Asymmetric hydroformylation catalysed by platinum complexes of new chiral bisphosphites

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Asymmetric hydroformylation of styrene using bis(phosphite)$PtCl_2$–$SnCl_2$ systems gives branched aldehydes with high enantioselectivity (up to 91%).

Asymmetric hydroformylation is a convenient synthetic method for obtaining optically active aldehydes from olefinic substrates.[1] These aldehydes are attractive building blocks in organic synthesis.[2] Most compounds which have been developed for chiral modification of catalysts are chiral derivatives of aryl- or alkyl-phosphines; less work has been done with less electron-rich ligands such as phosphites. For asymmetric hydroformylation of olefins, chiral diphosphine–Rh^I,[3] diphosphine–Pt^{II},[4] bisphosphite–Rh^I[5] or phosphinephosphite–Rh^I[6] have mostly been used. Surprisingly, however, there have been no reports on the application of bisphosphite–Pt^{II}–$SnCl_2$ complexes for asymmetric hydroformylation. This system may reasonably be expected to represent an alternative to the diphosphine system because the less electron-rich phosphites may cause dramatic changes in the reactivity and selectivity.

Here we report the synthesis and spectroscopic characterization of new bisphoshites, which afforded highly active platinum catalysts for asymmetric hydroformylation. The highest enantioselectivity (91%) was obtained with the platinum(ii)–$SnCl_2$ catalytic system associated with (2*S*,4*S*)-bis(*S*)-**1** and its enantiomer (2*R*,4*R*)-bis(*R*). These ligands are of particular interest, because they contain a chiral centre in the backbone and a chiral axis in the terminal groups. In this regard, these model ligands show the exploration of chiral cooperativity.

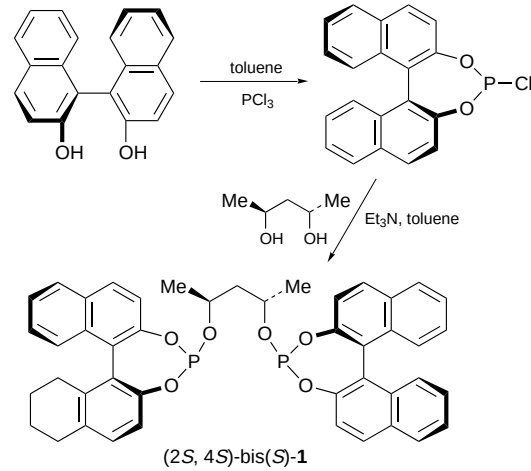
The reaction of racemic 1,1′-bi-2-naphthol with excess PCl_3 in toluene catalysed by 1-methylpyrrolidin-2-one gave phosphorochloridite (*S*,*R*)-6-chlorodinaphtho[*d*,*f*][1,3,2]dioxaphosphepine. Two equivalents of the racemic dioxaphosphepine were reacted with optically pure (2*R*,4*R*)-pentane-2,4-diol in the presence of triethylamine to give a diastereoisomeric mixture of 2,4-bis[dinaphtho[*d*,*f*][1,3,2]dioxaphosphepin-6-yloxy]-pentane. Diastereoisomers were obtained in a 1 : 2 : 1 ratio showing that the chiral pentanediol does not induce diastereoselectivity in the bisphosphite formation. Separation of the diastereoisomers was not successful.

In the ^{31}P NMR{^1H} spectrum of the product at ambient temperature, six lines are observed with relative intensities and splitting consistent with the expected three diastereoisomers. An explanation is that four resonances arise from the *meso* form, (2*R*,4*R*)-(*S*,*R*) = (2*R*,4*R*)-(*R*,*S*). The 2D homonuclear ^{31}P COSY NMR spectrum of the product confirms the existence of coupling ($^6J_{P–P}$ 9.5 Hz) between the P atoms (δ 149.0 and 153.6) six bonds apart.[7] Two singlets [δ 153.6 for (2*R*,4*R*)-bis(*R*)-**1** and 147.1 for (2*R*,4*R*)-bis(*S*)-**2**]) are attributed to the presence of the other two diastereoisomers. This was supported by the NMR spectra of the optically pure diastereoisomers obtained from (*S*)-6-chlorodinaphtho[*d*,*f*]-[1,3,2]dioxaphosphepine and (2*S*,4*S*)- (Scheme 1) or (2*R*,4*R*)-pentane-2,4-diol, respectively. In these cases the other two diastereoisomers were not detected by ^{31}P NMR. This implies that the diastereoisomers (**1** and **2**) were obtained in optically pure form. Optical resolution of 1,1′-bi-2-naphthol was carried out by using (*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*′,*N*′-tetramethylsuccinamide as a host compound[8] or (8*S*,9*R*)-(−)-*N*-benzylcinchonidium chloride as a resolving agent.[9]

Phosphites **1** and **2** in CD_2Cl_2 form phosphite–platinum complexes. The ^{31}P NMR{^1H} spectrum of $PtCl_2$[(2*S*,4*S*)-bis(*S*)-**1**] yields a characteristic satellite 'triplet' pattern (δ 87.5, $J_{Pt–P}$ = 5672 Hz) and of $PtCl(SnCl_3)$[2*S*,4*S*)-bis(*S*)-**1**] exhibits a P–P coupling pattern ($J_{P–P}$ = 20 Hz) with well separated chemical shifts (δ 98.0 and 89.1) and large inequivalent P–Pt coupling constants (5580 and 4420 Hz) as expected for inequivalent P atoms in positions *trans* to the chloro and $SnCl_3$ ligands, respectively. Reaction of $PtCl_2(PhCN)_2$ with both **1** and **2** afforded only the expected *cis* mononuclear eight-membered complexes without any oligomeric species. Oligomeric platinum complexes of diphospholes, dibenzophospholes and bisbinaphthophospholes have been reported with *trans* P–Pt–P disposition.[10]

