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Platinum complexes of malonate-derived monodentate phosphines and their application in the highly chemo- and regioselective hydroformylation of styrene

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ABSTRACT

Neutral complexes of the formula $PtCl_2L_2$ (where L = diethyl 2-diphenylphosphino-malonate (**1**), diethyl 2-methyl-2-diphenylphosphinomalonate (**2**), dibenzyl 2-diphenylphosphinomalonate (**3**), 1,3-dihydroxy-2-methyl-2-diphenylphosphinopropane (**4**)) were prepared. These proved to be precursors to active catalysts for the hydroformylation of styrene. The platinum-containing catalytic systems prepared from ligand **4** provided the highest activity, while the platinum compounds prepared from other ligands all showed similar levels of reactivity to each other. The matching of high chemo- and regioselectivities were observed in most cases. Surprisingly, the complexes were practically inactive in imidazolium-type ionic liquids. ^{31}P NMR studies on the $PtCl_2L_2$ complexes revealed that the stereoselectivity of the *cis*/*trans* geometrical isomers is strongly dependent on the structure of the ligand.

1. Introduction

Carbonylation reactions encompass several types of processes. Among these, hydroformylation is considered to be that process with the highest industrial importance [1]. Cobalt- and rhodium-containing catalysts have successful industrial scale application [2] and have seen detailed mechanistic investigations [2]. Hydroformylation activity has also been noted for platinum-phosphine-tin(II) halide systems [3]. When based on the application of $PtCl_2$(chiral diphosphine) precursors, these complexes have proved efficient enantioselective hydroformylation catalysts [4–11]. The high regioselectivities obtained with 1,1-disubstituted olefins [12] and the facile route developed towards optically active 2-aryl-propanal derivatives, the direct precursors of 2-phenyl-propionic acid derivatives (such as the non-steroidal anti-imflammatory drug ibuprofen [13–16]) using hydroformylation transformations, render such systems useful as catalysts of synthetically important reactions.

The search for higher-activity platinum hydroformylation catalysts has led to the application of novel achiral diphosphines [17]. Xantphos [18] and its analogues [19] have been tested in platinum–phosphine–tin(II) chloride systems. Investigations into the role of the co-catalyst have resulted in the development of tin(II) halide-free hydroformylation catalysts based on platinum-alkyl/aryl complexes and boron additives [20].

This paper describes the synthesis of platinum complexes with malonate-derived monodentate phosphines 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 [21]. Toluene was 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 ^1H 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 ^1H and ^{31}P NMR spectroscopy, respectively.

The ligands **1**–**4** and their borane adducts were synthesised as follows.

2.2. General procedure for the synthesis of the malonate ligands

Diethylmethylmalonate (0.22 mL, 0.43 mmol) was placed into a Schlenk tube and dissolved in 21 mL of dry THF. The solution was cooled to 0 °C and 65 mg (0.516 mmol) of NaH were added and the mixture was stirred for half an hour. The solution was cooled to

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−78 °C and 0.16 mL (0.29 mmol) of chlorodiphenylphosphine were added and the reaction mixture was left to stir overnight. The solution was brought to 0 °C using an ice bath and 1.02 mL (0.34 mmol) of borane–THF complex were added. The mixture was left to stir for 2 h after which it was warmed to room temperature and stirred for a further 10 min. TLC was performed to check the progress of the reaction. Slow addition of water quenched the reaction and excess THF solvent was removed *in vacuo*. The reaction mixture was extracted with EtOAc and washed twice with water. The organic layer was dried over $MgSO_4$ and the excess solvent removed *in vacuo*.

2.2.1. Diphenyl(diethylmalonyl)phosphine borane (**1**)

The pure product was isolated in the form of a white solid (54%).

