Journal of Organometallic Chemistry 695 (2010) 2381–2384

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Platinum complexes of 2-diphenylphosphinobenzaldehyde-derived P-alkene ligands and their application in the hydroformylation of styrene

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ARTICLE INFO

Article history:
Received 26 May 2010
Accepted 16 July 2010
Available online 23 July 2010

Keywords:
Hydroformylation
Platinum
Monodentate phosphine
NMR

ABSTRACT

Neutral complexes of the formula $PtCl_2L_2$ (where L = diethyl 2-diphenylphosphino-benzylidene-malonate (**1**), diisopropyl 2-diphenylphosphino-benzylidene-malonate (**2**), di-*tert*-butyl 2-diphenylphosphino-benzylidene-malonate (**3**), methyl *E*-2-(2′-diphenylphosphinophenyl)-acrylate (**4**), *tert*-butyl *E*-2-(2′-diphenylphosphinophenyl)acrylate (**5**)) were prepared. These complexes proved to be excellent precursors to active catalysts for the hydroformylation of styrene. The platinum-containing catalytic systems prepared from malonate-based ligands **1** and **2** provided the highest activity. Chemoselectivities of up to 87% were obtained, while the two aldehyde regioisomers were formed in almost equimolar ratio. The *in situ* studies by using lower ligand to Pt ratios resulted in slight decrease in both regio- and chemoselectivities.

^{31}P NMR studies on the $PtCl_2L_2$ complexes revealed that the formation of *trans* isomers is highly preferred in the case of benzylidene malonate-type ligands with two ester functionalities (**1**–**3**) probably due to steric hindrance. A mixture of *cis*/*trans* geometrical isomers (on the Pt) with a predominance of the *trans* isomer was formed when acrylate-type ligands with one ester functionality (**4** and **5**) were used.

1. Introduction

The hydroformylation reaction is a catalysed transformation with practical industrial importance. The highly regioselective hydroformylation of propene to the linear aldehyde regioisomer, *n*-butyraldehyde, in the presence of cobalt- and rhodium-containing catalysts, has successful industrial-scale application and has seen detailed mechanistic investigations [1]. The hydroformylation of alkenes making use of platinum–phosphine–tin(II) halide systems has also seen quite some research activity [2]. Although notable ee's were obtained in the asymmetric hydroformylation of alkenes (mainly of butene isomers as test substrates) using $PtCl_2$(chiral diphosphine) precursors, the efficacy of these systems was better in the enantioselective hydroformylation of vinylaromatics (mainly styrene) and of unsaturated carboxylic acid derivatives (acrylates and itaconates). The platinum–phosphine–tin(II)halide systems are useful as catalysts in two synthetically important reactions. The first is represented by the high regioselectivities obtained with 1,1-disubstituted olefins [3]. The second includes a facile route towards the synthesis of optically active 2-arylpropanal derivatives, the direct precursors of 2-arylpropionic acid derivatives (such as the non-steroidal anti-inflammatory drug ibuprofen [4–7]).

The search for higher-activity platinum-based hydroformylation catalysts has led to the application of novel achiral diphosphines [8]. In particular, xantphos [9] and its analogues [10] have proven the most successful for these transformations. The applicability of tin(II) halide-free hydroformylation catalysts based on platinum–alkyl/aryl complexes and boron additives was shown in our laboratory [11]. Recently, malonate-derived monodentate phosphines (2-diphenylphosphino-malonic acid derivatives) were used as efficient ligands in the highly chemo- and regioselective hydroformylation of styrene [12].

This paper describes the synthesis of novel platinum complexes based on 2-diphenylphosphinobenzaldehyde-derived P-alkene ligands containing ester functionality(ies) and their application in platinum-catalysed hydroformylation of styrene.

2. Experimental

2.1. General

The $PtCl_2(PhCN)_2$ precursor was synthesised from $PtCl_2$ (Aldrich) according to a standard procedure [13]. Toluene was

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doi:10.1016/j.jorganchem.2010.07.022

distilled and purified by standard methods and stored under argon. Styrene was freshly distilled immediately before use. All reactions were carried out under argon using standard Schlenk techniques.

