Journal of Organometallic Chemistry, 213 (1981) 503—512
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE HYDROFORMYLATION REACTION: CATALYSIS BY PLATINUM(II)-TIN(II) SYSTEMS

HOWARD C. CLARK and JULIAN A. DAVIES

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, University of Guelph, Guelph, Ontario N1G 2W1 (Canada)

(Received August 1st, 1980)

Summary

The complexes $[Pt(ER_3)(CO)Cl_2]$ (E = P, As; R = aryl, alkyl) are active precursors for the catalytic hydroformylation of olefins in the presence of added tin(II) chloride. The yield of aldehyde may be maximized by systematic parameter variation and is shown to be limited by the degree of steric crowding at the metal centre. Terminal aliphatic monoenes are hydroformylated readily with a high n : iso ratio; hindered internal olefins, cyclic and conjugated aromatic olefins are less readily hydroformylated, but with no competing hydrogenation. The catalyst system is active under mild conditions of temperature and pressure.

Introduction

Since the discovery that olefins may be activated towards hydroformylation by certain transition metal complexes [1], much has been done to elucidate the parameters which govern this industrially important reaction [2—5]. Most studies have been concerned with systems catalyzed by cobalt or rhodium carbonyl complexes, or their phosphine-modified analogues [5]. Indeed, the relative activities of the most studied transition metal carbonyls have been shown to decrease in the order $Rh > Co > Ru > Mn > Fe > Cr \sim Mo \sim W \sim Ni$ [6]. Although the non-inclusion of platinum in such a series has been recognized as a serious omission [5], very few studies of hydroformylation with platinum catalysts have been reported [7—13]. From these few studies, it appears that certain platinum(II)-tin(II) halide systems are especially active [8,10,13], the most striking results being [5] those of Hsu and Orchin [10] who obtained a turnover number (T.N.) of forty moles of olefin converted to aldehyde per mole of catalyst per hour in the hydroformylation of pent-1-ene at 100°C using a pressure of 3000 psi of H_2/CO (1/1). The catalyst in this system was described as $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (Ph = phenyl), although its instability prevented differentiation between the possible neutral five-coordinate and ionic four-coordinate species.

We have recently reported the preliminary results of our systematic studies on the platinum(II)-tin(II) halide catalyzed hydrogenation of olefins [14,15] and now present results of our work on a related system for olefin hydroformylation. The catalyst precursors are the complexes *cis*-$[Pt(ER_3)(CO)Cl_2]$ (E = P, As; R = alkyl, aryl), which show exceedingly high catalytic activity in the presence of tin(II) chloride. In a typical experiment, we find that the terminal monoene hex-1-ene may be converted to n-heptanal and its α-methyl isomer with an n : iso ratio of 12 : 1 and a turnover number of 223 moles of olefin converted to aldehyde per mole of catalyst per hour (T.N. = 223), using the precursor $[Pt(P^nBu_3)(CO)Cl_2]$ (Bu = butyl) in the presence of two equivalents of tin(II) chloride (Pt : Sn = 1 : 2) at 80°C using pressures as low as 600 psi of H_2/CO (1/1). Hindered olefins are also hydroformylated, but somewhat less readily. Below we report the results of systematic parameter variation on the efficiency of the catalytic system.

Results and discussion

In the platinum(II)-tin(II) halide-catalyzed hydrogenation of olefins, the platinum(II) : tin(II) ratio can affect both the efficiency and stability of the catalyst [14—16]. In our hydroformylation system, we find (Table 1) that the precursor $[Pt(PPh_3)(CO)Cl_2]$ alone shows no activity for the hydroformylation of hex-1-ene at 80°C under 600 psi of H_2/CO (1/1) in acetonitrile solution. In the presence of one equivalent of tin(II) chloride, slight activity is observed (T.N. = 14) which increases dramatically upon addition of a second equivalent (T.N. = 139). The activity remains approximately constant with up to five equivalents of tin(II) chloride added (T.N. = 150) and in the presence of larger excesses, such as ten equivalents, a slight decrease in activity is noted (T.N. = 116). The n : iso ratio under these conditions reaches a maximum of 11 : 1 with a Pt : Sn ratio of 1 : 2. These results are in contrast to those reported for $[Pt(PR_3)_2Cl_2]$-tin(II) chloride systems [8,13], which require a Pt : Sn ratio of 1 : 5 to maintain catalyst stability.

