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Asymmetric hydroformylation of styrene catalysed by platinum–tin complexes with chiral bis-binaphthophosphole ligands

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Abstract

A set of novel bidentate ligands **2**, **3** and **4**, which have two axially chiral binaphthophospholyl (BNP) substituents connected through a carbon chain of different lengths (two to four atoms), has been synthesised by alkylating the binaphthophospholyl anion with the appropriate diiodide or ditosylate. In solution the free diphospholes display fluxional behaviour because of the ready atropisomerisation of the binaphthyl backbone. Consistent with their structure, the reaction of the bis(BNP) compounds with platinum(II) derivatives gives either *cis* chelate mononuclear complexes or *trans* phosphorus-bridged polynuclear derivatives. The latter can be converted into the mononuclear species by warming them in the presence of $SnCl_2$. Coordination to platinum enhances the conformational stability of **3** and **4** and separate diastereomeric complexes can be detected in solution up to about 50°C. In the presence of $SnCl_2$, the platinum complexes containing **3** and **4** give rise to catalysts which exhibit remarkable activity in the hydroformylation of styrene. Under optimum conditions, reaction takes place with unprecedently high branched selectivity (80%–5%) and moderate enantioselectivity (up to 45% e.e.).

Keywords: Chiral phospholes; Atropisomeric ligands; Asymmetric hydroformylation; Platinum catalysts

1. Introduction

The asymmetric hydroformylation of olefins holds enormous potential for the synthesis of optically active aldehydes. These are valuable intermediates in the preparation of a great variety of biologically active compounds [1]. Unfortunately, of the enantioselective processes catalysed by transition metal complexes, hydroformylation is one of the most difficult to assess for several reasons. There are chemoselectivity problems since hydrogen is one of the reagents and hydroformylation catalysts are also able to promote hydrogenation and double-bond migration. There are regioselectivity problems since the reaction involves the addition of non-symmetric groups to the double bond of a usually non-symmetric substrate. There are obviously stereoselectivity problems also related to the efficiency of transfer of the chiral information from the catalyst to the substrate. An appropriate balance of these parameters is necessary to obtain efficient asymmetric hydroformylation and this requires that favourable conditions for all three kinds of selectivity, as well as for the catalytic activity, have to be met at the same time.

The asymmetric hydroformylation of styrene has received particular attention since it is the model reaction for the synthesis of α-arylpropanoic acids, an important class of non-steroidal anti-inflammatory agents. Both rhodium and platinum–tin complexes with chiral ligands have been employed successfully as catalysts in this reaction. For a long time rhodium catalysts have been believed to be more chemo- and regio-selective, whereas platinum catalysts have been assessed to be more stereoselective. This now seems about to change following the recent reports by Takaya who obtained quite high e.e. values (73%–95%) in the asymmetric hydroformylation of terminal [2] as well as internal olefins [3] with rhodium complexes containing ligand with a binaphthyl-core and mixed phosphine–phosphite. Comparably high enantioselectivities have been obtained in a few instances with Pt-based catalysts [4,5]. However, when bidentate phosphines are

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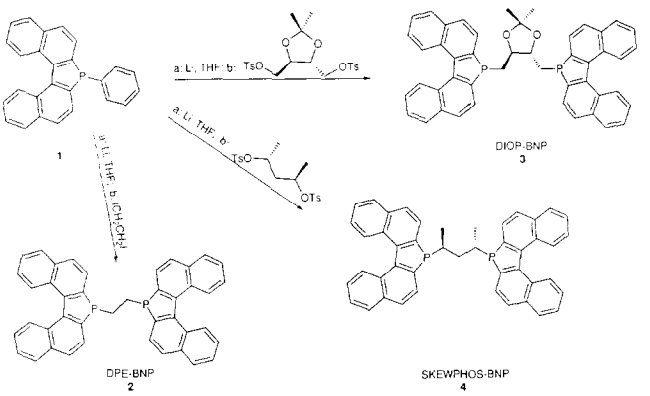
employed, the regioselectivity of the reaction is poor and the amount of the branched aldehyde is fairly low [branched/linear (B/L) = 0.5]. This trend can be reversed by exchanging the diphenylphosphino groups of the ligand for dibenzophosphole. Even then, branched selectivity is not very high with the best B/L ratio not exceeding 4, and the overall yield of the chiral aldehyde is still unsatisfactory because of competitive hydrogenation of the substrate.

