# Atropisomeric Binaphthalene-Core Phosphacyclic Derivatives in Coordination Chemistry and Homogeneous Catalysis

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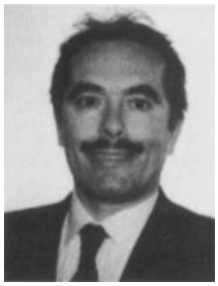
Binaphthophospholes and binaphthophosphepines have recently been synthesized. These are the first representatives of a new class of chiral ligands that include within the same structure an endocyclic phosphorus donor, a local $C_2$ symmetry and an axially chiral core. In this review we discuss the synthesis, chemical behaviour and first applications in asymmetric catalysis of these novel derivatives.

**Contents**



## Introduction

Axially chiral auxiliaries based on the atropisomeric 1,1'-binaphthalene backbone have enjoyed considerable success in recent years due to the remarkable efficiency that many of them have shown in a variety of asymmetric reactions, both stoichiometric and catalytic[1]. Among these, phosphorus derivatives play a prominent role because they are the most popular chiral inducers in transition-metal-



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**MICROREVIEWS:** This feature introduces Berichte's readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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catalysed enantioselective reactions. The asymmetric hydrogenation of olefins and ketones by Rh(I) and Ru(II) catalysts with BINAP[2], the enantioselective hydroformylation of vinylarenes by Rh(I) complexes containing mixed phosphinophosphito ligands[3], the asymmetric hydroboration of alkenes by rhodium catalysts with the P,N-heterodonor ligand QUINAC developed by Brown[4], and the enantioselective hydrosilylation of olefins by Pd catalysts with the monodentate 2-(1,1'-binaphthyl)diphenyl phosphane[5] (or the 2'-methoxy analogue, MOP[6]) provide remarkable examples of the versatility of these derivatives in asymmetric catalysis.

The hindered rotation around the σ-bond connecting the naphthyl groups is at the basis of the atropisomerism of these products. Their optical stability is determined by the steric hindrance of the substituents in the 8,8'- and 2,2'-positions of the binaphthyl moiety, which in most cases efficiently prevents interconversion between the two atropisomeric conformations. Sometimes, however, racemization may take place. This can occur through two different reaction pathways: a *syn* process, involving close contacts of the groups in the 2,2'- and 8,8'-positions, or an *anti* process, with close contacts of the groups in the 2',8- and 2,8'-positions. Computational studies have indicated that the preferred pathway may change depending on the structure of the substrate[7]. The *anti* process is slightly preferred in the case of unsubstituted 1,1'-binaphthyl, but the *syn* pathway is by far the more favourable when bulky substituents like bromine are present in the 2,2'-position.

During recent years a large part of our research efforts in the field of asymmetric catalysis has been aimed at exploiting the potential of binaphthalene-core phosphacyclic derivatives in asymmetric catalysis. These compounds possess an endocyclic phosphorus donor embedded in the $C_2$-symmetric environment created by the axially chiral diaryl backbone. This combination of structural elements appeared to us particularly attractive because of the excellent stereoselectivities recorded in the asymmetric hydrogenation and hydroformylation of olefins with, respectively, rhodium[8] and platinum–tin catalysts[9] containing $C_2$-symmetric phospholes or phospholanes as bidentate ligands.

At the time we started this investigation[10], binaphthalene-core phosphacyclic derivatives had no precedent in the literature. It later turned out that we were not the only people to be attracted by them. Much to our surprise, while our first contribution to this topic was in press[11], a paper by B. Wild and co-workers, reporting on binaphthophospholes and -arsoles, appeared in *The Journal of Organometallic Chemistry*[12]. A few months later a further report on a Pd complex with *P*-phenylbinaphthophosphole was published in the same journal by a Japanese group[13]. As occurs sometimes, various groups were independently and simultaneously pursuing similar objectives in a serendipitous competition.

## 2. Binaphthophospholes and Binaphthophosphepines

### 2.1. Synthesis and Reactivity

Binaphthophosphole (BNP) derivatives have been prepared according to three different procedures. Methods A and B provide for the building up of the heterocyclic core, whereas method C relies on the preformed phosphacyclic derivative **2b** as the substrate (Table 1).

*P*-phenyl BNP (**2b**) can be obtained in low yield (20–25%) by cycloaddition reaction of 3,4,3',4'-tetrahydro-1,1'-binaphthalene [bis(dialine), **1**] with dichlorodiphenylphosphane[10]. This cycloaddition, sometimes called the McCormack reaction, proceeds at fairly high temperature and is plagued by the formation of several side products. The main by-product is *P*-phenyl tetrahydrobinaphthophosphole (**3**). Only the stereoisomer with the *cis* fusion of the highly distorted phospholene and cyclohexene rings could be isolated. This finding provides some clue as to the stereochemistry of the hydrogen-transfer process following the McCormack reaction.

Reaction of the appropriate dichlorophosphane with 2,2'-dilithio-1,1'-binaphthalene (**4**) provides a straightforward entry into the BNP nucleus and, not surprisingly, this procedure (method B) was utilized by all the groups who prepared *P*-phenylbinaphthophosphole **2b**. This process is much more expedient and better yielding than the previous one and should be considered the method of choice for the preparation of binaphthophopholes whenever the dichlorophosphane is easily available[14].

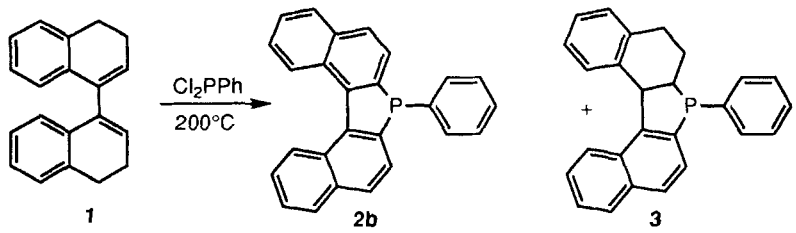
*P*-phenylbinaphthophosphole (**2b**) is itself a valuable source of new BNP derivatives. On treatment with lithium it undergoes, with complete chemoselectivity, heterolytic cleavage of the phenyl carbon–phosphorus bond to produce the corresponding phospholyl anion. This reaction is remarkable in that it leads exclusively to loss of the *P*-phenyl group, with no cleavage of the naphthyl substituents on the phosphorus atom being detected. The BNP anion reacts smoothly at room temperature with primary and secondary alkyl halides or with tosylates to afford the corresponding *P*-alkyl substituted phospholes in yields of 50–85% (Method C). In the latter case, net inversion at the stereogenic carbon centre takes place.

