JOM 23150

Hydroformylation of norbornene and 2,5-norbornadiene catalysed by platinum(0)-alkene complexes in the presence of methanesulfonic acid: determination of the stereochemistry of the reaction

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(Received April 6, 1992)

Abstract

The hydroformylation of norbornene catalysed by $[Pt(C_2H_4)(dppb)]/CH_3SO_3H$ (dppb = 1,4-bis(diphenylphosphino)butane) occurs under standard *oxo* conditions giving the *exo*-norbornanecarboxaldehyde exclusively. The deuteroformylation of this olefin shows that the addition of H and CHO groups is *cis*. As for the chemoselectivity of the monohydroformylation of 2,5-norbornadiene, the catalytic system affords better results than the more common catalytic precursors of rhodium and platinum/tin complexes; the regioselectivity towards the *exo*-aldehyde is lower.

1. Introduction

Complexes of the type $[L_2Pt(olefin)]$ (L = phosphine) in the presence of an organic acid such as methanesulphonic acid are precursors for olefin hydroformylation catalysts with interesting chemo- and regio-selectivity [1,2].

A study of the mechanism of this catalytic process necessarily requires knowledge of the stereochemistry CHO and hydrogen addition to the olefinic double bond.

In hydroformylation reactions with cobalt [3], rhodium carbonyls [4] and with platinum/tin catalytic precursors [5], the addition of the two groups took place rigorously *cis*, independent of the transition metal used. This implies the intermediacy of a catalytically active species where both a hydride and a carbon monoxide are bound, and also a suprafacial attack of the two groups on the olefinic linkage [6].

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However, implication of a *cis*-stereochemistry for our catalytic system may be unreliable, since the acid co-catalyst can act as hydrogen source, and hence a *trans* electrophilic attack of the proton to the coordinated olefin cannot be excluded.

To determine the stereochemistry of this hydroformylation, we chose norbornene as substrate, because it has the following advantages:

(i) It shows a fairly good reactivity with our catalytic system, probably due to the release of the ring strain that occurs during aldehyde formation [7];

(ii) It does not isomerize under *oxo* conditions.

However, the hydroformylation of norbornene generates simultaneously three chiral centres, and hence two diastereomeric norbornanecarboxaldehydes, *exo* and *endo* isomers respectively, are expected (Scheme 1).

Norbornene has been previously hydroformylated with various catalysts [8,9]; in all cases the formation of the *exo* aldehyde was claimed. However, to our knowledge, only in the hydroformylation of this olefin with $[RhH(CO)(PPh_3)_3]$ has a reliable determination of the configuration of the *oxo*-aldehydes been carried out;

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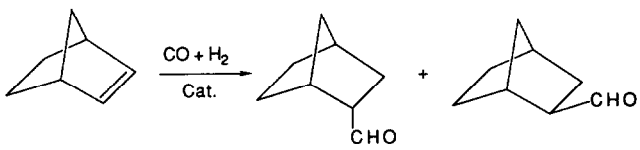


Scheme 1

GLC analysis of a mixture of *exo*- and *endo*-2-chloromethylbicyclo[2.2.1]heptane derived from the hydroformylation product and of the same halides obtained from a commercially available mixture of 2-hydroxymethylbicyclo[2.2.1]hept-5-ene (85% *endo* and 15% *exo*) showed that the norbornanecarboxaldehyde was about 97% *exo* [10]. Consequently, it appeared interesting to evaluate our catalytic system using norbornene and 2,5-norbornadiene as substrates, to ascertain both the stereochemistry of the reaction and the configuration of the monoaldehyde obtained.

2. Results and discussion

2.1. Norbornene

A set of hydroformylation reaction experiments was carried out, to determine the configuration of the chiral centre directly bound to the aldehyde function. Table 1 summarizes the results obtained. Our catalytic system shows an activity and a chemo-selectivity close to those of the catalytic precursors of rhodium and platinum/tin complexes [9]. Only the *exo*-aldehyde was obtained with $[Pt(C_2H_4)(dppb)]/CH_3SO_3H$ (1:1) (I) as the catalytic precursor, at 100°C and 100 atm ($CO/H_2 = 1$), similar to the results found with rhodium and platinum catalysts under analogous reaction conditions.