Quite recently, the preparation of binaphthophospholes such as **1** has been reported [6,7]. These compounds have a phosphole ring merged within the atropisomeric binaphthyl backbone and contain in an unique structure some of the main features which are assumed to be at the basis of highly efficient chiral ligands: axial chirality, C_2 local symmetry and endocyclic phosphorus centre. Some aspects of the chemistry of this new class of phosphacyclic derivative have been discussed [8,9] and the ability of *P*-phenylbinaphthophosphole (**1**) to act as a unidentate ligand towards d^8 metal centres has been demonstrated [10,11]. During the course of these investigations, it emerged that binaphthophospholes undergo fast atropisomerization of the binaphthyl framework in solution at room temperature, both in the free and bound state, and therefore they cannot be regarded as appropriate chiral inducers for enantioselective reactions. Despite this conformational lability, we thought that chelating phosphacyclic ligands where two binaphthophosphole units are connected by a chiral alkyl backbone of suitable length might display some interesting properties in enantioselective catalysis and we decided to prepare this novel kind of donor.

In this paper, we report the synthesis of the new bis-(binaphthophosphole) donors **2**, **3** and **4** as well as the preparation, NMR behaviour and catalytic activity in the hydroformylation of styrene of their platinum complexes.

2. Results and discussion

For the synthesis of the chelating bis-(binaphthophosphole) (BNP) compounds, *P*-phenylbinaphthophosphole (**1**) was used and the preparation was carried out as depicted in Scheme 1.Reductive cleavage of **1** with lithium leads to the selective loss of the *P*-phenyl group, producing the corresponding phospholyl anion in almost quantitative yield. This reacts smoothly at 0°C with 1,2-diiodoethane as well as with the enantiopure ditosylates **5** and **6** affording the potentially bidentate donors **2**, **3** and **4**. These are the BNP analogues of the well-known diphosphines DPE, DIOP and SKEWPHOS [12], respectively. They were isolated as crystalline powders in 50%–60% yield after flash chromatography, and their identity was confirmed



Scheme 1. Preparation of 1, *n*-bis-(binaphthophospholyl)alkanes.

by elemental analyses and multinuclear NMR spectroscopy. As a consequence of the fast atropisomerisation of the binaphthyl framework, these ligands all display fluxional behaviour in solution. For instance, the NMR spectrum of compound **2** at room temperature shows the methylene protons as a very broad peak at ca. δ 1.6 ppm, the phosphorus resonance as a sharp singlet at −3.78 ppm and the aliphatic carbons as a doublet at 21.27 ppm (J_{P-C} = 28 Hz). At 223 K all these signals are split into two separate sets of peaks. This also occurs to the most deshielded peaks of the ^{1}H NMR spectrum: the doublet observed at room temperature (δ 8.46 ppm, J = 7.5 Hz) is split into two sharply distinct resonances at δ 8.42 ppm (d, J = 7.5 Hz) and δ 8.50 ppm (d, J = 7.5 Hz) at 223 K. A similar splitting of resonances was observed in the variable-temperature NMR spectra of **3** and **4**.