TLC: R_f 0.15 (10:1 hexane:EtOAc); m.p: 74–76 °C; IR: ν_{max} ($CHCl_3$)/cm^{-1} 3009, 2390, 1732, 1256; ^1H NMR: (300 MHz, $CDCl_3$) δ_H 7.84–7.78 (m, 4H), 7.49–7.39 (m, 6H), 4.58 (d, 1H, J = 11.1 Hz), 3.97 (q, 4H, J = 7.1 Hz), 0.99 (t, 6H, J = 7.2 Hz), 1.62–0.58 (v br m, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ_C 164.2 (2C), 133.1 (d, 4C, J = 9.9 Hz), 131.7 (d, 2C, J = 2.3 Hz), 128.5 (d, 4C, J = 10.5 Hz), 126.5 (d, 2C, J = 55.0 Hz), 62.2 (2C), 52.3 (d, 1 C, J = 21.6 Hz), 13.4 (2C); ^{31}P NMR: (121 MHz, $CDCl_3$) δ_P 24.9 (br d, 1P, J = 41.1 Hz); CIMS: m/z 357 (M^+−1, 15%), 345 (M^+−BH_3+H, 100%); EIMS: m/z 357 (M^+−1, 5%), 344 (M^+−BH_3, 35%), 201 (M^+−$C_7H_9O_4$, 100%).

2.2.2. Diphenyl(methyldiethylmalonyl)phosphine borane (**2**)

The pure product was obtained via flash chromatography as a turbid oil (64%).

TLC: R_f 0.18 (10:1 hexane:EtOAc); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3011, 2395, 1730, 1256, 1105; ^1H NMR: (300 MHz, $CDCl_3$) δ_H 7.91–7.85 (m, 4H), 7.48–7.37 (m, 6H), 4.05 (q, 4H, J = 7.1 Hz), 1.71 (d, 3H, J = 14.7 Hz), 1.06 (t, 6H, J = 7.1 Hz), 1.58–0.61 (v br m, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ_C 168.3 (2C), 134.1 (d, 4C, J = 9.4 Hz), 131.4 (d, 2C, J = 2.6 Hz), 128.2 (d, 4C, J = 10.5 Hz), 127.1 (d, 2C, J = 54.3 Hz), 62.3 (2C), 55.3 (d, 1C, J = 20.2 Hz), 20.3 (d, 1C, J = 2.6 Hz), 13.5 (2C); ^{31}P NMR: (121 MHz, $CDCl_3$) δ_P 34.7 (broad d, 1P, J = 39.7 Hz); CIMS: m/z 371 (M^+−1, 25%), 359 (M−BH_3+H, 100%); EIMS: m/z 371 (M^+−1, 10%), 358 (M−BH_3, 20%), 329 (M−C_2H_7B, 100%), 188 (M−$C_8H_{17}O_4B$, 50%).

2.2.3. Diphenyl(dibenzylmalonyl)phosphine borane (**3**)

The pure product was isolated in the form of a clear sticky oil (67%).

TLC: R_f 0.19 (5:1 hexane:EtOAc); IR: ν_{max} ($CHCl_3$)/cm^{-1} 3009, 2390, 1734, 1216; ^1H NMR: (300 MHz, $CDCl_3$) δ_H 7.74–7.67 (m, 4H, aromatic H), 7.49–7.43 (m, 2H), 7.37–7.22 (m, 12H), 7.11–7.07 (m, 4H), 4.98 (d, 2H, J = 17.1 Hz), 4.94 (d, 2H, J = 17.4 Hz), 4.68 (d, 1H, J = 10.8 Hz), 1.80–0.56 (v br m, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ_C 164.0 (d, 2C, J = 2.5 Hz), 134.3 (2C), 133.1 (d, 4C, J = 10.0 Hz), 131.7 (d, 2C, J = 2.5 Hz), 128.6 (d, 4C, J = 10.6 Hz), 128.4 (4C), 128.4 (4C), 128.3 (2C), 126.1 (d, 2C, J = 55.2 Hz), 68.1 (2C), 52.3 (d, 1C, J = 20.5 Hz); ^{31}P NMR: (121 MHz, $CDCl_3$) δ_P 25.7 (br d, 1P, J = 20.1 Hz); CIMS: m/z 481 (M^+−1, 3%), 469 (M^+−BH_3+H, 20%), (M^+−$C_{22}H_{20}O_4PB$, 100%).