The *exo* configuration of the norbornane carboxaldehyde was inferred by a careful ^1H NMR analysis, which allows us to determine unequivocally the chemical shifts of all the hydrogen atoms of the molecule. A

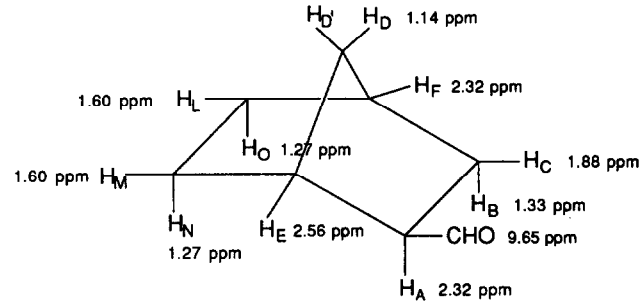


Fig. 1. Chemical shifts of the norbornanecarboxaldehyde protons.

set of measurements of proton intramolecular NOE effects was carried out. The saturation of the CHO proton produced remarkable enhancement of the resonances centred at 2.32 ppm and 1.88 ppm. As the former resonance is due to the proton coupled to the CHO (H_A), the latter can be simply assigned to the vicinal proton nearer to the CHO, H_C. By irradiating the proton H_C at 1.88 ppm, relevant NOEs were observed at 9.61 ppm (CHO absorption) and at 1.33 ppm; this last signal can be assigned to the proton H_B, geminal to H_C; the minor NOEs at 2.32 ppm and 1.14 ppm are attributed to H_F and H_D, respectively.

The saturation of the H_D protons at 1.14 ppm gave a significant NOE of the CHO group and H_C absorption. Thus both the formyl group and H_C are *exo*. On irradiation of H_D enhancements of the resonances at 2.32 ppm (H_F), 2.56 ppm (H_E) and 1.60 ppm, due to the *exo* protons H_L and H_M, were observed. This also indicates that the chemical shifts of the protons H_D and $H_{D'}$ are nearly coincident (1.14 ppm). As a consequence, the other signals at 1.27 ppm must be attributed to the *endo* protons H_N and H_O.

It is well documented that reactions of this type afford products with an *exo* configuration almost exclusively. This was first attributed to a favourable configuration of the transition state [11] or to a higher steric hindrance encountered upon *endo* attack [12]. We favour an interpretation based on more recent

TABLE 1. Hydroformylation of norbornene catalyzed by rhodium and platinum complexes [a]

Exp.	Catalytic precursor	Conv. (%)	T (°C)	P (atm)	t (h)	Aldehyde yield (%)	By-product yield (%)
1	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	35.7	50	100	46	34.6	1.1
2	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	99.3	100	100	5	97.8	1.5
3	$[RhH(CO)(PPh_3)]_3$	99.6	100	100	1	99.6	–
4	$[Pt(dppb)Cl_2]/SnCl_2$	99.1	100	100	1	98.2	0.9
5	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	93.1	100	50	5	93.1	–

[a] Norbornene: 16 mmol; norbornene/$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$ = 320 : 1 : 1; norbornene/$[Pt(dppb)Cl_2]/SnCl_2$ = 320 : 1 : 5, norbornene/$[RhH(CO)(PPh_3)_3]$ = 1000/1; solvent (toluene) = 20 ml; $P(CO)$ to $P(H_2)$ ratio = 1:1.

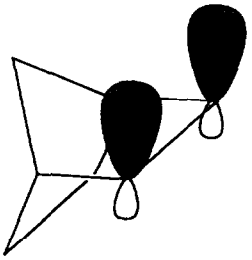


Fig. 2. π-HOMO of norbornene.

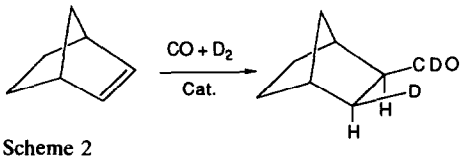
studies by Inaki, Fujimoto and Fukui. They inferred different conformations of the p orbitals of the two faces of the double bond of norbornene, the occupied molecular orbital at higher energy (p-HOMO) having the lobes more developed in the *exo* direction than in the *endo* direction [13].