TABLE 1

EFFECTS OF THE Pt^{II} : Sn^{II} RATIO ON THE HYDROFORMYLATION OF HEX-1-ENE [a]

Pt^{II} : Sn^{II} ratio	Terminal aldehyde (%)	Internal aldehyde (%)	C_6 compounds	n : iso ratio	Turnover number [b]
1 : 0	0.0	0.0	100.0	—	0
1 : 1	3.0	trace	97.0	—	14
1 : 2	28.0	2.5	69.5	11 : 1	139
1 : 5	30.0	3.0	67.0	10 : 1	150
1 : 10	23.0	2.5	74.5	9 : 1	116

[a] Catalysis by $[Pt(PPh_3)(CO)Cl_2]$ in acetonitrile solution containing hex-1-ene (Pt : Olefin : 1 : 910) at 80°C under 600 psi CO/H_2 (1/1) for 2 hours. [b] Moles of olefin converted to aldehyde per mole of platinum per hour.

TABLE 2

SOLVENT DEPENDENCE OF THE CATALYTIC HYDROFORMYLATION OF HEX-1-ENE [a]

Solvent	Terminal aldehyde (%)	Internal aldehyde (%)	C_6 compounds	n : iso ratio	Turnover number [b]
THF	0.0	0.0	100.0	—	0
Methanol	0.0	0.0	100.0	—	0
Acetonitrile	28.0	2.5	69.5	11 : 1	139
Acetone	34.0	2.0	64.0	17 : 1	164

[a] Catalysis by $[Pt(PPh_3)(CO)Cl_2]$ in the given solvent containing $SnCl_2 \cdot 2\,H_2O$ (Pt : Sn = 1 : 2) and hex-1-ene (Pt : olefin = 1 : 910) at 80°C under 600 psi H_2/CO (1/1) for 2 hours. [b] Moles of olefin converted to aldehyde per mole of platinum per hour.

Variation in solvent can also affect the efficiency of homogeneous catalytic systems, many of which are believed to function via formation of weakly bonded coordinated solvent complexes [17]. This effect is evident in the present system (see Table 2). The precursor $[Pt(PPh_3)(CO)Cl_2]$, in the presence of two equivalents of tin(II) chloride, shows no catalytic activity for the hydrofomylation of hex-1-ene at 80° C under 600 psi of H_2/CO (1/1) using either methanol or tetrahydrofuran (THF) as solvent. The use of solvents which are known to complex more efficiently with platinum(II) [17] such as acetonitrile (T.N. = 139) or acetone (T.N. = 164) gives rise to efficient catalysis. Again, these results contrast with those reported for $[Pt(PR_3)_2Cl_2]$-tin(II) chloride systems [8,13] where donor solvents, such as acetonitrile, inhibit hydroformylation.

It is, of course, desirable to utilize a catalyst system at the lowest temperature at which efficient hydroformylation can be maintained. Our results on temperature variation (Table 3) show that acetonitrile solutions of the precursor $[Pt(PPh_3)(CO)Cl_2]$ in the presence of two equivalents of tin(II) chloride show a marked increase in catalytic activity with temperature. Thus, at 30° C hex-1-ene is not hydroformylated; at 60° C hydroformylation is slight (T.N. = 20) and by 80° C catalysis occurs smoothly and efficiently (T.N. = 139). No attempt has been made to investigate the efficiency of the catalyst at more elevated temperatures as related systems are known to suffer from catalyst decom-

TABLE 3

TEMPERATURE VARIATION EFFECTS ON THE HYDROFORMYLATION OF HEX-1-ENE [a]