Addition of DPE–BNP (**2**) to a refluxing benzene solution of $[(PhCN)_2PtCl_2]$ led to the formation of a nearly insoluble precipitate. The ^{31}P NMR spectrum of this product at room temperature showed that three different species are present in dilute CD_2Cl_2 and $CDCl_3$ solutions. The first (A) has δ 43.5 ppm, ^1J(Pt—P) = ca. 2500 Hz in $CDCl_3$ and δ 43.1 ppm, ^1J(Pt—P) = ca. 2500 Hz in CD_2Cl_2. The second (B) shows δ 47.2 ppm, ^1J(Pt—P) = ca. 2560 Hz in $CDCl_3$ and δ 46.4 ppm, ^1J(Pt—P) = ca. 2500 Hz in CD_2Cl_2. The third (C) shows δ 49.6 ppm, ^1J(Pt—P) = 3524 Hz in $CDCl_3$ and δ 50.2 ppm, ^1J(Pt—P) = 3514 Hz in CD_2Cl_2. Both the main and the satellite peaks of species A and B appear as very broad lines (line half-width ca. 40 and 90 Hz for A and B, respectively), whereas the spectrum of C is characterised by very sharp resonances in all cases. Addition of $SnCl_2$ caused the separation of an orange precipitate and the disappearance of the signals corresponding to A and B while the spectrum of C was unaffected.

When the original precipitate was dissolved in DMSO-d_6, a golden coloured, fairly concentrated homogeneous solution was obtained. The ^{31}P NMR spectrum of the crude reaction mixture showed the pres-

ence of three species, characterised by approximately the same chemical shifts and coupling constants as those obtained in chlorinated solvents. A: δ 14.1 ppm, ^1J(Pt—P) = ca. 2500 Hz (broad lines); B: δ 47.5 ppm, ^1J(Pt—P) = ca. 2500 Hz (broad lines); C: δ 52.3 ppm, ^1J(Pt—P) = 3513 Hz. The DMSO solution as obtained at room temperature consisted of the above species in the ratio A B C = 55:22:23. This composition was slightly modified by the addition of 3 equiv. of $SnCl_2$ (A B C = 45:12:43) and was substantially shifted towards compound C on heating the mixture at 90°C for 2 h (A B C = 5: < 1:95). No $SnCl_2$ insertion into the Pt—Cl bond was observed during this treatment, even in the presence of a fivefold excess of $SnCl_2$.

From these results, it is readily apparent that all three complexes A, B and C are 1:1 Pt–binaphthophosphole adducts and that all possess two equivalent phosphorus atoms. The presence of Pt satellites demonstrates that each P atom is bonded to the metal. From the magnitude of the J(Pt—P) coupling constants, a *trans* P—Pt—P geometry can be confidently attributed to both A and B, while for C a *cis* P—Pt—P disposition must be assumed. These spectral data suggest that A and B are polynuclear complexes, oligomers or cyclo-oligomers, with the bisphosphole derivative acting as a bridging ligand between two different metal centres. The formation of similar oligomeric platinum complexes with diphospholes or dibenzophospholes has been already reported [13,14]. In contrast, C appears to be a mononuclear chelate complex with DPE–BNP acting as a normal bidentate ligand. Upon warming for a few hours in DMSO solution in the presence of $SnCl_2$, A and B underwent depolymerisation and were converted into C.

Reaction of $[(PhCN)_2PtCl_2]$ with both DIOP–BNP (**3**) and SKEWPHOS–BNP (**4**) afforded only the expected mononuclear chelate complexes without any polymeric species. In $CDCl_3$ solution, both these complexes showed a fluxional behaviour as demonstrated by variable-temperature ^{31}P NMR spectroscopy. The complex $[PtCl_2$(SKEWPHOS–BNP)] (**9**), for example, shows at room temperature three different phosphorus resonances at room temperature at δ 14.8, 13.0 and 10.2 ppm with J(Pt—P) ca. 3300 Hz in about 6:3:1 ratio. From the values of the coupling costants a *cis* P—Pt—P arrangement is postulated for each of these species. A similar pattern was observed in the case of $[PtCl_2$(DIOP–BNP)] (**8**). At room temperature, three compounds in ca. 2:1:1 ratio having phosphorus resonances at δ 8.8 ppm [J(Pt—P) = ca. 3490 Hz], δ 7.5 ppm [J(Pt—P) = ca. 3450 Hz] and δ 3.9 ppm [J(Pt—P) = ca. 3560 Hz], respectively, were observed in $CDCl_3$ solution. The fact that each resonance is accompanied by Pt satellites in the 3500 Hz range is consistent with a *cis* square-planar arrangement around the metal for each species. Coalescence of the ^{31}P resonances into a more-or-less broad signal was observed when solutions of **8** and **9** were warmed to about 50°C. The original spectra could be reproduced on cooling the samples down to room temperature. These spectra were also unaffected by the addition of $SnCl_2$ to the solutions.