Therefore the predominant formation of the *exo* aldehyde in the hydroformylation of norbornene can be ascribed to an electrophilic attack of the platinum at the more electron-rich face of the molecule.

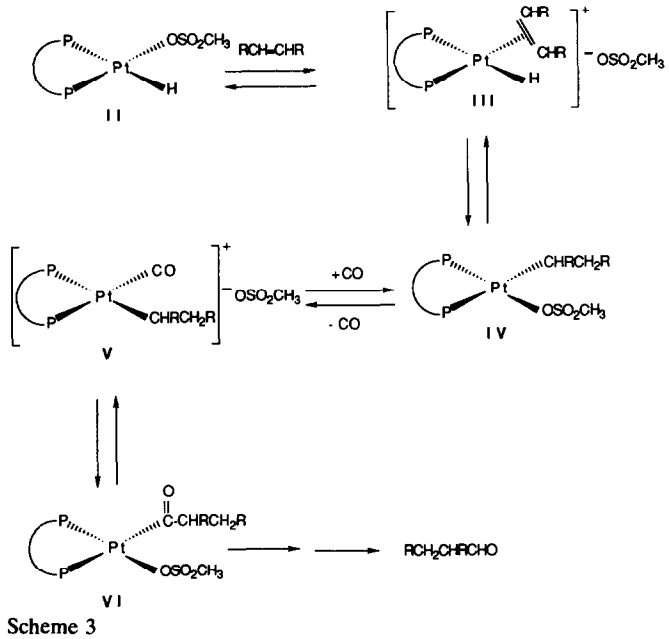
A deuteroformylation of norbornene was accomplished using **I** as the catalytic system, at 100°C and 50 atm ($CO/D_2 = 1$). The expected aldehyde was obtained in 81% yield with practically quantitative chemoselectivity. This compound contained only two deuterium atoms and its ^1H NMR spectrum confirmed the absence of scrambling between the hydrogen atoms of the molecule and D_2.

Comparison of the ^1H NMR spectra of the non-deuterated and di-deuterated aldehydes confirms the assignment of the resonances to the *cis* and *exo* groups CHO (9.65 ppm) and H_C (1.88 ppm) (Scheme 2).

The *cis* stereochemistry for the addition of CHO and H to the double bond of norbornene is unequivocally established. Both hydrogen and carbon monoxide attack on the coordinated olefinic bond occur through



Scheme 2



Scheme 3

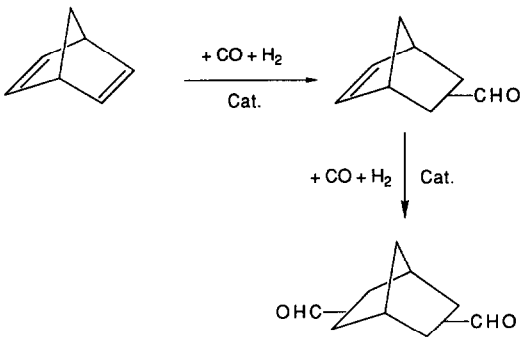
a suprafacial transfer from a catalytically active intermediate. The formation of the σ-acyl platinum complex, precursor of the *oxo* aldehyde, can be tentatively depicted in the step shown in Scheme 3.

The hydrido-complex **II** has been recently postulated as the intermediate species in the formation of **IV** from a [Pt(alkene)(diphosphine)] complex [14].

TABLE 2. Hydroformylation of 2,5-norbornadiene catalyzed by rhodium and platinum complexes [a]