Method C is complementary to the phosphannulation procedures A and B and expands the synthetic horizons to include even those BNP derivatives for which the corresponding alkylphosphane dichloride is hardly accessible. By this procedure chiral alkyl substituents such as 2-methylbutyl and neomenthyl were introduced onto the phosphorus atom and the unsubstituted binaphthophosphole **2a** was prepared by quenching the phospholyl anion with a protic reagent. Whereas 1*H*-phospholes dimerize rapidly[15], compound **2a** was isolated by flash chromatography, is fairly stable even in solution, and was characterized completely by multinuclear NMR[14].

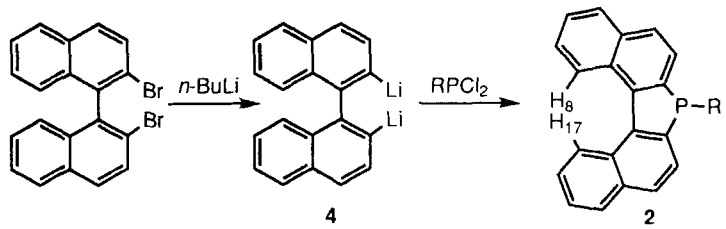
The utility of method **C** was also demonstrated in the preparation of the bidentate ligands **5**, **6** and **7** (Scheme 2), which were obtained by alkylation with the appropriate diiodide or ditosylate[16]. These chelating ligands have two

*Scheme 1.* Synthesis of binaphthophospholes

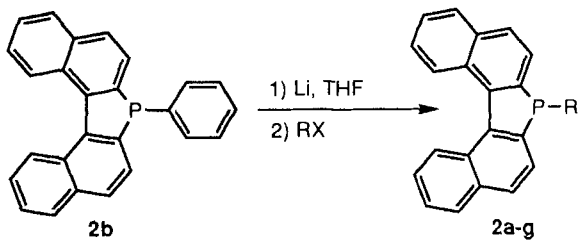
Method A. McCormack reaction




Method B. Phosphanulation of 2,2′-binaphthalene




Method C. Alkylation of binaphthophospholyl anion




| 2 | R |
|---|---|
| a | H |
| b | Ph |
| c | $CH_3$ |
| d | $CH_2CH_3$ |
| e | $CH_2Ph$ |
| f | $CH_2CH(CH_3)CH_2CH_3$ |
| g | *neomenthyl* |

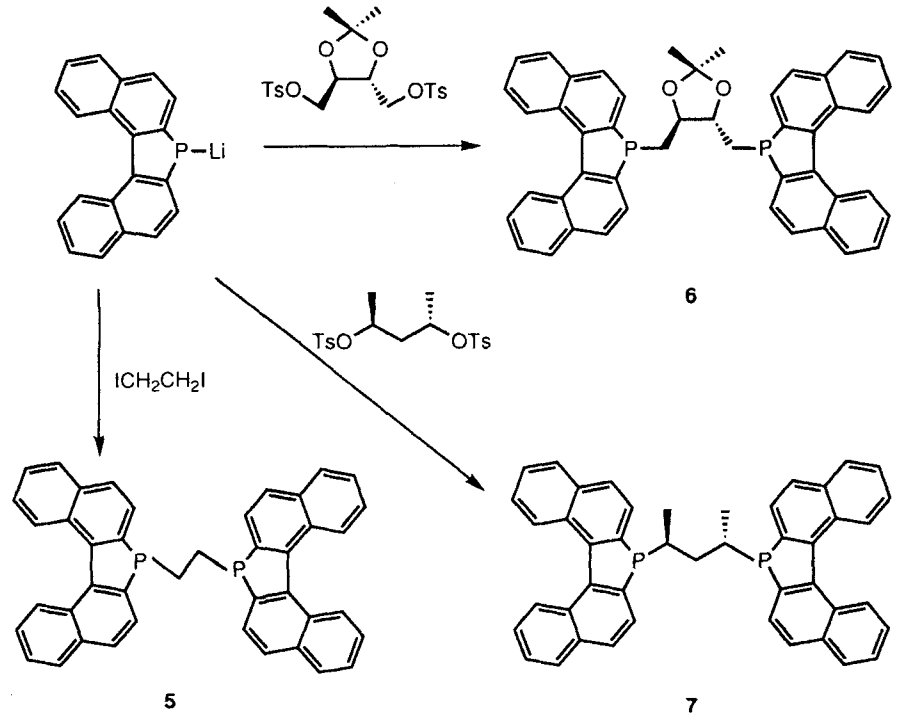
BNP groups connected through a suitable, sometimes chiral, carbon chain of variable length and are the BNP analogues of the well-known diphenylphosphanes DPE, DIOP and SKEWPHOS, respectively.

Binaphthalene-core phosphacyclic derivatives apart from phospholes have attracted much less attention thus far. Compounds with a six-membered phosphacyclic ring are still unknown, although two seven-membered compounds have been prepared[17]. Both the binaphthophosphepines so far reported have a three-atom chain with a central phosphorus atom connecting the 2,2′-carbons of the two naphthyl rings. They differ only in the substituent at the phosphorus atom, which is a methyl and a phenyl group in **8a** and **8b**, respectively. Their preparation is readily accomplished by metallation of 2,2′-dimethyl-1,1′-binaphthalene with superbase followed by quenching of the relevant dianion with the suitable dichlorophosphane (Table 1). The yield is modest (30–35%), but the method is straightforward (Scheme 3).

A common feature of binaphthophospholes **2** and phosphepines **8** is that, although they are devoid of $C_2$ symmetry, the P atom is not a stereogenic centre because it is located on the $C_2$-symmetry axis of the binaphthyl substituent. As a consequence, in these substrates pyramidal inversion at phosphorus, if it occurs, does not affect the chirality of the molecule, which is determined exclusively by the atropisomeric array of the binaphthyl framework.