Temperature (°C)	Terminal aldehyde (%)	Internal aldehyde (%)	C_6 compounds (%)	n : iso ratio	Turnover number [b]
30	0.0	0.0	100.0	—	0
60	4.5	trace	95.5	—	20
80	28.0	2.5	69.5	11 : 1	139

[a] Catalysis by $[Pt(PPh_3)(CO)Cl_2]$ in acetonitrile solution containing $SnCl_2 \cdot 2\,H_2O$ (Pt : Sn = 1 : 2) and hex-1-ene (Pt : olefin = 1 : 910) at the given temperature under 600 psi H_2/CO (1/1) for 2 hours. [b] Moles of olefin converted to aldehyde per mole of platinum per hour.

TABLE 4

EFFECT OF GAS COMPOSITION ON THE EFFICIENCY AND PRODUCT DISTRIBUTION OF THE HYDROFORMYLATION OF HEX-1-ENE [a]

H_2 pressure (psi)	CO pressure (psi)	Terminal aldehyde (%)	Internal aldehyde (%)	n-Hexane (%)	Hex-1-ene (%)	*cis*- and *trans*-hex-2-enes (%)	n : iso ratio	Turnover [b] number
200	400	19.0	1.5	0.0	67.5	12.0	12.5 : 1	93
300	300	29.0	2.5	0.0	59.0	9.5	12.5 : 1	139
400	200	26.0	2.0	2.0	59.0	11.0	13 : 1	127
500	100	26.0	2.0	2.5	58.5	11.0	13 : 1	127

[a] Catalysis by $[Pt(PPh_3)(CO)Cl_2]$ in acetonitrile solution containing $SnCl_2 \cdot 2\,H_2O$ (Pt : Sn = 1 : 2) and hex-1-ene (Pt : olefin = 1 : 910) at 80°C under 600 psi gas pressure of the given composition for two hours. [b] Moles of olefin converted to aldehyde per mole of platinum per hour.

position [8,13], and additionally the high reaction rates observed at elevated temperatures can readily cause an artificial lowering of the carbon monoxide and hydrogen concentrations in solution, thus opposing the normal effect of increased temperature [5].

In the cobalt carbonyl-catalyzed hydroformylation of olefins, the most influential parameter on both reaction rate and product composition has been shown to be the carbon monoxide partial pressure [18]. The present system also shows variation in rate and composition with variation in the H_2 : CO ratio (Table 4). The highest turnover number is obtained using equal pressures of H_2 and CO; either an increase or a decrease in the partial pressure of CO from this optimum value causes a significant decrease in the amount of hydroformylation of hex-1-ene using $[Pt(PPh_3)(CO)Cl_2]$ as the catalyst precursor in the presence of two equivalents of tin(II) chloride at 80° C with a constant total pressure of 600 psi. The n : iso ratio appears to be approximately independent of variation in gas composition and is constant at 12.5 : 1 to 13 : 1 under these conditions. The extent of isomerization of the remaining olefin to *cis*- and *trans*-hex-2-enes is also invariant, with a ratio of hex-1-ene : hex-2-enes of 5 : 1 to 6 : 1. The major variation in product composition is the amount of n-hexane formed by hydrogenation of the olefins. The results show that high partial pressures of carbon monoxide inhibit the reaction and significant amounts of n-hexane are only produced when the ratio of H_2 : CO is 2 : 1 or greater. Thus, under the conditions necessary for maximum hydroformylation (where H_2 : CO = 1 : 1), hydrogenation of the olefin is not a competitive reaction and thus none of this unwanted by-product is formed. These results are supported by our earlier observations on related catalytic systems for olefin hydrogenation, where it was observed that the reaction was grossly inhibited by carbon monoxide [19].