2.2.4. (2-Methyl-1,3-propanediol-2-yl)diphenylphosphine borane (**4**)

A suspension of 244 mg (6.44 mmol, 4 equiv.) of lithium aluminium hydride and 22 mL of ether was stirred at room temperature for 45 min. The suspension was cooled to 0 °C and a solution of **2** (600 mg, 1.61 mmol, 1 equiv.) in 14 mL of ether was added drop wise to the $LiAlH_4$/ether mixture using Schlenk syringe methods. The mixture was stirred at room temperature for 30 min, after which it was heated under reflux for a further 8 h. TLC was performed to assess the reaction progress. Slow addition of small pieces of ice destroyed the residual lithium aluminium hydride to quench the reaction. The product was extracted with DCM, citric acid and brine. The organic layer was dried over $MgSO_4$ and excess solvent was removed *in vacuo*. The desired pure product was obtained via flash chromatography as a white solid, (55%).

TLC: R_f 0.35 (1:1 hexane:EtOAc); m.p: 79–81 °C; IR: ν_{max} ($CHCl_3$)/cm^{-1} 3485, 3008, 2385, 1437, 1067; ^1H NMR: (300 MHz, $CDCl_3$) δ_H 7.92–7.86 (m, 4H), 7.51–7.42 (m, 6H), 4.03 (dd, 2H, J = 11.7 and 8.7 Hz), 3.64 (dd, 2H, J = 15.5 and 11.9 Hz), 2.46 (br s, 2H), 1.12 (d, 3H, J = 12.9 Hz), 1.65–0.50 (v br m, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ_C 134.0 (d, 4C, J = 8.6 Hz), 131.5 (d, 2C, J = 2.6 Hz), 128.7 (d, 4C, J = 9.9 Hz), 126.2 (d, 2C, J = 53.6 Hz), 66.5 (d, 2C, J = 5.6 Hz), 41.4 (d, 1C, J = 29.6 Hz), 17.4 (1C); ^{31}P NMR: (121 MHz, $CDCl_3$) δ_P 25.2 (br d, 1P, J = 69.5 Hz); CIMS: m/z 287 (M^+−1, 50%), 275 (M^+−BH_3+H, 100%), 257 (M^+−BH_3O, 15%); EIMS: m/z 287 (M^+−1, 5%), 274 (M−BH_3, 50%), 183 (M−$C_4H_{11}O_2B$, 60%), 108 (M−$C_{10}H_{17}O_2B$, 100%).

The decomplexation of the borane adducts using DABCO (1,4-diaazabicyclocyclo [2,2,2]octane) was carried out on the basis of previous studies [22] and, owing to several observed differences in reactivity, is detailed below.

2.3. General method for the synthesis of $PtCl_2$(monophosphine)$_2$ complexes (monophosphine = **1**–**4**)

To a three-necked flask equipped with a gas-inlet and a reflux condenser with a balloon at the top was added a degassed solution of $PtCl_2(PhCN)_2$ (236 mg, 0.5 mmol) and the borane adduct of **1** (1.05 mmol; or of **2**, **3** or **4**) in benzene (20 mL). This solution was heated to reflux under argon. A bright yellow homogeneous mixture resulted. Upon addition of DABCO (1.05 mmol) a white precipitate formed. The mixture was heated for 24 h. The small amount of precipitate was filtered off, the benzene was evaporated from the filtrate and the residue dried under vacuum for 2 h. The pale yellow highly viscous material was crystallised from a hexane–chloroform mixture. The target complexes were obtained as white powder-like solid materials.

*cis-$PtCl_2$(**1**)$_2$ (**1b**).* Yield: 67%. Anal. Calc. for $C_{38}H_{42}O_8P_2Cl_2Pt$ (954.68): C, 47.81; H, 4.43. Found: C, 47.96; H, 4.59%. For NMR data see Table 1.

*trans-$PtCl_2$(**2**)$_2$ (**2a**).* Yield: 70%. Anal. Calc. for $C_{40}H_{46}O_8P_2Cl_2Pt$ (982.73): C, 48.89; H, 4.72. Found: C, 48.97; H, 4.89%. For NMR data see Table 1.

*trans-$PtCl_2$(**3**)$_2$ (**3a**) and cis-$PtCl_2$(**3**)$_2$ (**3b**) (isolated as a mixture).* Yield: 79%. Anal. Calc. for $C_{58}H_{50}O_8P_2Cl_2Pt$ (1202.96): C, 57.91; H, 4.19. Found: C, 58.06; H, 4.30%. For NMR data see Table 1.