Compounds **2** and **8** share some common reactivity traits. Both are easily alkylated at the phosphorus atom by primary iodides, affording in high yield the relevant phosphonium salts **11** and **9**. Upon treatment with suitable nucleophiles, these salts undergo ready opening of the phos-

Scheme 2. Synthesis of bis(binaphthophospholes)




Scheme 3. Synthesis of binaphthophosphepines

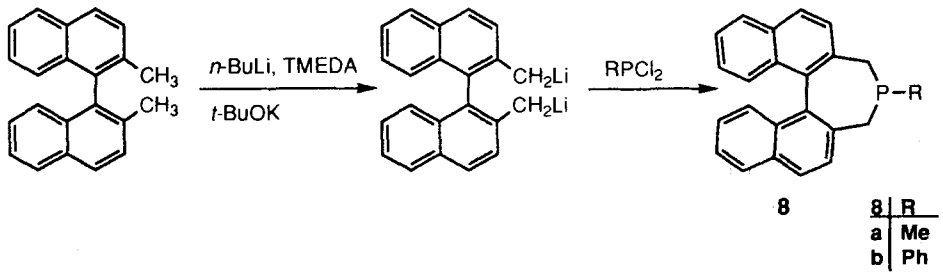


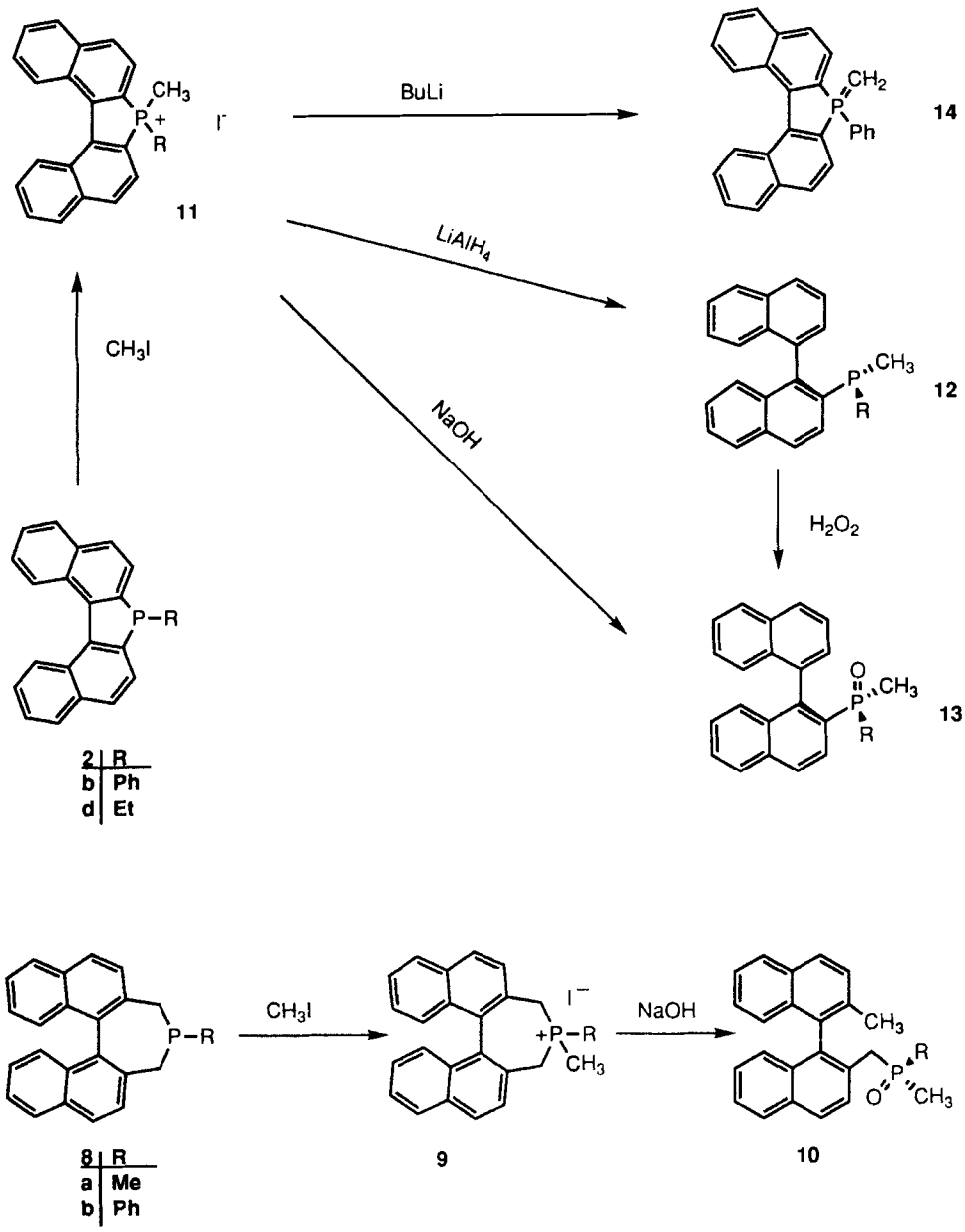

Table 1. Synthesis of P-substituted binaphthophospholes, bis(binaphthophospholes) and binaphthophosphepines

| Entry | Comp. | Method | Yield (%) | m.p. (°C) | $^{31}$P NMR[a] |
|---|---|---|---|---|---|
| 1 | **2a** | C | 68 | 102–103 | –60.81 |
| 2 | **2b** | A; B | 22; 85 | 157–158 | –4.69 |
| 3 | **2c** | B; C | 80; 50 | 102–103 | –19.66 |
| 4 | **2d** | B; C | 82; 56 | 122–124 | –3.32 |
| 5 | **2e** | C | 73 | 110–112 | –5.42 |
| 6 | **2f** | C | 60 | 142–143 | –11.20 |
| 7 | **2g** | C | 60 | 117–118 | –0.87 |
| 8 | **5** | C | 55 | 107–108 | –3.78 |
| 9 | **6** | C | 50 | 145–147 | 6.28 |
| 10 | **7** | C | 47 | 170–172 | 7.52 |
| 11 | **8a** | – | 30 | 186–187 | 62.83 |
| 12 | **8b** | – | 30 | 189–190 | 6.97 |

[a] In $CDCl_3$ solution at room temperature.

phacyclic ring. This occurs through cleavage of the naphthyl carbon–phosphorus bond in the case of phospholium salts **11**, whereas it is the methylene carbon–phosphorus bond that is broken in phosphepinium derivatives **9** (Scheme 4).