The ^{1}H and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer or a Varian Gemini 300 MHz instrument. Chemical shifts are reported in ppm relative to TMS (downfield) or 85% H_3PO_4 (0.00 ppm) for ^{1}H and ^{31}P NMR spectroscopy, respectively.

The P-alkene ligands **1**–**5**, which generate unusual Pd-based Suzuki catalysts [14], were synthesised as described in our previous paper [14].

2.2. General method for the synthesis of $PtCl_2$(monophosphine)$_2$ complexes (monophosphine = **1**–**5**)

In a typical experiment, a three-necked flask equipped with a gas-inlet and a reflux condenser with a balloon at the top was used. A degassed solution of $PtCl_2(PhCN)_2$ (131.6 mg, 0.30 mmol) and one of ligands **1**–**5** (0.60 mmol) in benzene (20 mL) was added to the flask. This solution was heated to reflux under argon. A bright yellow homogeneous solution resulted. The mixture was further heated for 1 h. A white precipitate formed which was filtered off and dried under vacuum for 2 h. The target complexes were obtained as white powder-like solid materials.

trans-$PtCl_2$(**1**)$_2$ (**1a**)

Yield: 71%. Analysis: Calculated for $C_{52}H_{50}O_8P_2Cl_2Pt$ (1130.90): C: 55.23; H: 4.46. Found: C: 55.06; H: 4.58. For NMR data see Table 1.

trans-$PtCl_2$(**2**)$_2$ (**2a**)

Yield: 63%. Analysis: Calculated for $C_{56}H_{58}O_8P_2Cl_2Pt$ (1187.01): C: 56.66; H: 4.93. Found: C: 56.79; H: 4.79. For NMR data see Table 1.

trans-$PtCl_2$(**3**)$_2$ (**3a**)

Yield: 80%. Analysis: Calculated for $C_{60}H_{66}O_8P_2Cl_2Pt$ (1243.11): C: 57.97; H: 5.35. Found: C: 58.16; H: 5.51. For NMR data see Table 1.

trans-$PtCl_2$(**4**)$_2$ (**4a**) and *cis*-$PtCl_2$(**4**)$_2$ (**4b**) (isolated as a 78/22 mixture)

Yield: 51%. Analysis: Calculated for $C_{44}H_{38}O_4P_2Cl_2Pt$ (958.72): C: 55.12; H: 4.00. Found: C: 55.02; H: 4.14. For NMR data see Table 1.

trans-$PtCl_2$(**5**)$_2$ (**5a**) and *cis*-$PtCl_2$(**5**)$_2$ (**5b**) (isolated as a 92/8 mixture)

Yield: 73%. Analysis: Calculated for $C_{50}H_{50}O_4P_2Cl_2Pt$ (1042.88): C: 57.59; H: 4.83. Found: C: 57.73; H: 4.97. For NMR data see Table 1.

2.3. Hydroformylation experiments

In a typical experiment, a solution of 0.01 mmol of $PtCl_2$(monophosphine) (monophosphine = ligands **1**–**5**) and 0.02 mmol (3.8 mg) of tin(II) chloride in toluene (10 mL) containing styrene (**6**, 1.0 mmol, 0.115 mL) was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurised to 80 bar total pressure ($CO/H_2 = 1:1$) and placed in an oil bath (100 °C) and the mixture was stirred with a magnetic stirrer for 24 h. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analysed by GC–MS.

3. Results and discussion

3.1. Synthesis of the complexes and their NMR investigation

Neutral complexes of general formula $PtCl_2$(phosphine)$_2$ were synthesised by the reaction of $PtCl_2(PhCN)_2$ with two equivalents of the respective phosphines **1**–**5** [14] (Fig. 1). The various triarylphosphine ligands show different selectivities regarding complex formation. The three diester derivatives (**1**–**3**) reacted with the $PtCl_2(PhCN)_2$ precursor selectively leading to the corresponding *trans*-$PtCl_2(P)_2$-type complexes **1a**, **2a** and **3a**, respectively. However, the use of monoester derivatives (**4** and **5**) resulted in the formation of the *cis*/*trans* mixture of 22/78 (**4b**/**4a**) and 8/92 (**5b**/**5a**), respectively. It seems that the bulkier diesters (**1**–**3**) are forced to exclusively occupy the *trans* positions resulting in the sterically less hindered square-planar *trans* arrangement of the ligands.