Exp.	Catalytic precursor	Conv. (%)	T (°C)	t (h)	Mono-aldehyde yield (%)	*Exo* mono-aldehyde select. (%)	Di-aldehyde yield (%)	By-product yield (%)
1	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	81.7	100	4	67.8	89.4	10.6	3.3
2	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	100	100	19	13.3	26.3	85.8	0.9
3	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	21.5	70	8	19.5	96.4	2.0	–
4	$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$	61.0	70	22	50.1	86.0	9.6	1.3
5	$[Pt(dppb)Cl_2]/SnCl_2$	99.3	100	0.5	4.4	95.4	79.1	15.8
6	$[RhH(CO)(PPh_3)_3]$	99.6	100	0.5	4.3	95.3	95.3	–
7	$[RhH(CO)(PPh_3)_3]$	25.1	50	6	21.5	99.1	3.6	–
8	$[Pt(dppb)Cl_2]/SnCl_2$	44.9	50	4	39.2	100	5.7	–
9	$[Pt(dppb)Cl_2]/SnCl_2$	23.9	50	7	22.4	100	1.5	–
10	$[Pt(dppb)Cl_2]/SnCl_2$	100	50	22	8.4	96.4	73.8	17.8

[a] 2,5-Norbornadiene: 16 mmol; 2,5-norbornadiene/$[Pt(C_2H_4)(dppb)]/CH_3SO_3H$ = 320 : 1 : 1; 2,5-norbornadiene/$[Pt(dppb)Cl_2]/SnCl_2$ = 320 : 1 : 5; 2,5-norbornadiene/$[RhH(CO)(PPh_3)_3]$ = 1000 : 1; solvent (toluene) = 20 ml; P(CO) to $P(H_2)$ ratio = 1 : 1 (total pressure 100 atm).



Scheme 4

2.2. 2,5-Norbornadiene

Several hydroformylation reactions of 2,5-norbornadiene are reported in the literature [15]; different mixtures of diastereomeric dialdehydes were generally formed. However, the selective production of the monoaldehyde (bicyclo[2.2.1]hept-2-carboxaldehyde-5-ene) appeared important owing to its applications as a synthon [16] (Scheme 4).

We have subjected the diene to hydroformylation catalysed by classical rhodium and platinum/tin complexes, and by **I**. The results are given in Table 2.

Rhodium and platinum/tin catalyst precursors promote monoaldehyde formation only at low conversion while, in the presence of our catalytic system **I**, a fairly good monoaldehyde yield was obtained even at 81.7% substrate conversion.

As for the configuration of the monoaldehyde produced, rhodium and platinum/tin catalysts show a very high stereoselectivity towards the formation of the *exo*-isomer (> 95%). The process catalysed by our system is stereoselectively comparable only if it is carried out both at lower temperature and at lower conversion. An increase in temperature, reaction time and hence of the substrate conversion causes a dramatic drop in stereoselectivity (only 26% *exo*-isomer). This can be explained assuming that the *exo*-monoaldehyde is hydroformylated faster than the *endo*-isomer, giving the dialdehyde products. The fact that the stereoselectivity to the *exo*-aldehyde generally decreases with increased conversion could also be due to the formation at low concentration of intermediate species where both double bonds are coordinated.

The monoaldehyde configuration was determined by GLC analysis of a mixture of 89.4% *exo* and 10.6% *endo* monoaldehyde produced in the *oxo* reaction and of a sample of almost exclusively *endo*-monoaldehyde obtained by the Diels–Alder reaction from an equimolecular mixture of cyclopentadiene and acrolein [17].

3. Experimental details

GLC analyses were carried out on a Hewlett Packard HP 5890 gas chromatograph using 2 m × 0.5 mm CW 20 M column. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer, in $CDCl_3$ as solvent, at 25°C. The NOE experiments were performed on carefully degassed samples (10% w/v) in the difference mode. The decoupler was adjusted at the required frequency to saturate the proton in question. The decoupler power used was the minimum required to saturate the spin of interest. A delay varying from 10 to 30 s was used to allow the system to reach equilibrium. Each NOE experiment was repeated at least four times. Norbornene and 2,5-norbornadiene were used as received from Fluka AG. Methanesulphonic acid (Janssen Chimica) and $SnCl_2 \cdot 2H_2O$ (C. Erba Analyticals) were used as received. Dppb (Strem Chemicals) and PPh_3 (Aldrich) were used as received. $[Pt(C_2H_4)(dppb)]$ [18], $[PtCl_2(dppb)]$ [18] and $[RhH(CO)(PPh_3)_3]$ [19] were synthesized according to literature procedures. Toluene was purified by a standard method [20]. Reaction products were identified by comparing their GLC retention times, and NMR and IR spectra with those of authentic samples.