In order to examine the effect of varying the ligand, ER_3, in the complexes *cis*-$[Pt(ER_3)(CO)Cl_2]$ on the catalytic activity of these precursors and to gain some insight into the rôle of the ER_3 ligand in the catalytic cycle, we have prepared and examined the activity of a range of complexes (Table 5). Complexes of the type $[Pt(ER_3)(CO)Cl_2]$ may be simply prepared by the bridge-cleavage

TABLE 5

EFFECTS OF VARIATION IN THE ER_3 LIGAND IN THE PRECURSORS $[Pt(ER_3)(CO)Cl_2]$ ON THE HYDROFORMYLATION OF HEX-1-ENE [a]

E	R	Terminal aldehyde (%)	Internal aldehyde (%)	C_6 Compounds (%)	n : iso ratio	Turnover [b] number
P	p-FC_6H_4 [c]	47.0	3.0	50.0	15.5 : 1	225
P	^nBu	45.0	4.0	51.0	11.0 : 1	223
P	Et	37.0	3.0	60.0	12.0 : 1	182
P	Ph	34.0	2.0	64.0	17.0 : 1	164
P	p-$CH_3C_6H_4$	34.0	2.0	64.0	17.0 : 1	164
P	Cy	27.0	4.0	69.0	7.0 : 1	141
As	Ph [d]	11.0	1.0	88.0	11.0 : 1	55

[a] Catalysis by $[Pt(ER_3)(CO)Cl_2]$ in acetone solution containing $SnCl_2 \cdot 2H_2O$ (Pt : Sn = 1 : 2) and hex-1-ene (Pt : olefin = 1 : 910) at 80°C under 600 psi H_2/CO for two hours. [b] Moles of olefin converted to aldehyde per mole of platinum per hour. [c] Mean values (see text). [d] Not comparable with other values (see text).

reaction of the dimeric species $[Pt_2(ER_3)_2Cl_4]$ with carbon monoxide [20], providing the ER_3 ligand is not sterically demanding. In order to prepare complexes of bulky ligands [21], such as PCy_3 (Cy = cyclohexyl), we have adapted an uncommon literature preparation [22]. Chloroform solutions of the diolefin complex $[Pt(COD)Cl_2]$ (COD = 1,5-cyclooctadiene), saturated with carbon monoxide, react with one equivalent of ER_3 under an atmosphere of carbon monoxide to yield the desired complexes in high yield via displacement of the olefinic moiety [23]. The effect which an ER_3 group imposes upon the reactions of its complexes can often be attributed to either steric or electronic effects, or to a combination of the two [21]. From the cone angle data of Tolman [21], which give a rough measure of relative size, the steric constraints imposed by our selection of phosphine ligands lie in the order.

$$PCy_3 > P(p\text{-}FC_6H_4)_3 \sim PPh_3 \sim P(p\text{-}CH_3C_6H_4)_3 > P^nBu_3 \sim PEt_3 \qquad (1)$$

(Et = Ethyl).

Their basicities, which describe electronic effects, lie in the order:

$$PCy_3 > P^nBu_3 > PEt_3 > P(p\text{-}CH_3C_6H_4)_3 > PPh_3 > P(p\text{-}FC_6H_4)_3 \qquad (2)$$

The extent of hydroformylation induced by their complexes (Table 5) follows neither series and thus is probably determined by a combination of both steric and electronic effects. The data in Table 5 do, however, indicate that hydroformylation is favoured by ligands which are small in size (PEt_3, P^nBu_3). Additionally, for ligands of similar basicities, the smaller ligand is more effective (PEt_3, $P^nBu_3 > PCy_3$) whilst for ligands of similar size, the least basic is more effective ($P(p\text{-}CH_3C_6H_4)_3$, $PPh_3 < P(p\text{-}FC_6H_4)_3$). As small changes in catalytic systems (such as use of substrates of different reactivities) can open new pathways in the catalytic cycle [24], it seems possible that the variation in activity described here may not be an effect of changing the rate of the reaction but rather a change in the catalytic cycle itself. As catalysis is hindered by bulky ligands which restrict substrate coordination and yet favoured by less basic ligands, which may act as leaving groups, both coordinate and dissociative pathways may be possible, depending upon a combination of the steric and electronic properties of the ligands.

