179. Stereochemistry of the Platinum Catalyzed Hydroformylation of Olefins

by **Paul Haelg, Giambattista Consiglio** and **Piero Pino**

Technisch-Chemisches Laboratorium der Eidgenössischen Technischen Hochschule, Universitätstrasse 6, CH-8092 Zürich

(15.VI.81)

Summary

The deuterioformylation of (*Z*)- or (*E*)-2-butene catalyzed by [DIOP]Pt($SnCl_3$)Cl[1]) gives predominantly *erythro*- or *threo*-1,3-[^{2}H]$_2$-2-methylbutanal respectively. Hence, hydroformylation by this catalytic system must take place with *cis*-stereochemistry.

Introduction. – The hydroformylation of olefins where L_2PtCl_2–$SnCl_2$ (L = phosphine ligand) is used as the catalyst precursor [1] [2] offers an interesting alternative to the better known rhodium or cobalt catalyzed reaction [3]. In connection with the research on the mechanism of asymmetric hydroformylation with the above platinum containing catalysts [4–6], it is important to know the stereochemistry of the addition of the CHO-group and of hydrogen to the olefinic bond. On the basis of previous experience of hydrocarbonylation reactions with rhodium [7], cobalt [8] and palladium [9] catalysts, a *cis*-addition would be expected. However, with platinum-tin catalytic systems, this extrapolation is particularly uncertain, since the homogeneous hydrogenation using similar catalytic systems is sometimes non-stereospecific [10].

The first attempts to determine the stereochemistry of the platinum-catalyzed hydroformylation were carried out using (*Z*)- and (*E*)-3-methyl-2-pentene as the substrate and $(Ph_3P)_2PtCl_2$ and $SnCl_2 \cdot 2\,H_2O$ or [DIOP]Pt($SnCl_3$)Cl[1]) [11] as the catalyst precursor. Unfortunately 4-methylhexanal and 3-ethylpentanal are the main products (~90% of the aldehydic products) and they do not give any information about the stereochemistry of the reaction *(Table 1)*.

Table 1. *Hydroformylation of (Z)- and (E)-3-methyl-2-pentene.* Composition (%) of reaction mixtures.

Reaction mixture	Starting olefin	
	(*E*)-3-Methyl-2-pentene	(*Z*)-3-Methyl-2-pentene
4-Methylhexanal	33	32
3-Ethylpentanal	58	57
2,3-Dimethylpentanal *erythro*	9 (21)	11 (32)
2,3-Dimethylpentanal *threo*	(79)	(68)

[1]) DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis (diphenylphosphino)butane.

0018-019X/81/6/1865-05$01.00/0

Table 2. *Hydro- (HF) and deuterioformylation (DF) of (Z)- and (E)-2-butene by platinum and rhodium catalysts*

Substrate	Catalyst precursor	Reaction Type	Reaction conditions			Conversion %[a]	Isomeric composition of the recovered olefin (%)[b]			Isomeric composition of the aldehydic products (%)[b]	
			t (°C)	p_{H_2} (atm)	p_{CO} (atm)		1-Butene	(Z)-2-Butene	(E)-2-Butene	Pentanal	2-Methyl-butanal
(Z)-2-Butene	[DIOP]Pt($SnCl_3$)Cl	HF	60	40	40	32	0	75	25	24	76
(E)-2-Butene						36	0	12	88	23	77
(Z)-2-Butene	[DIOP]Pt($SnCl_3$)Cl	DF	80	35	90	5	0	97	3	30	70
(E)-2-Butene						5	0	2	98	20	80
(Z)-2-Butene	$RhH(CO)(PPh_3)_3$	DF	80	50	150	70	n.d.	n.d.	n.d.	0	100
(E)-2-Butene						70	n.d.	n.d.	n.d.	0	100

[a]) Based on gas absorption. [b]) See experimental section. n.d. = not determined.