*trans-$PtCl_2$(**4**)$_2$ (**4a**) and cis-$PtCl_2$(**4**)$_2$ (**4b**) (isolated as a mixture).* Yield: 57%. Anal. Calc. for $C_{32}H_{38}O_4P_2Cl_2Pt$ (814.58): C, 47.18; H, 4.70. Found: C, 47.32; H, 4.84%. For NMR data see Table 1.

3. Hydroformylation experiments

In a typical experiment, a solution of 0.01 mmol of $PtCl_2$(monophosphine) (monophosphine = ligands **1**–**4**) and 0.02 mmol of tin(II) chloride in 10 mL toluene containing 1 mmol of styrene (**7**)

Table 1
NMR data of the platinum complexes containing monodentate phosphines **1**–**4**.[a]

Complex	δ_P[b] (ppm)	^1J(Pt,P) (Hz)	Yield of isomer[b] (%)
trans-$PtCl_2$(**1**)$_2$ (**1a**)	27.0	2845	5
cis-$PtCl_2$(**1**)$_2$ (**1b**)	3.1	3551	95
trans-$PtCl_2$(**2**)$_2$ (**2a**)	29.7	2872	100
trans-$PtCl_2$(**3**)$_2$ (**3a**)	27.5	2530	45
cis-$PtCl_2$(**3**)$_2$ (**3b**)	3.3	3578	55
trans-$PtCl_2$(**4**)$_2$ (**4a**)	39.0	2980	47
cis-$PtCl_2$(**4**)$_2$ (**4b**)	25.4	4079	53

[a] Measured in $CDCl_3$ (room temperature).
[b] Obtained by reacting 2 equiv. of phosphine with $PtCl_2(PhCN)_2$.

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 and the mixture was stirred with a magnetic stirrer for the given reaction time. 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.

4. Results and discussion

4.1. Synthesis of the complexes and their NMR investigation

The monodentate ligands (**1**–**4**) used in this study are depicted in Fig. 1. These ligands were prepared by treatment of Ph_2PCl with the relevant malonate anion obtained by reaction of the malonate ester with sodium hydride. Smooth conversion to the diphenylmalonylphosphine ensued and the borane adducts could be readily prepared by adding borane–THF to the reaction mixture, allowing isolation of the desired compounds. Reduction to the diol **4** was effected by treatment of the malonate derivative with $LiAlH_4$ in diethylether, without loss of the borane protecting group.

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 phosphine. Since the ligands are air sensitive they were stored as their borane adducts and deprotected immediately prior to (during) the preparation of the corresponding platinum precursors in a one-pot reaction, to avoid formation of the corresponding phosphine oxides. Both diethylamine and DABCO were used for the deborylation procedure of the $R_3P \cdot BH_3$ adducts; the DABCO system proved superior, providing clean reactions and the Pt complexes in acceptable yields.

Rather surprisingly, the diaryl-monoalkyl type phosphines of similar structure show different selectivities regarding complex formation. The two diethylmalonate derivatives (**1** and **2**) reacted with the $Pt(PhCN)_2Cl_2$ precursor selectively leading to the corresponding bis(monophosphino) complexes $PtCl_2(P)_2$ with *cis*-(**1b**, 95%) and *trans*-(**2a**, 100%) geometries, respectively. The use of the dibenzylmalonate **3** and the dihydroxy phosphine **4** resulted in the formation of the *cis*/*trans* mixture of 55/45 and 53/47, respectively.

The $PtCl_2(P)_2$-type complexes **1a–4a** and **1b**, **3b** and **4b** each showed a single central signal (flanked by platinum satellites, in a ratio of 1:4:1) in the ^{31}P NMR spectra thereof (Table 1). In these spectra, the coupling constants are diagnostic, showing values of 2800–3000 Hz or 3500–4100 Hz for the P-*trans* and P-*cis* complexes, respectively. The ^{31}P NMR spectra of platinum complexes provide a sensitive probe for the structures of complexes, even in complicated mixtures. The magnitude of the one-bond interactions, i.e. $^1J(^{195}Pt,^{31}P)$ coupling constants, has been shown to depend strongly on whether the P atom has another P atom or a chlorine atom as ligand in the position *trans* to it on the Pt. The P atom *trans* to chloro ligand possesses $^1J(^{195}Pt,^{31}P)$ coupling constants larger than 3500 Hz, while P nuclei *trans* to another P atom display typical platinum-phosphorus coupling constants of 2500–3000 Hz [23].

