interest to learn what role, if any, the oxidation state of the metal catalyst, as well as the presence of suitable added ligands, has on the regiochemistry of the alkene–formate ester

Table 1. Palladium catalysed alkene–formate ester carbonylation reactions.[a]

Alkene	HCO₂R' R' =	Catalyst[b]	Additive,[f] mmol	Yield of esters[c]/ %	Linear/ branched ratio
p-MeC₆H₄CH=CH₂	Buⁿ	A	—	37	~ ;7
		A	P(OPh)₃, 0.3	20	'
		A	PPh₃, 0.2	35	1.4
		A	PPh₃, 0.5	30	1.5
		A	dppm, 1.0	4	0.8
		A	dppe, 1.0	0	—
		A	dppb, 0.25	36	3.6
		A	dppb, 0.50	42	4.3
		A	dppb, 1.0	67	6.5
		B	—	40	0.04
		B	PBu₃, 1.0	35	0.06
		B	[(CH₃)₂N]₂CO, 1.0	39	0.05
	Prⁿ	A	dppb, 1.0	38	5.7
	Buˢ	A	dppb, 1.0	27	4.5
o-MeC₆H₄CH=CH₂	Buⁿ	A	dppb, 1.0	49	14.0
p-MeOC₆H₄CH=CH₂	Buⁿ	A	dppb, 0.5	51	4.7
		B	—	53	0.20
p-ClC₆H₄CH=CH₂	Buⁿ	A	dppb, 1.0	26	2.0
		B	—	30	0.24
p-BrC₆H₄CH=CH₂	Buⁿ	A	dppb, 1.0	7	4.6
2,4Me₂C₆H₃CH=CH₂	Buⁿ	A	dppb, 1.0	48	11.5
2-Vinylnaphthalene	Buⁿ	A	dppb, 1.0	32	5.0
		B	—	41	0.04
C₆H₁₃CH=CH₃	Buⁿ	A	dppb, 0.5	23	5.1
		A	dppb, 2.0	64	10.8
		B	C₈H₁₇I, 0.2	45	0.6
		C	dppb, 1.0	45	8.0
		D	—	10	7.1
		D	C₈H₁₇I, 0.2	20	4.2
	Prⁿ	C	dppb, 0.5	59	16.0
	Buˢ	C	dppb, 0.1	45	9.7
C₈H₁₇CH=CH₂	Buⁿ	C	dppb, 0.1	48	7.0
cis-Dec-2-ene	Buⁿ	C	dppb, 0.1	50	0.4[d]
trans-Dec-2-ene	Buⁿ	C	dppb, 0.1	42	0.4[e]

[a] *Reaction conditions*: alkene (2.2—2.5 mmol), HCO₂R' (15 mmol), catalyst (0.05 mmol), except Pd(dba)₂ (0.1 mmol), added ligand (if any); PhMe (1.0 ml); 150 °C; 82 atm. CO. A reaction time of 3 days was used, except entries 14 and 22 (2 days). [b] A = Pd(PPh₃)₄, B = (Ph₃P)₂PdCl₂, C = Pd(dba)₂, D = Rh(CO)Cl(PPh₃)₂. [c] Products were identified by comparison of spectral results [i.r., n.m.r. (¹H, ¹³C), m.s.] with literature data as well as, in most cases, by the addition of authentic materials to g.c. samples. [d] Isomer distribution of esters: 1-, 2-, 3-, 4- 29:63:7:1. [e] Isomer distribution of esters: 1-, 2-, 3-, 4- 29:57:11:3. [f] dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, dppb = bis(diphenylphosphino)butane.

$$RCH = CH_2 + HCO_2R' \xrightarrow[\substack{CO, \; dppb, \; PhMe \\ 82 \; atm, \; 150°C}]{Pd(PPh_3)_4 \; or \; Pd(dba)_2} RCH_2CH_2CO_2R'$$

major

CO, PhMe   (Ph₃P)₂PdCl₂
82 atm   150 °C

$$\begin{array}{c} RCHMe \\ | \\ CO_2R' \end{array}$$

major

reaction under non-acidic conditions. We now report that one can tune the reaction, with good regiochemical control for the linear or branched chain ester, by judicious choice of metal catalyst and added ligand.