Scheme 4. Synthesis and reactions of binaphthophospholium and binaphthophosphepinium salts

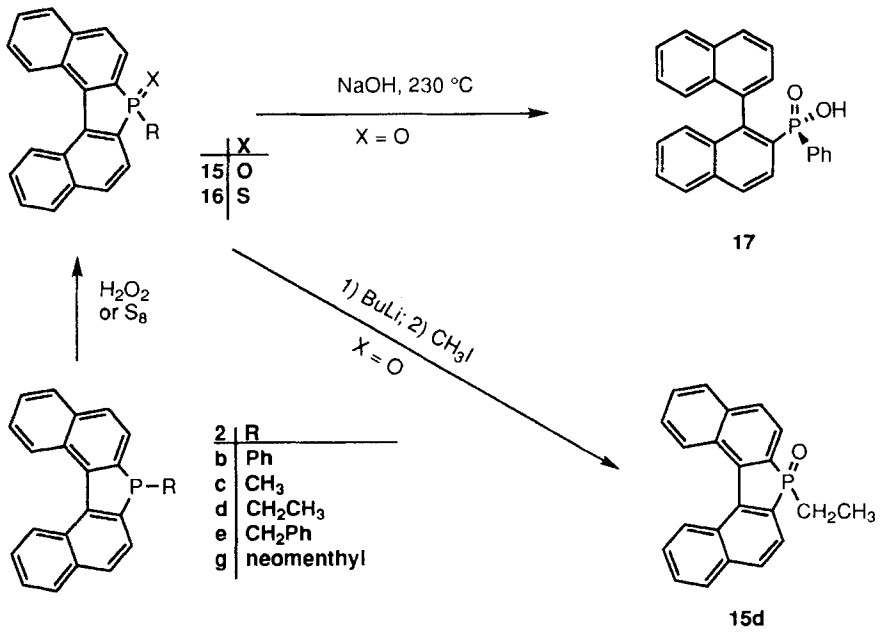



The structure of the open-ring product depends on the nature of the nucleophile. Treatment of phospholium salts **11** with lithium aluminium hydride leads to binaphthyl-substituted phosphanes **12**, whereas the analogous phsophane oxides **13** are obtained by reaction with oxygenated nucleophiles[18]. The stereochemistry of the ring-opening reaction is apparently unaffected by the nature of the nucleophile, because mixtures of diastereoisomers of the same relative configuration (and similar composition) have been obtained with lithium aluminium hydride and with potassium hydroxide.

The ring-opening reactions of phosphonium salts **11** and **9** provide a useful synthetic route to binaphthyl-substituted phosphanes **12** and phosphane oxides **13** and **10**, which are otherwise hardly accessible. These compounds are diastereomorphic due to the presence of the axially chiral binaphthyl residue and the stereogenic phosphorus. Because they may be considered to be configurationally stable below 100°C[18], compounds **12** can be regarded as the first representatives of a new class of chiral phosphane ligands characterized by this unprecedented combination of chiral elements.

There are also some reactions where the phosphole nucleus is preserved. Deprotonation of methyl phospholium salt **11b** with butyl lithium provides the corresponding ylid **14**, which behaves like a Wittig olefination reagent (Scheme 4). Reaction of binaphthophospholes with *m*-chloroperbenzoic acid or with sulphur in chloroform affords the corre-

Scheme 5. Reactivity of binaphthophospholes




sponding oxides **15** or thiono derivatives **16** (Scheme 5). Deprotonation-alkylation of the methyl group converts the phosphole oxide **15c** into the ethyl derivative **15d**.

Opening of the phosphole ring may also occur on phosphane oxide substrates. Heating the oxide **15b** with sodium hydroxide at high temperature affords the phosphinic acid **17**. All these facts are indicative that the phosphole ring in BNP derivatives is subjected to some torsional strain.

Binaphthophospholes and phosphepine sometimes differ in their chemical behaviour. Reaction of *P*-phenylphosphepine **8b** with lithium, instead of removing the *P*-phenyl group, leads to opening of the phosphacyclic ring through cleavage of the C–P bond at the methylene carbon, and eventually results in the complete removal of phosphorus from the substrate. Similarly, deprotonation of the methyl phosphepinium salts **9a** and **9b** does not take place at the methyl group, but rather at one of the methylenes.

### 2.2 Structure and Dynamic Behaviour

Two independent X-ray structures of *P*-phenylbinaphthophosphole **2b** are reported in the literature. Both were determined on enantiomorphic crystals obtained by spontaneous resolution, respectively from EtOH (*P* configuration)[19] and MeOH (configuration unknown, most probably the same)[14]. The two structures show almost identical parameters and the only significant difference concerns the short contact calculated for the *peri* hydrogens H(8) and H(17) (2.05 vs. 2.33 Å, respectively).

In the solid state *P*-phenylbinaphthophosphole **2b** shows a pyramidal geometry at phosphorus and a modest distortion of the phosphole ring from planarity. As expected, the naphthyl rings are significantly bent and each naphthalene ring is considerably folded. The endocyclic C–P bond lengths (1.81 Å) and the C–P–C angle (89.3°) are comparable to those of other ring-substituted phospholes[20]. The exocyclic C–P bond is slightly longer (1.83 Å) and this probably contributes to the selectivity observed in the reaction of **2b** with lithium.