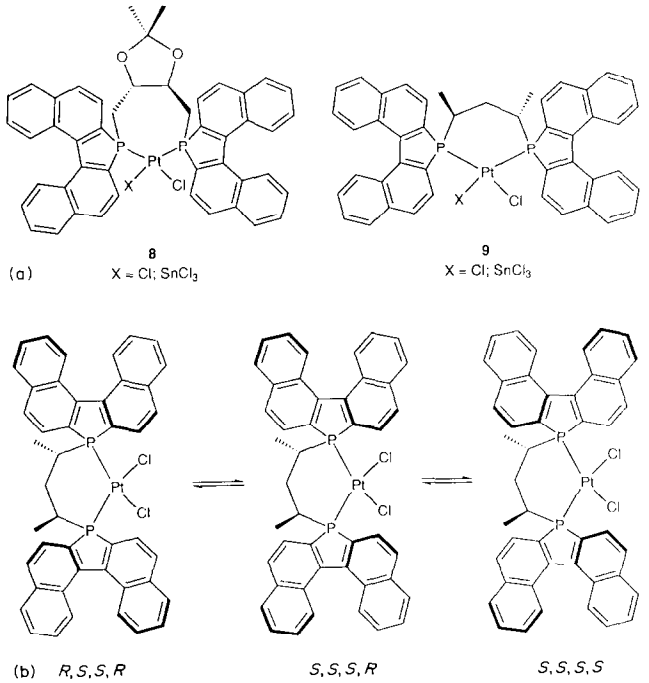
The variable-temperature NMR experiments suggest that the fluxional behaviour observed in the case of $[PtCl_2$(SKEWPHOS–BNP)] (**9**) and $[PtCl_2$(DIOP–DNP)] (**8**) is a consequence of the atropisomerisation experienced by the binaphthyl groups. Below the coalescence temperature, this equilibrium is frozen and different complexes should result depending on the relative chirality assumed by the binaphthyl substituents of the ligands. In the case of SKEWPHOS–BNP and DIOP–BNP, which contain equivalent stereogenic centres in the carbon backbone, three diastereoisomers can be expected, one in which the two binaphthyls have opposite chirality (*R*, *S* or *S*, *R*) and two where the binaphthyls have the same chirality (*R*, *R* and *S*, *S*). The structures of complexes **8** and **9** and of the species involved in the dynamic equilibrium are reported in Scheme 2.

Complexes **7**, **8** and **9** were tested for catalytic activity in the hydrofomylation of styrene. The catalytic

Table 1
Hydroformylation of styrene in the presence of $[PtCl_2$(bis(binaphthophosphole)$]$ + $SnCl_2$ catalysts [a]

Run	Catalyst	Time (h)	Temp. (°C)	Conv. (%)	RCHO [b]	Branched [c]	e.e. (%) [d]
1	**7** + $SnCl_2$	24	90	6	48	72	–
2	**8** + $SnCl_2$	20	85	97	64	63	20
3	**8** + $SnCl_2$	20	58	50	74	68	44
4	**8** + $SnCl_2$	40	38	22	73	66	39
5	**8** + $SnCl_2$ [e]	380	32	77	78	63	43
6	**9** + $SnCl_2$	22	58	45	76	68	17
7	**9** + $SnCl_2$	22	34	10	71	65	18
8	**9** + $SnCl_2$ [e]	93	32	97	73	78	24
9	**9** + $SnCl_2$ [f]	70	32	89	68	80	24
10	**9** + $SnCl_2$ [g]	70	32	95	55	85	20

[a] Reaction conditions: Pt/substrate = 1:1750; Pt/$SnCl_2$ = 1:2; solvent, toluene; $p(CO) = p(H_2) = 40$ atm.
[b] Aldehydes/(aldehydes + ethylbenzene) × 100. [c] Branched aldehyde/(branched + normalaldehydes) × 100. [d] The predominant enantiomer always had an *S*-configuration. [e] 55 atm H_2 + 40 atm CO. [f] 80 atm H_2 + 40 atm CO. [g] 100 atm H_2 + 20 atm CO.