The data shown in Table 5 were found to be reproducible within a small experimental error for all complexes except for the most active precursor, $[Pt(P\{p\text{-}FC_6H_4\}_3)(CO)Cl_2]$. Under experimentally "identical" conditions, this complex failed to show reproducible catalytic activity; for example, four consecutive experiments gave turnover numbers of 291, 193, 175 and 243 (mean = 225) for the hydroformylation of hex-1-ene. Whilst each of these results represents a higher absolute yield of aldehyde than analogous experiments with PPh_3 or $P(p\text{-}CH_3C_6H_4)_3$ complexes, the presence of the electron-withdrawing fluoro group in the *para* position of the aryl ring appears to render the complex extremely sensitive to small variations in reaction conditions (possibly due to residual traces of dioxygen or water vapour in the system). Indeed, solutions of this precursor in the presence of two equivalents of tin(II) chloride show no catalytic activity whatsoever for the hydroformylation of hex-1-ene if purged with dioxygen for a few minutes or treated with trace amounts of distilled water prior to the attempted catalytic reaction. Accordingly, attempts to hydroformylate less reactive olefins were performed with the precursor [Pt(P^nBu_3)(CO)Cl_2], which was found to be more robust and only slightly less efficient.

Data for catalysis by the arsine complex [Pt($AsPh_3$)(CO)Cl_2] is included in Table 5 for completeness, but is not strictly comparable with the data for complexes of phosphine ligands as this complex was found to be unstable under hydroformylation conditions and some decomposition to metal occurred. Whilst it is extremely unlikely that hydroformylation is catalyzed heterogeneously in this case [5], the decrease in catalyst concentration caused by partial decomposition of the complex results in an anomolously low yield of aldehyde per mole of catalyst.

In order to examine the generally of our system we have examined olefins of several types (Table 6). Our data show that the terminal aliphatic monoene, hex-1-ene, is most readily hydroformylated to n-heptanal and its α-methyl isomer. The olefinic moiety of this monoene is the least hindered of any we have examined and this result again suggests that the degree of steric hindrance at the metal centre may be a major factor in determining the extent of hydroformylation. The hydroformylation of unsubstituted cyclic olefins, such as cyclohexene, can yield only a single product as no isomerization is possible. The internal olefin, *trans*-hex-3-ene, also yields a single detectable product, indicating that double-bond isomerization, followed by hydroformylation, is not a competitive reaction sequence. The low yields of aldehydes obtained for cyclic and internal olefins, in which the double bond is more hindered are comparable with results obtained for the cobalt carbonyl catalyzed hydroformylation reaction [25]. One major problem with cobalt carbonyl catalysts is the extent to which competitive reactions interfere with hydroformylation, demonstrated particularly with substrates containing a double bond conjugated to an aromatic system. In such cases, cobalt carbonyl catalysts lead to an extremely high degree of hydrogenation [4]. In the present system, styrene was found to yield 2-phenylpropanal with no interference by hydrogenation; the other possible isomeric product, 3-phenylpropanal, was not detected. This situation is mirrored by the activity of rhodium carbonyl catalysts which yield both isomers when operating under conditions of high temperature and pressure [26,27] but

TABLE 6

HYDROFORMYLATION OF VARIOUS SUBSTRATE-TYPES BY THE PRECURSOR [Pt(P^nBu_3)(CO)Cl_2] [a]

Substrate	Aldehyde(s) (%)	Turnover number [b]
hex-1-ene [c]	49.0	223
trans-hex-3-ene [d]	7.0	32
cyclohexene [d]	10.5	48
styrene [e]	6.0	27

[a] Catalysis by complex in acetone solution containing $SnCl_2 \cdot 2\ H_2O$ (Pt : Sn = 1 : 2) and the given olefin (Pt : olefin = 1 : 910) at 80°C under 600 psi H_2/CO (1/1) for two hours. [b] Moles of olefin converted to aldehyde per mole of platinum per hour. [c] With n : iso = 11.0 : 1. [d] Single product. [e] Only 2-phenylpropanal detected.

under milder conditions 2-phenylpropanal predominates [28] with little competitive hydrogenation.