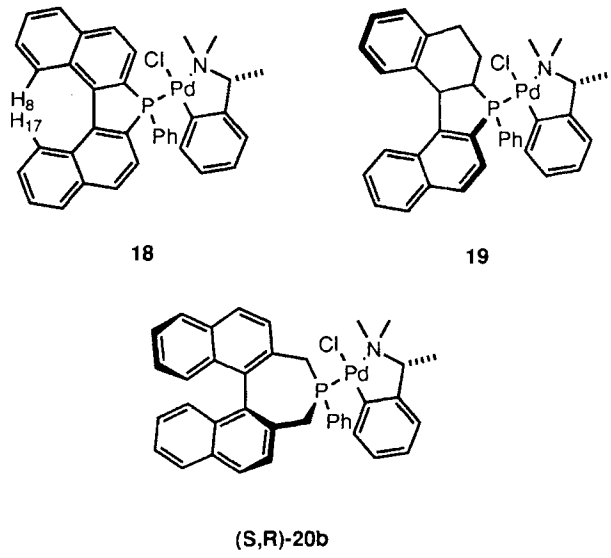
The dihedral angles between the mean planes of the outer and inner pairs of benzene rings are 38.2° and 18.7°, respectively. This corresponds to an average twist angle of 29.3° between the best-fit planes of the two naphthyl rings. As the same angle is as high as 75° in compound **3**[14], this difference gives a measure of the torsional strain inherent in the binaphthophosphole structure. This strain originates from the inclusion of the phosphole ring within the diaryl framework. The requirement of the five-membered heterocyclic ring to be as planar as possible conflicts with the demand of the binaphthyl residue to have its naphthyl groups in planes as orthogonal as possible. It is the relief of this torsional strain that provides the driving force to open ring products.

The geometry of *P*-phenyl BNP is only slightly altered when the phosphorus centre is coordinated to palladium, like in the complex **18** (Figure 1).

It is noteworthy that even in this case two separate X-ray structures of the same Pd complex are available. One incorporates the ligand as a racemate[21] and one as a pure enantiomer (*P* configuration)[13]. The main difference between these two structures still concerns the contact distance of the *peri* hydrogens. In both the structures, this is longer than in the free ligand (2.20 and 2.36 Å, respectively), due to the larger twist angle between the best-fit planes of the two naphthyl rings (33°).

The structural parameters of *P*-phenyl binaphthophosphepine **8b** can be inferred from the crystal structure of the

Figure 1. Chiral palladium complexes with binaphthophosphacyclic ligands




**18** **19**

**(S,R)-20b**

analogue palladium complex **20b**, containing the enantiopure (S)-**8b** (Figure 1). This shows a twist angle between the naphthalene rings of 63.8° and an intracyclic C–P–C angle of 100.6°[17]. These values are definitely greater than those observed in the analogous complex containing **2b**, and indicate that binaphthophosphepines are largely strain-free molecules. As expected for such a compound, the P atom is still pyramidal and the endocyclic C–P bonds are longer than the exocyclic one (1.845 vs. 1.82 Å).

The Tolman's cone angle[22] of these two ligands, as determined from the X-ray structures of these Pd derivatives, is 136° for **2b** and 151° for **8b**. The corresponding angle in triphenylphosphane is 145°.

Binaphthophospholes may in principle experience two different dynamic processes: atropisomerization of the binaphthalene backbone and pyramidal inversion at the phosphorus atom. While the former results in a net inversion of configuration and may cause racemization, the latter is a chirality-invariant process because the phosphorus atom is not a stereocentre.

Most BNP derivatives exhibit temperature-dependent NMR spectra and, when obtained by spontaneous resolution, undergo fast racemization at room temperature in solution. The energy barrier to this process can be determined by variable-temperature NMR, isolating the signals of a couple of diastereotopic centres. When the exchange is fast on the NMR *time scale*, the two resonances average to a single signal, whereas two separate peaks are observed when the atropisomerization is slow.

It is worth pointing out that atropisomerization can be detected and its rate measured only in cases where the phosphorus centre is configurationally stable, that is, when a high energy barrier is associated with the pyramidal inversion. If it occurs, this degenerate process would otherwise impart an apparent $C_2$ symmetry to the product, making the diastereotopic elements in the molecule indistinguishable. It follows that the dynamic process observed using VT NMR is due to interconversion between the two enantiomeric conformations of the binaphthalene backbone, and that the energy barrier of pyramidal inversion in BNP compounds is comparable with those recorded in benzoannulated phospholes (100–110 kJ mol$^{-1}$)[23].

This conclusion is further supported by the observation that the fluxional behaviour is mantained even when pyramidal inversion is rendered impossible by the presence of a fourth substituent at the phosphorus atom. Tetrasubstituted derivatives like the phospholium salts **11**, phosphole oxides **15** and phosphole–metal complexes **18**, **22**, **23** and **24** (vide infra), also have temperature-dependent NMR spectra attributable to the occurrence of atropisomerization.

The activation energies of this process have been determined by various groups for different binaphthophospholes, and the results are collected in Table 2. There is excellent agreement between the values recorded in separate experiments by independent groups. Regardless of the nature of the alkyl substitutent at the phosphorus atom, the energy barriers of phosphole derivatives lie in a fairly restricted range around 55–56 kJ mol$^{-1}$. Slightly higher values (of about 60 kJ mol$^{-1}$) have been recorded for the phosphole oxides **15b** and **15g**.

Table 2. Energy barriers to the atropisomerization of binaphthophosphole derivatives

| Entry | Comp. | Method | $\Delta E$ (kJmol$^{-1}$) | Ref. |
|---|---|---|---|---|
| 1 | **2f** | $^{31}$P NMR | 56 | [14] |
| 2 | **2g** | $^{31}$P NMR | 55 | [14] |
| 3 | **2b** | $^{1}$H NMR | 56 | [12] |
| 4 | **2c** | $^{1}$H NMR | 56 | [12] |
| 5 | **15g** | $^{1}$H NMR | 60 | [14] |
| 6 | **2b** | $^{13}$C NMR | 59.4 | [13] |
| 7 | **15b** | $^{13}$C NMR | 59.4 | [13] |
| 8 | **18** | $^{1}$H NMR | 65 | [13] |

The interconversion of the atropisomers involves close contact between the *peri*-hydrogen atoms H(8) and H(17), which must be forced past one another in the transition state of a *syn*-atropisomerization process. The fluxionality of binaphthophospholes must be related to the geometry of the five-membered phosphole ring, which tends to open the bite of the pentahelicene structure and to render it more flat. As a consequence, the outer benzene rings of each naphthalene are forced to move further apart, making the H(8) and H(17) atoms less sterically demanding.