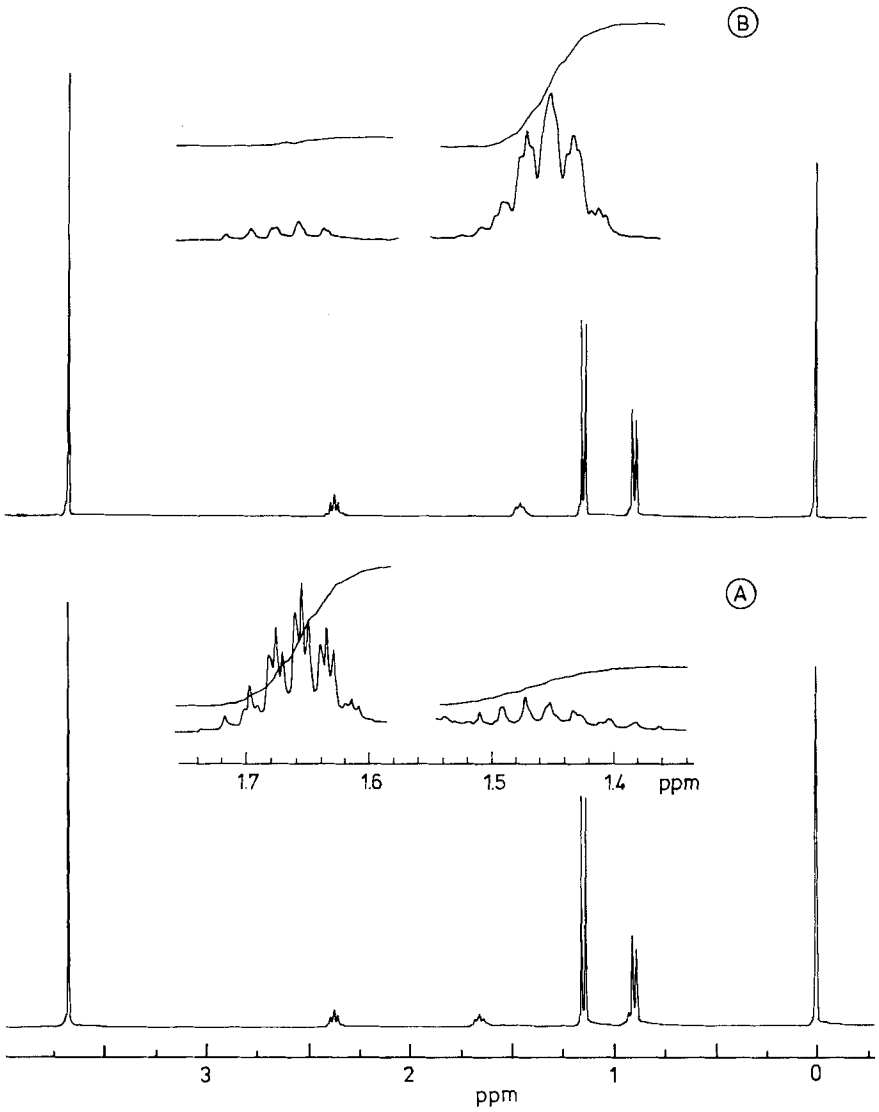


Figure. *^{1}H-NMR. spectrum (360 MHz) of methyl 2-methyl-3-[^{2}H]-butanoate arising from deuterioformylation of (Z)-2-butene* (Spectrum A) *and of (E)-2-butene* (Spectrum B)

During the investigation of the asymmetric hydroformylation of (*Z*)- and (*E*)-2-butene with [(−)-DIOP]Pt($SnCl_3$)Cl it was shown that 2-methylbutanal is indeed the main product (> 70%) if the reaction is carried out at low temperature and if conversion is kept low [12]. If under the same conditions a deuterioformylation is carried out, the relative amounts of *erythro*- and *threo*-1,3-[^{2}H]$_2$-2-methylbutanal formed are expected to give the desired information about the stereochemistry of the reaction.