As expected, each of the *trans*- and *cis*-$PtCl_2(P)_2$-type complexes **1a**–**5a** and **4b**, **5b**, respectively, exhibited a single central signal (flanked by platinum satellites, in a ratio of 1:4:1) in the ^{31}P NMR

Table 1
NMR data of the platinum complexes containing P-alkene phosphines (**1**–**5**).[a]

		^{31}P NMR	^{1}H NMR			
			δ [ppm] (multiplicity, J [Hz], integral)			
		δP [ppm]	^{1}J(Pt, P) [Hz]	Alkyl protons (OR)	Alkenyl protons (=CH–)	Aromatic protons
trans-$PtCl_2$(**1**)$_2$	**1a**	19.6	2618	1.17 (t, 7.1 Hz, 3H); 1.19 (t, 7.1 Hz, 3H) 4.12 (q, 7.1 Hz, 2H); 4.14 (q, 7.1 Hz, 2H)	8.52 (s, 1H)	7.98 (d, 5.8 Hz, 4H) 7.20–7.42 (m, 10H)
trans-$PtCl_2$(**2**)$_2$	**2a**	19.8	2625	1.16 (d, 6.2 Hz, 6H); 1.18 (d, 6.2 Hz, 6H) 4.98 (h, 6.2 Hz, 1H); 5.03 (h, 6.2 Hz, 1H)	8.38 (s, 1H)	7.99 (d, 5.8 Hz, 4H) 7.24–7.42 (m, 10H)
trans-$PtCl_2$(**3**)$_2$	**3a**	19.8	2633	1.38 (s, 9H); 1.41 (s, 9H)	8.15 (s, 1H)	7.88–8.02 (m, 4H) 7.22–7.65 (m, 10H)
trans-$PtCl_2$(**4**)$_2$	**4a**	19.2	2625	3.58 (s, 3H)	8.60 (d, 16.0 Hz, 1H) 6.06 (d, 16.0 Hz, 1H)	7.86–7.93 (m, 4H) 7.25–7.44 (m, 10H)
cis-$PtCl_2$(**4**)$_2$	**4b**	25.9	3100	3.80 (s, 3H)	6.29 (d, 12.0 Hz, 1H) 4.58 (d, 12.0 Hz, 1H)	8.00–8.06 (m, 4H) 7.06–7.64 (m, 10H)
trans-$PtCl_2$(**5**)$_2$	**5a**	18.8	2680	1.32 (s, 9H)	8.23 (d, 15.0 Hz, 1H) 6.00 (d, 15.0 Hz, 1H)	7.81–7.86 (m, 4H) 7.20–7.42 (m, 10H)
cis-$PtCl_2$(**5**)$_2$	**5b**	26.4	3210	1.30 (s, 9H)	8.10 (d, 15.0 Hz, 1H) 6.12 (d, 15.0 Hz, 1H)	8.00–8.06 (m, 4H) 7.06–7.64 (m, 10H)

[a] Spectra were measured in CDCl3 (under Ar at room temperature).

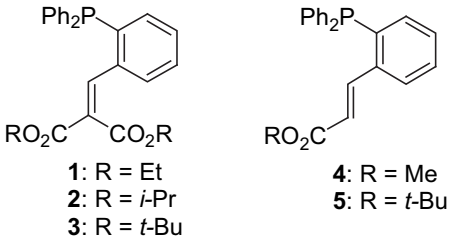


Fig. 1. The P-alkene ligands (**1**–**5**) used in this study.

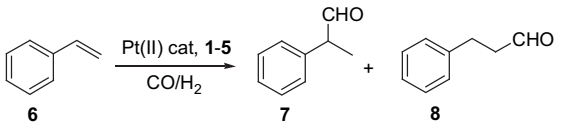
spectra thereof (Table 1). In these spectra, the coupling constants are diagnostic, showing values of 2600–2700 Hz or 3100–3200 Hz for the *trans* and *cis* complexes, respectively. The ^{31}P NMR spectra of the platinum complexes provide a sensitive probe for the structures of complexes, even in complicated mixtures. The magnitude of the $^{1}J(^{195}Pt, ^{31}P)$ coupling constants is strongly dependent on whether the P atom has another P atom or a chlorine atom as ligand in the position *trans* to it on the Pt. It is known from the literature that the *trans* P–Cl arrangement features $^{1}J(^{195}Pt, ^{31}P)$ coupling constants typically larger than 3500 Hz, while *trans*-P–P arrangement displays typical platinum–phosphorus coupling constants of 2500–3000 Hz [15].