This assumption is supported by the observation that, regardless of the nature of the heteroatom, conformational lability is a general property of heterocyclic compounds containing a five-membered ring merged within the atropisomeric binaphthyl backbone. Arsole[12], pyrrole[24], furane[24] and thiophene[24] derivatives are all fluxional at room temperature, and the relevant energy barriers, where determined, are slightly higher (59–65 kJ mol$^{-1}$ for arsoles) or slightly lower (45–48 kJ mol$^{-1}$ for thiophenes) than for the phosphorus compounds.

The energy barriers displayed by binaphthophospholes are too low to permit optical resolution of these compounds at room temperature and this make them unsuitable for use as chiral inducers as such. This was one of the reasons that induced us to take up the preparation of bis(binaphthophosphole) chelating ligands by connecting two BNP units to a chiral alkyl backbone of suitable length[16].

These derivatives also display fluxional behaviour in solution, because of the easy atropisomerization of the binaphthyl backbone. Due to the presence of configurationally stable stereogenic centres in the alkyl chain, this process results in epimerization and chirality in the ligand is not lost. This provides an opportunity to investigate the influence of BNP substitution in asymmetric catalysis.

As monitored by VT NMR, the equilibration of bis(BNP) ligands **5**, **6** and **7** occurs at a slower rate than in mono-BNP and proceeds with modest diastereoselectivity. Although the coalescence temperatures of the free ligands could not be carefully determined, they may be confidently estimated to lie in the range 0−20 °C depending on the alkyl chain. These values increase further upon coordination to a metal centre (vide infra).

Unlike the case of binaphthophospholes, binaphthophosphepine derivatives are expected to be configurationally stable because a few products with this structure have been obtained as pure enantiomers[25]. This expectation proved correct and the multinuclear NMR spectra of binaphthophephepines **8a** and **8b** provide clearcut evidence of this stability. In the $^1$H-NMR spectra both the compounds show twelve partially overlapping resonances for the aromatic protons and two sets of eight lines at $\delta$ = 2.10−3.00 for the diastereotopic methylene groups. These signals were unaffected by varying the temperature in the range ±60 °C. A single peak was observed in the $^{31}$P-NMR spectrum, and the $^{13}$C-NMR spectrum, besides the signals due to the aromatic carbons, was characterized by the presence of three (**8a**) or two (**8b**) doublets in the range $\delta$ = 10.10−35.00.

These spectral data indicate that no atropisomerization of the binaphthyl framework and no conformational equilibration of the seven-membered binaphthophosphepine ring occurs within the range of temperatures explored, and provide further confirmation that binaphthepine derivatives are configurationally stable.

### 2.3 Coordination Chemistry and Resolution

The coordination chemistry of binaphthophospholes **2**, **5**, **6** and **7** and binaphthophosphepines **8** towards transition-metal centres, mainly in $d^8$ electronic configuration, has been investigated in some detail (Scheme 6). Complexes of palladium(II), platinum(II) and iron(II) have been prepared and characterized. Particular attention has been paid to reactions with complexes containing chiral ancillary ligands, such as the chloride-bridged C,N-cyclopalladated complex **25** derived from enantiopure *N,N*-dimethyl-α-methylbenzylamine[26], in view of their ability to act as resolution agents for phosphorus compounds.

Complexation of both **2b** and the *P*-methyl analogue **2c** with iron(II) readily occurs through easy displacement of acetonitrile from the stereogenic metal centre of the enantiopure precursor **21**[12]. Interconversion between diastereomeric species is observed in complexes **22**. At 293 K compound **22b** shows a singlet for the cyclopentadienyl protons and three broad resonances for the phosphorus nuclei in the $^1$H- and $^{31}$P-NMR spectra. The first signal resolves into two sharp resonances in the ratio 1:2 at 246 K and the second resolves into overlapping 1:2 ABX systems at similar temperatures. The *P*-methyl complex **22c** displays the same NMR behaviour but with slight differences in temperature and in the diastereoisomeric ratio (257 K and 1.3:1, respectively). It is apparent that upon complexation to iron the conformational stability of the 1,1′-binaphthyl core increases slightly, but it is still prone to atropisomerize in solution even below room temperature.