The generally accepted rôle of the tin(II) chloride additive in catalytic hydrogenation by platinum chloride complexes involves initial insertion of $SnCl_2$ into a Pt—Cl bond to form a Pt—$SnCl_3$ complex. The $SnCl_3^-$ ligand has a high *trans*-influence and accordingly promotes five-coordination and hence labilization of the *trans* ligand. Substrate coordination is thus promoted and the catalysis enhanced.

Multinuclear NMR studies by Pregosin and coworkers [29—31] have shown that $[PtCl_2(PR_3)_2]/SnCl_2$ systems react as in eq. 3.

$$[\mathrm{PtCl_2(PR_3)_2}] \xrightarrow{\mathrm{SnCl_2}} \underset{\mathrm{(I)}}{[\mathrm{PtCl(SnCl_3)(PR_3)_2}]} \xrightarrow{\mathrm{SnCl_2}} \underset{\mathrm{(II)}}{[\mathrm{Pt(SnCl_3)_2(PR_3)_2}]} \qquad (3)$$

The complex I may be *cis* or *trans*, depending upon the nature of R. Complex II is of *trans* geometry and reacts with hydrogen to give *trans*-$[Pt(H)SnCl_3(PR_3)_2]$. The hydride has been shown to react with activated unsaturates to yield insertion products [30].

The system described in this paper shows many differences in behavior from that of the $[PtCl_2(PR_3)_2]/SnCl_2$ system and so it seemed worthwhile to undertake an NMR study to determine the nature of the catalyst precursor and to investigate its stoichiometric reactions.

Our initial results have yet to define the precursor exactly, but undoubtedly show that the chemistry described by equation 3 is not followed. Titration of *cis*-$[PtCl_2(CO)(PPh_3)]$ with $SnCl_2 \cdot 2\ H_2O$ in acetone was monitored by $^{31}P\{^1H\}$ NMR. The disappearance of the starting material (δ P = 9.05 ppm, $^1J(Pt, P)$ = 3057 Hz) was accompanied by formation of a single new product (δ P = 18.50 ppm, $^1J(Pt, P)$ = 2034 Hz). The reaction was monitored after addition of 1, 2, 5 and 10 equivalents of $SnCl_2$, although with 2 equivalents added, the new product was present in 100% abundance and no further reaction occurred. No coupling to ^{117}Sn and ^{119}Sn could be observed, even at low temperature. The magnitude of $^1J(Pt, P)$ suggests that the phosphine is *trans* to a strong σ-donor. The complex with two equivalents of $SnCl_2$ added was then examined by ^{119}Sn and ^{195}Pt NMR. The ^{119}Sn NMR spectrum showed a single species present, $\delta(^{119}Sn) = -126.8$ ppm, coupled to ^{195}Pt, $^1J(Pt, Sn)$ = 15,968 Hz. No coupling to ^{31}P was observed. The ^{195}Pt NMR spectrum showed a single species as a triplet (1 : 2 : 1) at —2822 ppm, coupled to ^{31}P, $^1J(Pt, P)$ = 2063 Hz. No coupling to ^{119}Sn was observed.

The most likely explanation of these data is that two species are present, one containing two equivalent (probably *cis*) phosphines on platinum and another containing the Pt—$SnCl_3$ moiety, but no phosphine ligands. Only the former species has been observed in the ^{195}Pt NMR within the range we have studied (—4400 to 2800 ppm). These preliminary results suggest a quantitative rearrangement reaction in which the phosphine and $SnCl_3^-$ ligands migrate to separate platinum centres. Further NMR studies on these and related systems are underway in an attempt to identify this catalyst precursor and so define a new rôle for the trichlorostannate ligand in homogeneous catalysis. In connection with the results of Pregosin [29—31] previously mentioned (eq. 3), it is noteworthy that stoichiometric quantities of $SnCl_2$ were used (not five equivalents as in the catalytic reaction) and that spectra obtained at room temperature were broadened, possibly an indication of exchange. Only at low temperatures could the couplings be observed and accordingly these experiments bear no resemblance whatsoever to the catalytic reaction in which conditions are totally different.