Scheme 2. (a) Platinum 1, *n*-bis(binaphthophospholyl)alkane complexes and (b) interconversion of bis-(binaphthophospholyl)platinum complexes through atropisomerisation.

reactions were run in toluene at constant substrate-to-metal ratio (1750:1) in the presence of 2 mol equiv. of $SnCl_2$ as promoter. It is assumed that hydroformylation is preceded by formation of trichlorostannylplatinum complexes such as **8** and **9** (X = $SnCl_3$). The most significant results are listed in Table 1.

Complex **7** produced a catalytic system of negligible activity (Run 1) confirming previous reports on the low catalytic activity in hydroformylation of platinum–diphosphine complexes containing a five-membered chelate ring [15]. In contrast, the catalysts obtained from **8** and **9** displayed remarkable activity. This allowed us satisfactory conversions in a reasonable time even at 32°C. The effect of temperature on the reaction rate was substantially different for **8** and **9**. As the reaction temperature decreased from 58°C to 32°C, the turnover frequency of the SKEWPHOS–BNP catalyst changed from 36 to 18 mol h^{-1} (Runs 6 and 8), while the reaction rate of the DIOP–BNP complex was reduced to one-tenth of the original value (Runs 3 and 5). The chemo- and regio-selectivities of the DIOP–BNP catalysts were almost independent of temperature below 60°C and were comparable with the values recorded with the analogous DIOP–DBP (dibenzophosphole) catalyst under similar conditions [16]. The enantioselectivity was also almost unaffected by temperature variations below 60°C, but was definitely lower than in the DIOP–BDP case. The configuration of the predominant enantiomer was opposite to that recorded with DIOP [17] and DIOP–DBP [5,16] catalysts.

The SKEWPHOS–BNP-based catalyst **9** was more active than **8** in the low-temperature range, while at high temperature the situation was reversed. The enantioselectivity of the reaction was consistently low and substantially unaffected by variations in the reaction parameters. Unlike the previous case, the branched isomer has the same configuration as obtained with SKEWPHOS [18]. Catalytic activity and branched selectivity were favourably influenced by hydrogen-rich gas mixtures (Runs 8, 9 and 10). This effect on the regioselectivity was particularly pronounced and regioselectivity could be improved to 85% when the reaction was run at low temperature (compare Runs 7 and 10).

3. Experimental details

3.1. General procedures

Melting points are uncorrected. IR spectra were recorded in KBr pellets on a BIO-RAD FTS-7PC spectrophotometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian VXL 5000 spectrometer at 300, 75.5 and 121.42 MHz, respectively, in CD_2Cl_2, $CDCl_3$ and DMSO-d_6 solution. Chemical shifts of protons and carbons are in δ (ppm) referred to TMS as internal standard; ^{31}P chemical shifts are in ppm with respect to H_3PO_4 as external standard. Mass spectra were recorded on a Hewlett Packard 5988A spectrometer. Elemental analyses were performed with a Perkin-Elmer Analyser 240B. The optical rotation of 2-phenylpropanal was measured in benzene solution on a Perkin-Elmer 241 polarimeter. GLC analyses were performed on a Hewlett Packard 5890A gas chromatograph using a 30 m cyclodex-β column (J & W Scientific). Flash column chromatographies were carried out using Merck silica gel 60 (230–400 mesh) according to literature methods [19]. Air- and moisture-sensitive reactions were performed with the usual inert-atmosphere techniques. Commercial chemical reagents were used as received and solvents were dried by standard procedures and stored over molecular sieves under an inert atmosphere. [$PtCl_2(PhCN)_2$] was prepared from $PtCl_2$ in hot benzonitrile by the standard method [20].