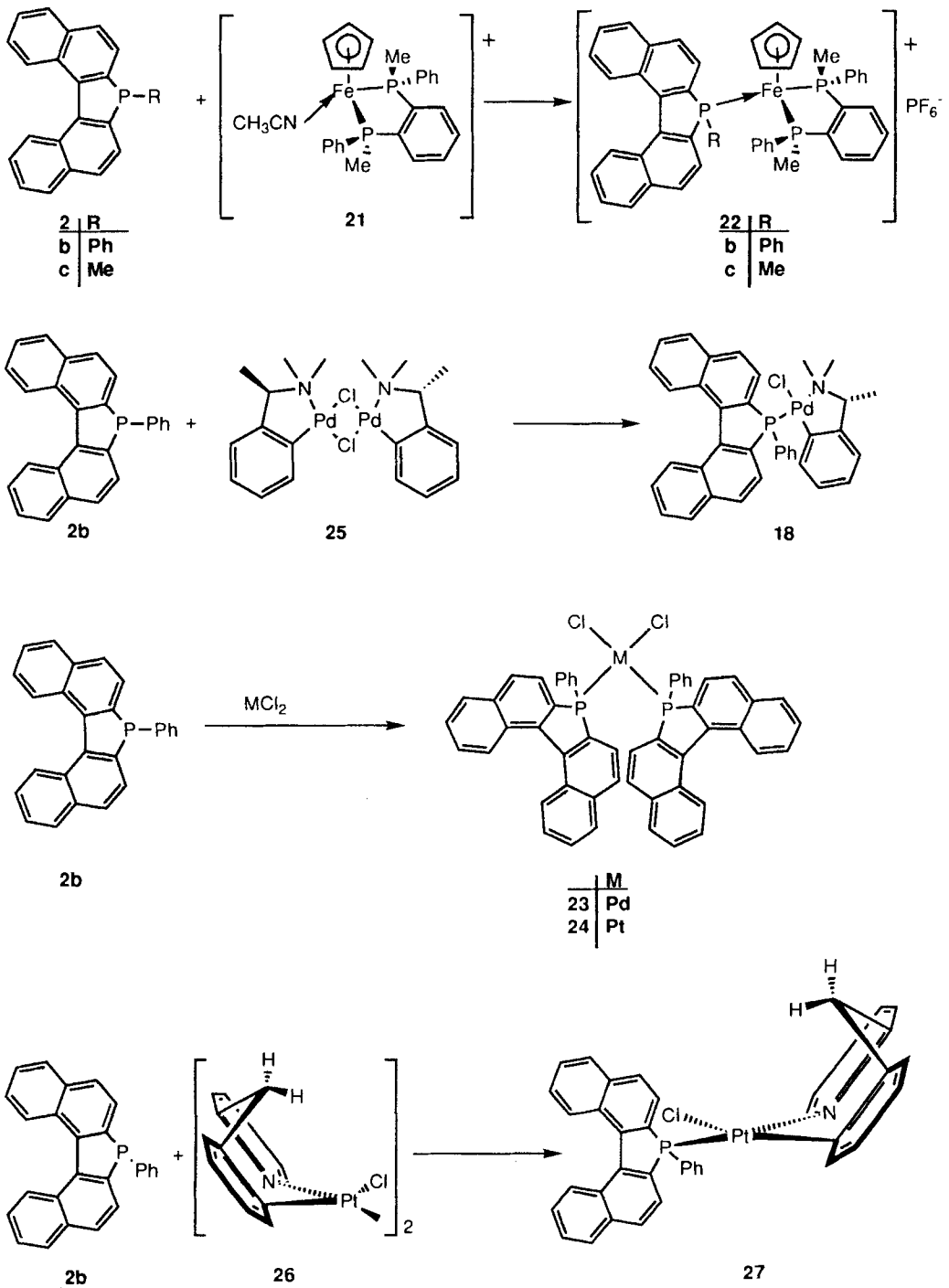
*P*-Phenyl BNP **2b** acts as a monodentate phosphorus ligand towards $d^8$ metal ions and readily substitutes neutral as well as anionic ligands coordinated to Pd(II) and Pt(II) centres. The reaction of **2b** with $K_2[PtCl_4]$ and $(PhCN)_2PdCl_2$ affords new complexes $(\mathbf{2b})_2MCl_2$, with exclusive (M = Pt; **24**) or predominant (M = Pd; **23**) *cis* geometry[21] as inferred from NMR studies. For instance, the $^{31}$P-NMR spectrum at room temperature of the Pt complex **24** shows one single broad resonance at $\delta$ = 12.1 with a $^{31}$P−$^{195}$Pt coupling constant of 3480 Hz, consistent with a *trans* P−Pt−Cl arrangement. This stereochemistry is confirmed in the solid state by IR spectroscopy[21].

Both the complexes **23** and **24** have temperature-dependent NMR spectra. When the $^{31}$P-NMR of **24** is recorded at 280 K, the resonance at $\delta$ = 12.1 is split into two separate signals ($\delta$ = 12.6 and $\delta$ = 9.3), each possessing satellite peaks ($J$ = 3480 and 3490, respectively). At the same temperature, a pair of triplets centred at $\delta$ = −4370 and $\delta$ = −4380, respectively, are observed in the $^{195}$Pt-NMR spectrum. This indicates that, in the bound state, the phosphole mantains the fluxional behaviour of the binaphthyl framework displayed in the free state. Albeit slower than in the free ligands, this process is fast on the NMR time scale at room temperature. When the equilibrium is frozen, two diastereomeric $(\mathbf{2b})_2MCl_2$ complexes result according to the relative chirality assumed by the coordinated ligands: a racemic derivative (*R,R* and *S,S*) and a meso compound (*R,S* and *S,R*).

The Pd complex **23** displays similar dynamic behaviour in its $^{31}$P-NMR spectrum. Since in this case coordination of **2b** affords a mixture of *cis* and *trans* complexes, two separate peaks are present in the spectrum at room temperature, both being split upon cooling.

Reaction of *P*-phenyl BNP **2b** with *ortho*-metallated chloride-bridged dinuclear $[(C-N)MCl]_2$ complexes [HC−N = 2-benzylpyridine, M = Pt, **26**; HC−N = *N,N*-dimethyl (*R*)-α-methylbenzylamine, M = Pd, **25**] promotes bridge splitting, leading to the mononuclear species (**2b**)(C−N)MCl, **27** and **18**, with a *trans* P−M−N arrangement[21,13].

Scheme 6. Metal complexes of binaphthophosphole




Some of the main features of the crystal structure of **18** have already been discussed above and it is only worth adding that coordination around the metal is essentially square planar with a slight tetrahedral distortion. Bond lengths and angles around palladium are in the normal range.

Complex **18** shows temperature-dependent NMR behaviour: the signals of the CMe, $NMe_2$ and CH coalesce at about 310 K and are split into two separate sets of peaks of different intensity at lower temperature. These modifications have been attributed to the interconversion between the two diastereoisomers produced by the atropisomerization of the coordinated BNP ligand[21]. The calculated energy barrier (about 65 kJ $mol^{-1}$[13]) is well in keeping with the values determined for the free ligand, given that coordination is expected to increase the configurational stability of BNP derivatives[12].

The alternative conclusion, that the dynamic behaviour of **18** is due to hindered rotation around the P–Pd bond[13] leading to inequivalent amounts of rotamers, is not substantiated by the accompaning experimental details and has been criticized[27]. The temperature-dependent NMR spectrum of the model achiral complex only demonstrates that a fall in temperature induces the formation of diastereotopic protons. This is just what happens when the atropisomerization of the diaryl framework is at the low-exchange limit.

No evidence of dynamic behaviour is found in the analogous Pd derivative **19** of the tetrahydrophosphole **3**. This was obtained in the form of an equimolar mixture of two diastereoisomers, which unfortunately could not be resolved by fractional crystallization[28].