Conclusions

The described catalytic system complements usefully the cobalt and rhodium carbonyl hydroformylation catalysts currently employed, combining some desirable features of both, including activity at modest temperatures and pressures, aldehyde formation with a high n : iso ratio and little interference by competitive hydrogenation. Steric hindrance at the metal centre appears to be a major factor in determining the extent of hydroformylation. The choice of ligand is thus critical in determining the absolute yield of aldehyde, whilst the ratio of H_2 : CO employed is the major factor in determining the extent of competitive hydrogenation. Spectroscopic studies on the catalytic system and related stoichiometric reactions will be reported in greater detail.

Experimental

Hex-1-ene (Aldrich, 99%), *trans*-hex-3-ene (Aldrich 99%) and styrene (Aldrich 99%) were passed down columns of Florisil (Fisher, 100—200 mesh) and alumina (Fisher, Basic Brockman activity 1, 80—200 mesh) and deoxygenated prior to use. Cyclohexene (Eastman Kodak) was vacuum distilled, passed down columns of Florisil and alumina and deoxygenated prior to use. Acetone (Fisher, spectranalysed), methanol (Fisher, spectranalysed) and acetonitrile (Fisher, certified) were deoxygenated and tetrahydrofuran (Fisher, certified) distilled from sodium hydride and deoxygenated prior to use. The complexes $[Pt(ER_3)(CO)Cl_2]$ were prepared and characterized by known methods [20,22,23]. Tin(II) chloride was recrystallized from hydrochloric acid. In a typical hydroformylation experiment, the complex precursor (0.0150 m*M*) and hydrated tin(II) chloride were weighed into a 50 cm^3 glass autoclave liner containing a Teflon-coated star-shaped magnetic stirrer. The solids were deoxygenated and the olefin (910 equivalents) added. The solvent (3 cm^3) was added and magnetically stirred until a homogeneous clear solution resulted. The glass liner was then transferred to the autoclave under a blanket of dry nitrogen. The autoclave was then flushed with carbon monoxide, pressurized with carbon monoxide and then hydrogen, and heated thermostatically to the desired temperature. The solution was then stirred for two hours, following which the entire autoclave was plunged into crushed ice to quench the reaction. The gases were then vented and the solution removed for analysis.

High pressure reactions were performed using an autoclave constructed in this department according to a design available from Dr. C.D. Schmulbach, Univeristy of Carbondale, S. Illnois, U.S.A.

Gas chromatographic analyses were performed on an Aerograph autoprep 700 chromatograph equipped with a 32 foot × 0.25 inch (O.D.) Carbowax 4000 (60—80 mesh) column by comparison with known standards. Integration of ^{1}H NMR spectra (δ(—CHO) vs δ(—CH=CH$_2$)) allowed confirmation and definite identification of the aldehydic products.

^{31}P NMR spectra were obtained on a Bruker WP60 instrument operating at 24.3 MHz. Chemical shifts are relative to external 85% H_3PO_4, more positive shifts represent deshielding. ^{119}Sn and ^{195}Pt NMR spectra were obtained on a Bruker 250 MHz instrument operating at 93 MHz and 53.75 MHz. ^{119}Sn chemical shifts are relative to Me_4Sn and ^{195}Pt chemical shifts are relative to K_2PtCl_4 (aq), more positive shifts represent deshielding.

Acknowledgments

Thanks are expressed to Dr. C.S. Wong for useful discussion and to the Natural Sciences and Engineering Research Council of Canada for financial support. The ^{119}Sn and ^{195}Pt NMR spectra were obtained through the cooperation of Bruker Spectrospin (Canada) and the assistance of Dr. M. Smith is acknowledged with thanks.

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