3.1. Hydroformylation of norbornene in the presence of $[Pt(C_2H_4)(dppb)] / CH_3SO_3H$

Norbornene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene, 0.05 mmol of $[Pt(C_2H_4)(dppb)]$ and an equivalent amount of CH_3SO_3H. The reactor was pressurized to 100 atm with synthesis gas ($CO/H_2 = 1:1$) and heated to 100°C (±0.1°C). After 5 h the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (99.3%), the aldehyde yield (97.8%) and the *exo/endo* isomer ratio (~ 100% *exo*).

3.2. Hydroformylation of norbornene in the presence of $[Pt(dppb)Cl_2] / SnCl_2$

Norbornene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene, 0.05 mmol of $[PtCl_2(dppb)]$ and a five-fold amount of $SnCl_2 \cdot 2H_2O$. The reactor was pressurized to 100 atm with synthesis gas ($CO/H_2 = 1:1$) and heated to 100°C (±0.1°C). After 1 h the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (99.1%), the aldehyde yield (98.2%) and the *exo/endo* isomer ratio (~ 100% *exo*).

3.3. Hydroformylation of norbornene in the presence of [RhH(CO)(PPh$_3$)$_3$]

Norbornene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene and 0.016 mmol of [RhH(CO)(PPh$_3$)$_3$]. The reactor was pressurized to 100 atm with synthesis gas (CO/H$_2$ = 1:1) and heated to 100°C (±0.1°C). After 1 h the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (99.6%), the aldehyde yield (99.6%) and the *exo/endo* isomer ratio (~ 100% *exo*).

3.4. Deuteroformylation of norbornene in the presence of [Pt(C$_2$H$_4$)(dppb)] / CH$_3$SO$_3$H

Norbornene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene, 0.05 mmol of [Pt(C$_2$H$_4$)(dppb)] and an equivalent amount of CH$_3$SO$_3$H. The reactor was pressurized to 50 atm with CO and D$_2$ (CO/D$_2$ = 1:1) and heated to 100°C (±0.1°C). After 5 h the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (81.1%), the aldehyde yield (81.1%) and the *exo/endo* isomer ratio (~ 100% *exo*).

3.5. Hydroformylation of 2,5-norbornadiene in the presence of [Pt(C$_2$H$_4$)(dppb)] / CH$_3$SO$_3$H

2,5-Norbornadiene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene, 0.05 mmol of [Pt(C$_2$H$_4$)(dppb)] and an equivalent amount of CH$_3$SO$_3$H. The reactor was pressurized to 100 atm with synthesis gas (CO/H$_2$ = 1:1) and heated to 100°C (±0.1°C). After 4 h the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (81.7%), the monoaldehyde yield (67.8%), the *exo* monoaldehyde isomer selectivity (89.4%) and the dialdehydes yield (10.6%).

3.6. Hydroformylation of 2,5-norbornadiene in the presence of [Pt(dppb)Cl$_2$]SnCl$_2$

2,5-Norbornadiene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene, 0.05 mmol of [PtCl$_2$(dppb)] and a five-fold molar quantity of SnCl$_2$ · 2H$_2$O. The reactor was pressurized to 100 atm with synthesis gas (CO/H$_2$ = 1:1) and heated to 100°C (±0.1°C). After 30 min the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (99.3%), the monoaldehyde yield (4.4%), the *exo* monoaldehyde isomer selectivity (95.4%) and the dialdehyde yield (79.1%).

3.7. Hydroformylation of 2,5-norbornadiene in the presence of [RhH(CO)(PPh$_3$)$_3$]

2,5-Norbornadiene (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene and 0.016 mmol of [RhH(CO)(PPh$_3$)$_3$]. The reactor was pressurized to 100 atm with synthesis gas (CO/H$_2$ = 1:1) and heated to 100°C (±0.1°C). After 30 min the reactor was cooled to room temperature, the residual gases removed and the reaction mixture analysed by GLC to determine the conversion (99.6%), the monoaldehyde yield (4.3%), the *exo* monoaldehyde isomer selectivity (95.3%) and the dialdehyde yield (95.3%).

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