It is worth mentioning that although the ligands used in the present study can be considered as *ortho*-substituted PPh_3 analogues, the $^{1}J(^{195}Pt,^{31}P)$ coupling constants for **4b** and **5b** are significantly smaller than that observed in the corresponding *cis*-$PtCl_2(PPh_3)_2$ (3678 Hz, 14.7 ppm) [16]. Interestingly, the $^{1}J(^{195}Pt,^{31}P)$ coupling constants for **1a**–**5a** are almost the same as that measured in case of the *trans*-$PtCl_2(PPh_3)_2$ (2605 Hz, 22.0 ppm) complex [17]. Accordingly, on the basis of NMR investigations, a weaker interaction between our P-ligands and the platinum(II) centre can be envisaged for the *cis* complexes than in case of the triarylphosphines investigated earlier [16,17]. Indeed, similarly weak interactions can be invoked on the basis of the $^{1}J(^{195}Pt,^{31}P)$ coupling constants for the *trans* complexes. This phenomenon is probably due to the small effect of the *ortho*-substituents that would be minimised between the phosphine ligands occupying *trans* positions on the metal centre.

Interestingly, in our earlier work [14] using these P-alkene ligands with Pd, each was shown to bind in a bidentate (P-binding and alkene-binding to the metal) fashion to the Pd centre. This was manifested by significant upfield shifts of the resonances characteristic of the alkene hydrogen atom(s) in the ^{1}H NMR spectra of the Pd-complexes when compared to the free ligands. For example, free ligand **4** gives resonances at 8.44 ppm and 6.27 ppm for the alkene protons, while the Pd complex thereof gave resonances at 5.95 ppm and 4.44 ppm, respectively. In general in the present instance, it appears as if the P-alkene ligands prefer a monodentate binding fashion to the Pt centre, as evidenced by the low field resonances for the alkene protons that are reflective of a free alkene moiety in the ligand. In only one case is this not so, namely for complex **4b**, where the alkene signals for the bound ligand shows similar upfield shifts as those observed for the Pd complex, namely showing resonances at 6.29 ppm and 4.58 ppm, respectively, indicating a bidentate binding mode to the Pt ion.

3.2. Hydroformylation reactions

Pre-formed complexes $PtCl_2(L)_2$ (where L = **1**–**5**, Fig. 1) were used as catalysts for the hydroformylation of styrene (Scheme 1) in the presence of 2 equivalents of tin(II) chloride per Pt under 'oxo-conditions' ($p(CO) = p(H_2) = 40$ bar, 100 °C, as described in Table 2).



Scheme 1.

In addition to the branched and linear aldehyde products **7** and **8**, respectively, some hydrogenation product (ethylbenzene, **9**) was also formed. Although the formation of aldehydes was highly favoured under all conditions, the presence of **9** was not negligible even under optimal conditions (*vide infra*).

The hydroformylation activity of the *in situ*-generated platinum–tin(II)chloride catalysts, obtained from $PtCl_2L_2$ (L = **1**–**5**) precursors, is moderate. The conversions obtained in 24 hours are strongly dependent on the structure of the ligand. The highest catalytic activity was obtained from the two diester derivatives **1** and **2**, resulting in 66 and 88% conversion (Table 1, entries 1 and 2). Lower conversions were obtained with the two monoester-type (**4**, **5**) and the di-*tert*-butyl ester (**3**) ligands (entries 3, 5 and 7). The activity of these catalysts is lower than those of the corresponding rhodium catalysts and most of the platinum–*diphosphine*–tin(II) chloride systems tested to date [8,11]. Nevertheless, the novel ligand-containing catalysts are of interest from several theoretical points of view.