When p-methylstyrene was treated with n-butyl formate and a catalytic amount of tetrakis(triphenylphosphine)palladium(0) [40:1 ratio of alkene:Pd⁰] in toluene for 2—3 days at 150 °C and 82 atmospheres of carbon monoxide, the linear and branched chain esters were obtained in a ratio of 0.37 (37% yield). While repetition of the reaction in the presence of a monodentate ligand such as triphenylphosphine or triphenyl phosphite (Table 1) results in the formation of the straight-chain ester as the main product, the regioselectivity is not high and the yield of esters did not increase appreciably. Added bidentate ligands such as bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane act as inhibitors, but the presence of 1,4-bis(diphenylphosphino)butane (dppb) markedly affects the regioselectivity of the reaction with the esters formed in both good yield [67% using 2:1 ratio of dppb:Pd(PPh₃)₄] and regioselectivity for the linear isomer (linear/branched = 6.5). The Pd(PPh₃)₄–dppb system is applicable to other formate esters as well as to other alkenes (e.g. oct-1-ene, see Table 1), affording linear esters as the principal product. Similar selectivity for the straight-chain ester was realized by the substitution of bis(dibenzylideneacetone)palladium [Pd(dba)₂] for Pd(PPh₃)₄. An exception occurs for the isomeric internal alkenes, cis- and trans-dec-2-ene, both of which give mainly the ester of 2-methyl-decanoic acid. The rhodium(I) complex, (PPh₃)₂Rh(CO)Cl, is catalytically active but product yields are low.

Change of the oxidation state of the metal complex by use of bis(triphenylphosphine)palladium dichloride as the catalyst (an added ligand has no beneficial effect) results in the generation of the branched-chain ester in high regioselectivity (Table 1), superior in some instances (e.g. p-methylstyrene) to the palladium chloride catalysed reaction effected in the

presence of hydrochloric acid.⁹ In this, as in the above reaction, carbon monoxide is required, with slower reaction occurring at lower pressures. No reaction takes place using a nitrogen atmosphere. It is conceivable that Pd(dba)₂ reacts with carbon monoxide and dppb to give (dba)Pd(CO)(dppb) (1) in which one of the two phosphorus atoms is co-ordinated to the metal. Oxidative addition of palladium to the carbon–hydrogen bond of the formate ester¹⁰ may then occur to give a metal hydride, followed by reaction with the alkene. The role of carbon monoxide may be to stabilize the hydridometallocarboxylate intermediate, by preventing decarbonylation to the corresponding alkoxypalladium hydride. The reason no reaction occurs under nitrogen is that (1) cannot be generated in the absence of carbon monoxide. Note that these processes depend on the pressure of carbon monoxide, with no reaction below 50 atm, and very slow reaction (6—8 days) at 50—60 atm., presumably because (1) is not easily generated at lower pressures.

In conclusion, use of a complex with the metal in the appropriate oxidation state, and an added ligand (if required), enables one to prepare linear or branched-chain esters in a regioselective manner, and usually in reasonable yields by a simple, new alkene–formate ester process effected under neutral conditions.

References

1 R. A. Sheldon, 'Chemicals from Synthesis Gas,' Reidel, Dordrecht, Holland, 1983, Ch. 5, and references cited therein.
2 I. Tkatchenko, in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, Pergamon Press, Elmsford, New York, 1982, Vol. 8, and references cited therein.
3 B. Despeyroux and H. Alper, *Ann. N.Y. Acad. Sci.*, 1984, **415**, 148.
4 S. B. Fergusson and H. Alper, *J. Chem. Soc., Chem. Commun.*, 1984, 1349.
5. H. Wada, Y. Kasori, and Y. Misu, Jpn. Pat. 62,161. 737 (17 Jul, 1987); *Chem. Abstr.*, 1988, **108**, 131037p.
6 T. Ikaraski, *Chem. Econ. Eng. Rev.*, 1980, **12**, 31.
7 P. Isnard, B. Denise, R. P. A. Sneeden, J. M. Cognion, and P. Durual, *J. Organomet. Chem.*, 1983, **266**, 135.
8 W. Ueda, T. Yokoyama, Y. Morikawn, Y. Moro-Okay and T. Ikawa, *J. Mol. Catal.*, 1988, **44**, 197.
9 M. Mlekuz, F. Joo, and H. Alper, *Organometallics*, 1987, **6**, 1591.
10 H. A. Zahalka, H. Alper, and Y. Sasson, *Organometallics*, 1986, **5**, 2497.