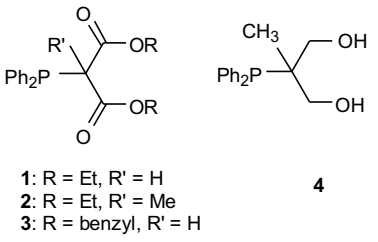


Fig. 1. The monodentate ligands (**1**–**4**) used in this study.

It is worth noting that the $^1J(^{195}Pt,^{31}P)$ coupling constants for the ligands possessing ester functionalities (**1**–**3**) fall in the typical ranges cited above. In contrast, both the *cis* and *trans* complexes of the dihydroxy derivative **4** possess larger couplings by about 400–500 Hz. Accordingly, direct interaction of the hydroxy functionalities with the central metal cannot be excluded.

4.2. Hydroformylation reactions

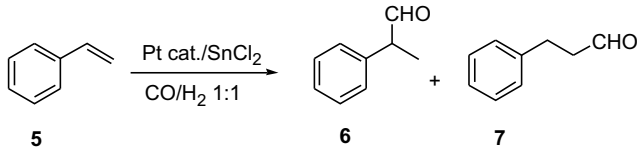
Pre-formed complexes $PtCl_2(L)_2$ (where L = **1**–**4,** Fig. 1) were used as catalysts for the hydroformylation of styrene (Scheme 1) in the presence of 2 equiv. of tin(II) chloride per Pt under 'oxo-conditions' ($p(CO) = p(H_2)$, 100 °C, as described in Table 2).

In addition to the aldehyde product regioisomers **6** and **7**, some hydrogenation product (ethylbenzene, **8**) may also be expected. Notwithstanding this possibility, the chemoselectivity towards aldehydes is very high and the formation of **8** is negligible (less than 0.5% in all cases and typically below than the GC–MS detection limit).

Although the activity of the platinum catalysts described here is lower than most of the platinum–*diphosphine*–tin(II)chloride systems tested to date [20], the novel ligand-containing catalysts are of interest from several theoretical points of view. The hydroformylation activity of the *in situ*-generated platinum–tin(II)chloride catalysts, obtained from $PtCl_2$(**1**), $PtCl_2$(**2**) and $PtCl_2$(**3**) precursors, is moderate and the conversions obtained in 24 h are nearly the same (Table 1, entries 1, 3 and 5). The regioselectivity towards branched aldehyde is high in all cases, especially with **1** and **2**, which give the highly sought after yet rarely observed exclusive formation of a single isomer. Higher conversions, accompanied by only a slight decrease in the regioselectivity, were observed in elevated reaction times as long as 120 h (entries 2, 4 and 6). It is worth mentioning that the application of the obvious analogues catalytic precursor, *cis*-$PtCl_2(PPh_3)_2$ resulted in much lower regioselectivity (entry 14). Similar results have been obtained by using the corresponding Pt–PPh_3–$SnCl_2$ '*in situ*' system for the hydroformylation of styrene [24].

Most interestingly, the analytical data for the Pt complexes of ligands **1** and **2** possess opposite stereochemistry: while that of **1** is *cis*, that of **2** is *trans*. The fact that the product formation is insensitive to this parameter implies one of several points. It is possible that the complex dissociates one of its P ligands to form structurally similar active catalysts for both instances, or the binding mode of the alkene to the Pt and the first step in the catalytic cycle is unaffected by the geometry of the Pt complex or that the geometry of one of the complexes changes to match the other *in situ*. It may be possible to elucidate which of these factors (or some other characteristic) determines this particular feature of the reaction outcome by attempting to isolate the Pt complex from the solution and investigating its structure. This aspect forms part of ongoing work in our laboratories.