The regioselectivity towards branched aldehyde varies between 50 and 55%. The introduction of an α-unsaturated mono/diester moiety into *ortho*-positions of one of the phenyl rings of PPh_3, yields catalysts that afford slightly higher branched selectivities than is obtained with PPh_3. (The application of the obvious analogous catalytic precursor, *cis*-$PtCl_2(PPh_3)_2$ resulted in 45% regioselectivity [12]. It is worth mentioning that similar results have been obtained by using the corresponding Pt–PPh_3–$SnCl_2$ '*in situ*' system for the hydroformylation of styrene [18].) It is worth noting that higher conversions and practically identical chemoselectivities, accompanied by a decrease in the regioselectivity, were observed for reaction times as long as 72 h (entries 4, 6 and 8).

The fact that both the *cis*-$PtCl_2(PPh_3)_2$ precursor, reported previously, and the *trans*-$PtCl_2L_2$ precursors in this study gave similar regioselectivities, *i.e.* almost equimolar formation of **7** and **8**,

Table 2
Hydroformylation of styrene with platinum complexes containing 2-diphenylphosphinobenzaldehyde-derived P-alkene phosphines (**1**–**5**).[a]

Entry	Catalyst	Conv. [%]	R_c[b] [%]	R_{br}[c] [%]
1	**1a** + $2SnCl_2$	66	87	50
2	**2a** + $2SnCl_2$	88	81	54
3	**3a** + $2SnCl_2$	43	82	55
4	**3a** + $2SnCl_2$[d]	70	84	52
5	**4a** + $2SnCl_2$	41	85	55
6	**4a** + $2SnCl_2$[d]	53	82	44
7	**5a** + $2SnCl_2$	36	86	54
8	**5a** + $2SnCl_2$[d]	48	84	44
9	$PtCl_2(PhCN)_2$ + **1** + $SnCl_2$[e]	46	79	45
10	$PtCl_2(PhCN)_2$ + **2** + $SnCl_2$[e]	35	79	48
11	$PtCl_2(PhCN)_2$ + **3** + $SnCl_2$[e]	58	80	56[e]
12	$PtCl_2(PhCN)_2$ + **4** + $SnCl_2$[e]	45	81	50
13	$PtCl_2(PhCN)_2$ + **5** + $SnCl_2$[e]	14	77	50

[a] Reaction conditions (unless otherwise stated): Pt/styrene = 1:100; 0.05 mmol Pt-complex precursor, 0.1 mmol $SnCl_2$; $p(CO) = p(H_2) = 40$ bar; $T = 100$ °C; $t = 24$ h; solvent: toluene.

[b] R_c = chemoselectivity towards aldehydes [(moles of **7** + moles of **8**)/(moles of **7** + moles of **8** + moles of **9**) × 100].

[c] R_{br} = regioselectivity towards branched aldehyde regioisomer [moles of **7**/(moles of **7** + moles of **8**) × 100].

[d] Reaction time: 72 h.

[e] Pt/ligand (**1**–**5**)/$SnCl_2$ = 1/0.55/1.5 was used.

implies several points regarding mechanistic details. (Apparently, the product formation seems to be insensitive to the *cis* or *trans* geometries of $PtCl_2L_2$-type precursors.) One of the possible explanations is the dissociation of one of the P-ligands to form structurally similar active catalytic intermediates. The other possibility is the isomerization of the *cis* complexes to the corresponding *trans* isomer. Less likely is that the activation of the alkene (styrene) by the platinum complex and its insertion into Pt–H bond, leading to platinum–alkyl intermediate, is almost unaffected by the geometry of the Pt complex.

The lower P-coordination seems to be supported by the fact that chemo- and regioselectivities similar to the above-mentioned ones can be obtained by lower P/Pt ratios. In fact, the application of the *in situ* systems obtained from $PtCl_2(PhCN)_2$ and the appropriate ligand **1**–**5** in a ratio of 1/0.55, resulted in slightly lower chemo- and regioselectivities (Table 2, entries 9–13).

In summary, the chemoselectivity of hydroformylation was moderate and very similar throughout, accompanied by low rates of reaction. The rate of the hydroformylation reaction is significantly influenced by the phosphorus ligands employed in this study. However, the two aldehyde regioisomers are formed in nearly equimolar ratios under all conditions investigated, implying catalyst insensitivity to the steric constraints brought about by the presence of the P-alkene ligands.

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