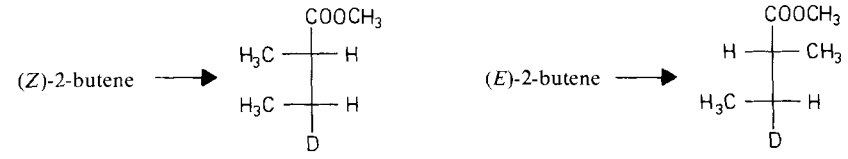
Results and discussion. – The results obtained in the hydroformylation of (*Z*)- and (*E*)-2-butene are reported in *Table 2.* The characterization of the reaction products (2-methylbutanal and pentanal) was carried out by ^{1}H-NMR. on the methyl esters of the corresponding acids, obtained from the hydroformylation products as previously described [13]. By using a high magnetic field (360 MHz) the two diastereotopic methylene protons of methyl 2-methylbutanoate give well separated signals centered at 1.47 and 1.67 ppm.

Deuterioformylation of the same substrates was carried out in the presence of the same catalyst precursor ([DIOP]Pt($SnCl_3$)Cl) at 80° under 125 atm of a mixture of $^2H_2$ and CO (in a 1 to 2.5 molar ratio) *(Table 2).* Conversion, monitored by gas absorption, was kept at about 5%. The methyl esters obtained from the aldehydic mixture were separated by preparative GC. as previously described [13]. MS. analysis of the methyl 2-methylbutanoate showed essentially monodeuteriation. The ^{2}H-atom is bound to the C-atom in the β-position with respect to the carboxyl group (^{1}H-NMR., *Figure*). From the ratio between the intensity of the signals at 1.47 ppm and 1.67 ppm the ratio between the epimers of methyl 3-[^{2}H]-2-methylbutanoate was calculated to be 83:17 for the product derived from (*Z*)-2-butene and 8:92 for that derived from (*E*)-2-butene. These values show that the platinum catalyzed deuterioformylation of (*Z*)- and (*E*)-2-butene under the conditions used is highly stereoselective. The apparent non-complete stereoselectivity of the reaction can in fact be derived from partial isomerization of the substrate to its diastereoisomer and, as evidenced by the formation of pentanal, to 1-butene.

The *cis* character of the stereoselective addition of H and CHO to the olefinic bond was proved by comparison of the above results with those obtained in the deuterioformylation of the same substrates in the presence of RhH(CO)(PPh_3)$_3$ as the catalyst precursor, which occurs with *cis*-stereochemistry *(Scheme)* [7] [8]. Only 2-methylbutanal is obtained with this catalytic system *(Table 2).* The ^{1}H-NMR. spectrum of the methyl ester derived from the product arising from (*Z*)-2-butene shows only one multiplet in the region of the methylene protons at 1.67 ppm. For the product derived from (*E*)-2-butene only the signal at 1.47 ppm is observed. Based on the established *cis*-stereochemistry of the reaction, the latter signal must be representative of *threo* methyl 2-methyl-3-[^{2}H]-butanoate and the former of *erythro* methyl 2-methyl-3-[^{2}H]-butanoate.

Considering the spectra reported in the *Figure* together with the above results it clearly appears that the platinum catalyzed hydroformylation of (*Z*)- and (*E*)-2-butene, similar to the cobalt- and rhodium-catalyzed reactions, takes place with prevailing *cis*-stereochemistry.

Scheme. *Products arising from deuterioformylation of* (Z)- *and* (E)-*2-butene after oxidation and esterification* (only one epimer is shown)