Ligand **4**, which is more electron rich than its ester analogues, enables higher hydroformylation activities to be observed than its ester counterparts. It is worth noting that the reaction is sensitive to pressure. While the conversion is negligible under 80 bar pressure (CO/H_2 = 1:1), complete conversion may be obtained under 110 bar pressure (compare entries 7, 8 and 9).



Scheme 1.

Table 2
Hydroformylation of styrene with platinum complexes containing malonate-derived monodentate phosphines (**1**–**4**).[a]

Run	Catalyst	Solvent	Pressure (bar) p(CO)/p(H_2)	Conv. (%)	Products formed[b]			R_{br}[d] (%)
					Olig.[c] (%)	**6** (%)	**7** (%)	
1	$PtCl_2$(**1**)$_2$ + 2$SnCl_2$	Toluene	60/60	23	0	23	0	100
2	$PtCl_2$(**1**)$_2$ + 2$SnCl_2$	Toluene	60/60[e]	67	0	65	2	97
3	$PtCl_2$(**2**)$_2$ + 2$SnCl_2$	Toluene	60/60	53	0	53	0	100
4	$PtCl_2$(**2**)$_2$ + 2$SnCl_2$	Toluene	60/60[e]	90	0	88	2	98
5	$PtCl_2$(**3**)$_2$ + 2$SnCl_2$	Toluene	60/60	23	0	21	2	91
6	$PtCl_2$(**3**)$_2$ + 2$SnCl_2$	Toluene	60/60[e]	85	0	77	8	90
7	$PtCl_2$(**4**)$_2$ + 2$SnCl_2$	Toluene	40/40	4	0	2	2	50
8	$PtCl_2$(**4**)$_2$ + 2$SnCl_2$	Toluene	55/55	76	0	65	11	86
9	$PtCl_2$(**4**)$_2$ + 2$SnCl_2$	Toluene	55/55[e]	100	0	85	15	85
10	$PtCl_2$(**4**)$_2$ + 2$SnCl_2$	[BMIM][PF_6]	40/40	100	100	0	0	-
11	$PtCl_2$(**4**)$_2$ + 2$SnCl_2$	[BMIM][BF_4]	40/40	39	39	0	0	-
12	$PtCl_2$(**4**)$_2$ + 5$SnCl_2$	[BMIM][BF_4]	40/40	100	100	0	0	-
13	$PtCl_2$(**4**)$_2$ + 5$SnCl_2$	[BMIM][BF_4]	60/60	58	55	2	1	67
14	$PtCl_2(PPh_3)_2$ + 2$SnCl_2$	Toluene	60/60	66	0	30	36	45

[a] *Reaction conditions*: Pt/styrene = 1:100; T = 100 °C; t = 24 h.
[b] The rest is unconverted substrate.
[c] Dimers, oligomers, polymers [determined by GC (dodecane internal standard)]; the amount of the recovered substrate **1** is not indicated.
[d] R_{br} = regioselectivity towards branched aldehyde regioisomer [moles of **6**/(moles of **6** + moles of **7**) × 100].
[e] *Reaction time*: 120 h.

Ionic liquids have been found useful in a number of catalyst systems for several reactions including metathesis [25] and hydroformylation [26] reactions. Ligand **4** was expected to be a suitable ligand in ionic liquid catalysis due to the presence of the two polar hydroxyl groups enabling good solubility. Nevertheless, and disappointingly, attempted hydroformylation under standard conditions set out herein led exclusively to styrene oligomerisation and no formyl products were detected at all (entries 10–12). Even the increase of the total pressure to 120 bar (p(CO) = p(H_2) = 60 bar) resulted in the formation of aldehydes in traces only (entry 13).

In summary, the chemoselectivity of hydroformylation was excellent throughout, notwithstanding relatively slow rates of reaction. Importantly, ethylbenzene could be detected by GC–MS analysis in traces only, implying high degrees of chemoselectivity and that the catalysts are poor hydrogenation promoters. The regioselectivity is significantly influenced by the phosphorus ligands, and the branched aldehyde (2-phenyl-propionaldehyde) prevails under all conditions investigated, with single isomers (100% branched product) being observed in some cases.

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