3.2. Synthesis of binaphthophospholes: general procedure

7-Phenylbinaphtho[2,1-b;1′,2′-d]phosphole (**1**) (0.30 g, 0.83 mmol) was added to a suspension of lithium (0.011 g, 1.66 mmol of a 25% mineral oil dispersion) in dry THF (10 ml) at room temperature under dinitrogen. The mixture was heated under reflux for 3 h, then cooled to room temperature and a solution of t-butyl chloride (0.09 ml, 0.83 mmol) in dry THF (5 ml) added. After warming under reflux for further 3 h, the dark-red solution was cooled to 0°C, 0.5 mmol of the appropri-

ate alkyl halide or tosylate (1,2-dilodoethane for **2**; (+)-2,3-*O*-isopropylidene-L-threitol ditosylate (**5**) for **3**; (2*R*, 4*R*)-2,4-pentanediol ditosylate 6 for **4**) in dry THF (5 ml) was added and the solution heated under reflux for 6 h. After cooling to room temperature, saturated aqueous ammonium chloride (100 ml) was added, THF was rotoevaporated and the residue was extracted several times with dichloromethane. The organic layer was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was purified by flash chromatography (9 : 1 hexane/dichloromethane as eluent) and recrystallised from dichloromethane/hexane.

1,2-Bis-(binaphtho[2,1-b;1′,2′-d] phospholyl)ethane, (DPE–BNP) (**2**): 57% yield; m.p. 107–108°C. ^{1}H NMR δ: 1.10 (d, $^2J_{PH}$ = 9.0 Hz, 4H, —CH_2); 7.47 (dd, J = 0.6, 7.2 Hz, Ar, 4H); 7.55 (dd, J = 1.2, 6.6 Hz, Ar, 4H); 7.80–8.20 (series of m, Ar, 8H); 8.05 (d, J = 7.5 Hz, Ar, 4H); 8.42 (d, J = 8.1 Hz, Ar, 4H) ppm. ^{31}P NMR δ: −3.78 (bs) ppm. Analysis: Calc. for $C_{42}H_{28}P_2$: C, 84.84; H, 4.75%. Found: C, 84.52; H, 4.48%. MS: 594.2 (M^+, 5%); 297.0 (9%); 280.9 (100%); 140.4 (7%).

(4*S*, 5*S*)-2,2-Dimethyl-4,5(binaphtho[2,1-b;1′,2′-d]phospholyl)-1,3-dioxolane, (DIOP–BNP) (**3**): 50% yield; m.p. 145–147°C. ^{1}H NMR δ: 1.60 (s, 6H, —CH_3); 2.05 (m, 4H; —CH_2—); 4.11 (m, 2H, —CH—); 7.27–7.65 (series of m, Ar, 8H); 7.70–8.25 (series of m, Ar, 12H); 8.37 (d, J = 8.4 Hz, Ar, 4H) ppm. ^{31}P NMR δ: 6.28 (bs) ppm. Analysis: Calc. for $C_{47}H_{36}O_2P_2$: C, 81.25; H, 5.22%. Found: C, 81.46; H, 5.02% MS: 694.7 (M^+, 4%); 354.0 (11%); 281.9 (100%); 251.9 (47%); 140.4 (13%).

(2*S*, 4*S*)-2,4-Bis-(binaphtho[2,1-b;1′,2′-d]phospholyl)pentane, (SKEWPHOS–BNP) (**4**): 47% yield; m.p. 170–172°C. ^{1}H NMR δ: 0.90 (m, 6H, —CH_3); 1.48 (m, 2H, —CH_2—); 2.35 (m, 2H, —CH—); 7.37–7.60 (series of m, Ar, 16H); 8.00 (d, J = 8.4 Hz, Ar, 4H); 8.40 (d, J = 8.4 Hz, Ar, 4H) ppm. ^{31}P NMR δ: 7.52 (bs) ppm. Analysis: Calc. for $C_{45}H_{34}P_2$: C, 84.89; H, 5.38%. Found: C, 84.56; H, 5.32%.