Experimental Part

Deuterioformylation of (E)-2-butene with platinum. The deuterioformylation was carried out in a 250 ml stainless steel autoclave with 36 g of (*E*)-2-butene and 80 mg of Pt[DIOP]($SnCl_3$)Cl in 25 ml of ethylbenzene at 80° under 35 atm of $^2H_2$ and 90 atm of CO. The reaction was stopped when gas absorption indicated a conversion of ~5% (pressure decrease 8 atm, 4.5 h). The composition of the residual olefin and of the product was determined by GC. using a dimethylsulfolan column at RT. and a *Carbowax* column at 100°. The reaction mixture was then oxidized [14] with 7.5 g Ag_2O and 1.5 g NaOH in 100 ml of water by stirring overnight at RT. After filtration and washing with ether the water layer was acidified and the acids were continuously extracted with ether for 12 h. Esterification with etheral diazomethane and evaporation of the solvent gave a crude mixture of methyl 2-methylbutanoate and pentanoate. Methyl 2-methylbutanoate was isolated by preparative GC. using a 4.5 m polypropylene-glucol column at 130°. The 360 MHz-NMR. spectrum was measured in $CDCl_3$ and a ratio of 92:8 was obtained for the intensity of the multiplets at 1.67 ppm and 1.47 ppm. The deuterium content of methyl 2-methylbutanoate was determined by MS. analysis of the corresponding anilide, which was prepared according to [15]: 9% D_0, 87% D_1, 3% D_2, 1% D_3.

Deuterioformylation of (Z)-2-butene with platinum. The procedure was the same as described for (*E*)-2-butene. The ratio of the methylene proton signals was 17:83 and the deuterium content was as follows: 13% D_0, 82% D_1, 3% D_2, 2% D_3.

Deuterioformylation of (E)- and (Z)-2-butene with rhodium. The deuterioformylations were carried out as described above using 10 g olefin, 50 mg Rh(H)(CO) $(PPh_3)_3$ and 100 mg PPh_3 in 20 ml benzene. The conditions are specified in *Table 2.*

Hydroformylation of (E)- and (Z)-3-methyl-2-pentene. The hydroformylations were carried out as described above treating 5 g of olefin, 80 mg of $Pt(PPh_3)_2Cl_2$ and 120 mg of $SnCl_2 \cdot 2\,H_2O$ in 25 ml benzene with 80 atm of CO and H_2 at 100° for 18 h. The reaction mixture was analyzed and oxidized as described [7]. The diastereoisomeric composition of methyl 2,3-dimethylpentanoate was determined by GC. using an *Apiezon L* coated capillary column at 80°.

REFERENCES

[1] *C. Y. Hsu & M. Orchin,* J. Am. Chem. Soc. *97,* 3553 (1975).
[2] *I. Schwager & J. F. Knifton,* J. Catal. *45,* 256 (1976).
[3] *P. Pino, F. Piacenti & M. Bianchi* in 'Organic Synthesis via Metal Carbonyls' Vol. II, I. Wender and P. Pino Eds., Wiley, New York 1977.
[4] *C. Y. Hsu,* Ph.D. Dissertation, University of Cincinnati 1974; Chem. Abstr. *82,* 154899 (1975).
[5] *G. Consiglio & P. Pino,* Helv. Chim. Acta *59,* 642 (1976).
[6] *Y. Kawabata, T. Hayashi & I. Ogata,* Chem. Lett. *1978,* 361.
[7] *A. Stefani, G. Consiglio, C. Botteghi & P. Pino,* J. Am. Chem. Soc. *95,* 6504 (1973).
[8] *A. Stefani, G. Consiglio, C. Botteghi & P. Pino,* J. Am. Chem. Soc. *99,* 1058 (1977).
[9] *G. Consiglio & P. Pino,* Gazz. Chim. Ital. *105,* 1133 (1975).
[10] *F. Van Rantwijk, A. P. G. Kiebson & H. Van Bekkum,* J. Mol. Catal. *1,* 27 (1975/76).
[11] *P. S. Pregosin & S. N. Sze,* Helv. Chim. Acta, *61,* 1848 (1978).
[12] *P. Haelg, G. Consiglio & P. Pino,* to be published.
[13] *G. Consiglio, D. A. von Bézard, F. Morandini & P. Pino,* Helv. Chim. Acta *61,* 1703 (1978).
[14] *P. Pino, S. Pucci, F. Piacenti & G. Dell'Amico,* J. Chem. Soc. (C) *1971,* 1640.
[15] *H. Ll. Bassett & C. R. Thomas,* J. Chem. Soc. *1954,* 1188.