In a typical experiment the autoclave was filled with solvent, alkene and the catalyst precursor. Catalysts were prepared *in situ* by simple mixing $PtCl_2(PhCN)_2$ in toluene or in dichloromethane with the ligands, while anhydrous $SnCl_2$ was used as co-catalyst. It was then purged with syn gas [$CO–H_2$ (1 : 1)] and pressurised. Catalytic reactions were carried out under classical conditions to give a mixture of the branched (*b*, 2-phenylpropanal) and the normal (*n*, 3-phenylpropanal) regioisomers and hydrogenated (ethylbenzene) products. At the end of the reaction the autoclave was cooled and depressurised. The reaction mixture was directly vacuum distilled to remove the catalyst. The reaction mixture and the distilled products were analysed by GC. The enantiomeric excess was determined by GC using a chiral capillary column.

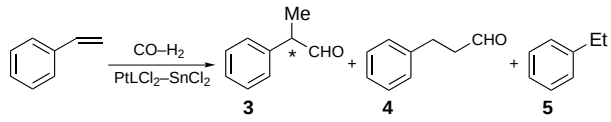
Some representative results are given in Table 1. When **1** or **2** was used as the ligand in platinum catalysed asymmetric hydroformylation of styrene, the absolute configuration of central chirality in the bridge is of primary importance in asymmetric induction (Table 1). In the case of (2*S*,4*S*)-bis(*S*)-**1**, there is a cooperative effect of the axial chirality of the terminal 1,3,2-dioxaphosphepine groups and the central chirality of the



(2*S*, 4*S*)-bis(*S*)-**1**

Scheme 1

Table 1 Enantioselective hydroformylation of styrene catalysed by bis(phosphite)$PtCl_2$-$SnCl_2$ complex [100 atm. of H_2–CO (1 : 1), P/Pt: 2.05, $SnCl_2$/Pt: 1.0][a]



3 **4** **5**

Ligand	*t*/h	*T*/°C	Solvent	Substr/Pt	Conv. (%)[b]	**5** (%)[b]	(*b*/*n*)[b]	Ee of **3** (%)[c]	Config.[d]
2	10	60	PhMe	2000	65	59	62/38	14	*S*
1	67	17	PhMe	2000	76	55	58/42	88	*R*
1	2	60	PhMe	2000	100	55	60/40	73	*R*
1	2	100	PhMe	2000	100	59	59/41	62	*R*
1	70	17	CH_2Cl_2	5000	90	54	60/40	91	*R*
1	4	60	CH_2Cl_2	5000	96	47	58/42	75	*R*
1	22	17	—	5000	50	48	58/42	89	*R*

[a] Reactions were carried out in the given solvent [*ca.* 2.5 mol dm^{-3}, except in CH_2Cl_2 (8.35 mol dm^{-3})] in a 20 ml stainless-steel autoclave under an atmosphere of H_2 and CO (1 : 1) at 100 atm. initial total pressure. [b] Conversions and composition of the reaction mixture (*b* : *n* : *h* branched : normal : hydrogenated) were determined by GC (SPB-1) using decane as an internal standard. [c] Determined by GC analysis (β-DEX, 30 m, id. 0.25 mm) of the corresponding acid. [d] Determined by the sign of optical rotation of the corresponding aldehyde.

backbone. The highest enantioselectivity (91% *R*) was obtained with the platinum(ii)–$SnCl_2$ catalytic system associated with (2*S*,4*S*)-bis(*S*)-**1** and its enantiomer (2*R*,4*R*)-bis(*R*)-**1** (matched constellation).[11] Reactions with (2*R*,4*R*)-bis(*S*)-**2** (mismatched constellation) resulted in much lower enantioselectivities. Up until now the highest enantioface discrimination (86.3% ee) has been reported[4b] for the hydroformylation of styrene to hydratropaldehyde with the platinum–Sn system [(*R*,*R*)-BCO-DBP]$PtCl_2$ [BCO-DBP = 5,5′-(bicyclo[2.2.2]octane-2,3-diyldimethyl)bis(5*H*-benzo[*b*]phosphindole)].

Addition of $SnCl_2$ is essential for catalytic activity. The role of the $SnCl_2$ co-catalyst in promoting the key steps of Pt–Sn-catalysed hydroformylation, such as the alkene insertion, the CO insertion and the hydrogenolysis of acyl complexes, has been thoroughly investigated.[12] A dramatic increase in reaction rate and a slight decrease in enantioselectivity were found when the reaction temperature was increased. Regioselectivity was almost independent of reaction temperature.

In spite of the high hydrogenation activity of the catalyst, we were able to find a catalytic system with remarkably high hydroformylation activity. For example, in dichloromethane at 60 °C, hydroformylation rates of *ca.* 1100 and 530 turnovers h^{-1} at 54 and 88% of conversion were observed in combination with high enantioselectivity (75% ee), respectively. Surprisingly when $Rh(CO)_2(acac)$ was used as a catalytic precursor (100 atm. and 60 °C) both diastereoisomers afforded the same preferred *R* enantiomer in the product with the same regioselectivity (81 : 19 *b*/*n*), enantioselectivity (16% ee) and with complete chemoselectivity.

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Footnote

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