3.3. Preparation of binaphthophospholeplatinum complexes

To a refluxing yellow solution of 91.3 mg (0.193 mmol) of [$PtCl_2(PhCN)_2$] in benzene, a suspension of 115 mg (0.193 mmol) of DPE–BNP in 10 ml benzene was added under dinitrogen. After a few minutes time pale-yellow crystals were obtained. The mixture was heated under reflux for 12 h until no more free donor was present in solution. The solution was cooled to room temperature, the solid was filtered off, washed with benzene and dried under reduced pressure to give 150 mg (0.175 mmol; 91%) of [{$PtCl_2$(DPE–BNP)}]$_n$ as an oligomeric complex.

In the case of SKEWPHOS–BNP and DIOP–BNP, stirring for 1 h was sufficient to complete the reaction. [$PtCl_2$(SKEWPHOS–BNP)] (**8**) and [$PtCl_2$(DIOP–BNP)] (**9**) complexes were obtained in 89% and 94% yield, respectively. The complexes were identified by multinuclear NMR.

3.4. Hydroformylation experiments: general procedure

In a typical experiment, 0.005 mmol of [$PtCl_2$(bis-(dinaphtophosphole)}], 1.9 mg (0.01 mmol) of $SnCl_2$, 1 ml (8.7 mmol) of styrene and 10 ml of toluene were placed under dinitrogen into a 100 ml stainless steel autoclave. The autoclave was pressurised to 80 atm total pressure (CO H_2 = 1 : 1), placed in an oil bath and agitated by an arm shaker. After cooling and venting, the solution was removed and fractionally distilled to enable determination of the optical purity by polarimetry. The extent of conversion and composition of the reaction products were determined by GC (110°C). The e.e. was determined in the same manner on the corresponding carboxylic acids obtained by $KMnO_4$ oxidation [21] of a sample of the crude reaction mixture. The retention times (from 100°C to 170°C at 5°C min^{-1}) of (*S*)- and (*R*)-2-phenylpropanoic acid were 15.9 and 16.2 min, respectively.

4. Conclusions

Bidentate phosphacyclic ligands where two BNP units are connected by a chiral three or four carbon chain readily bind to platinum (II) affording mononuclear six- or seven-membered chelate complexes. The atropisomerisation of the binaphthyl frameworks of the ligands, which takes readily place at room temperature when unbound, is slowed by coordination and diastereomeric species are identified in solution up to 50°C. This is in keeping with the behaviour of simple mono-BNP derivatives [6,11].

The Pt complexes are the precursors of very efficient catalysts for the asymmetric hydroformylation of styrene. Almost quantitative conversions can be recorded even at a temperature as low as 32°C with a branched selectivity that, to the best of our knowledge [1], is the highest so far observed with a Pt catalyst. These favourable figures, however, contrast with the modest enantioselectivity of the process. This can be attributed either to the conformational lability of the BNP framework in runs over 50°C or, at lower temperatures, to the presence of different catalytic species in solution. Better results are expected for reaction at low temperatures in the presence of a single complex as the

[1] A higher branched selectivity (92%) is claimed in Ref. [14]. This was later corrected to 80% (see Ref. [5], p. 2048).

catalyst, and attempts to isolate a pure single diastereomeric species are in progress.

With both catalysts, the e.e. of the chiral isomer does not vary significantly upon changing the temperature. This trend is completely different from that observed in the SKEWPHOS case [22], where inversion of configuration takes place on increasing the reaction temperature. This may be related to the extreme rotational freedom of the diphenylphosphino substituent as compared to that of the BNP group. However, a BNP substituent plays a significant role in the stereochemical outcome of hydroformylation as demonstrated by the reversal of the enantioselection observed in the series of DIOP-related ligands.

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