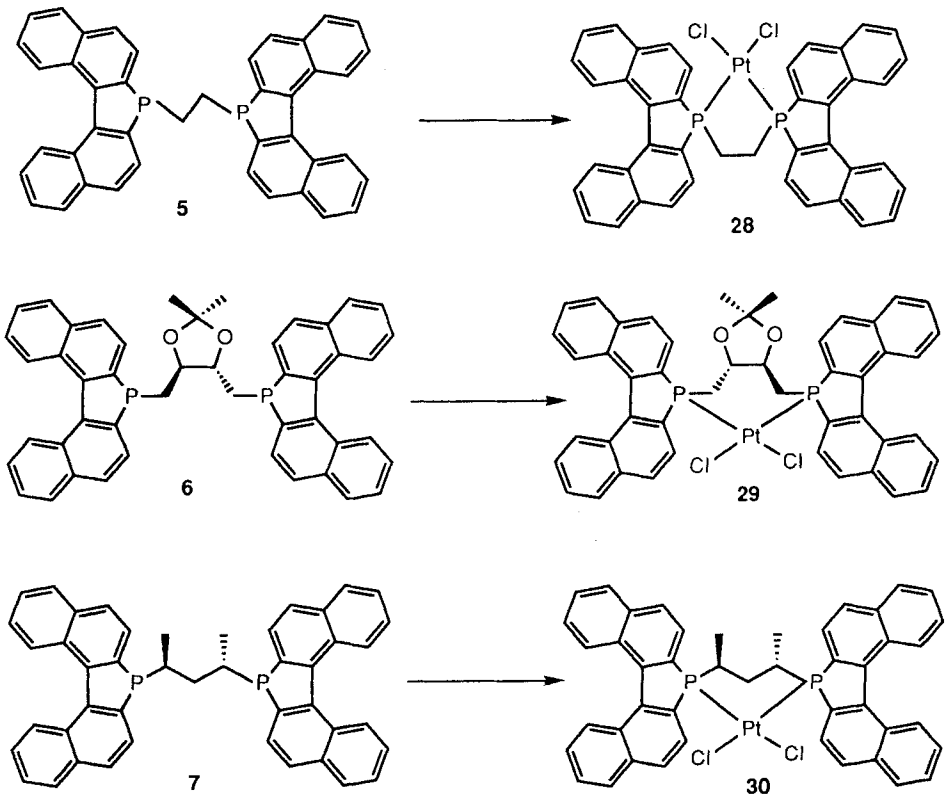
Complex **27** comprises two different, non-equilibrating species, which give rise to two separate sets of NMR resonances that do not show any variation between 223 and 323 K. Notably, the dynamic behaviour of the BNP ligand is no longer apparent in either of the species. This means that either the binaphthalene framework is stiff even at room temperature or that it is fluxional even at the lowest temperature. We prefer the first hypothesis because it seems more reasonable that in the bound state the ligand should increase its stiffness rather than its mobility.

Considerable steric hindrance between one naphthyl ring and the chloride ligand is readily apparent in **27** on inspection of molecular models. This led us to assume that the two species should be non-interconverting conformers arising from hindered rotation around the Pd–P bond[21]. Alternatively, diastereomeric complexes may originate from a severe tetrahedral distortion which makes the Pt atom a stereogenic centre. This does not seem to be the case, because similar complexes show an essentially square planar geometry around the metal[29]. One further possible explanation is that the agostic interaction involving the metal and the more deshielded methylene hydrogen, evidenced by the significant $^{1}H-^{195}Pt$ coupling ($^{4}J$ = 20 Hz), may induce stereogenicity at the benzyl carbon. This hypothesis can be neither proved nor disproved at the moment.

Binding of the bis(binaphthophosphole) ligands **5**, **6** and **7** to Pt(II) centres occurs readily upon reaction with $(PhCN)_2PtCl_2$. The expected mononuclear chelate complexes **28**, **29** and **30** (Scheme 7) show fluxional behaviour in $CDCl_3$ solution, which results in temperature-dependent $^{31}P$-NMR[16] spectra.

Complex **30**, for instance, shows at room temperature three different phosphorus resonances, at $\delta$ = 14.8, 13.0 and 10.2 in a ratio of approximately 6:3:1 with $J(Pt-P) \approx 3300$ Hz. From the coupling constants a *cis* P–Pt–P arrangement may be attributed to each of these three species. When the solution of **30** is warmed, coalescence of the $^{31}P$ resonances into a more or less broad signal is observed at about

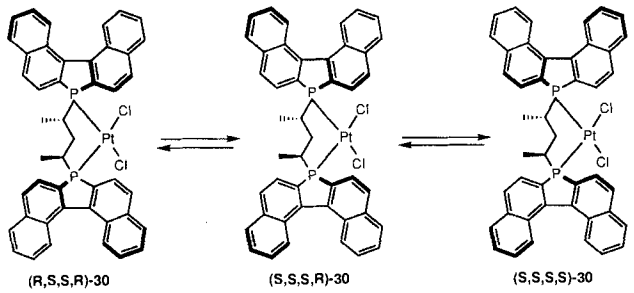
Scheme 7. Synthesis of Pt complexes of bis(binaphthophospholes)



50 °C. The original spectrum can be reproduced upon cooling the samples down to room temperature. A similar pattern, but with a higher coalescence temperature, is observed for complex **29**.

This fluxional behaviour is once more a consequence of the atropisomerization experienced by the binaphthyl groups of the ligands. In the case of complexes **29** and **30**, which contain two equivalent stereogenic centres in the carbon backbone, three diastereoisomers can be expected: one where 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 species involved in the dynamic equilibrium of complex **30** are reported in Scheme 8.

Scheme 8. Interconversion of Pt–bis(binaphthophosphole) complexes




Even in this case coordination to the metal increases the configurational stability of the ligands. The effect is particularly pronounced for complex **29**, where separate diastereomeric species are detectable in the $^{31}$P-NMR spectrum up to 50 °C.

The conformational lability displayed by binaphthophosphole metal complexes make them unsuitable for optical resolution with the aid of the C,N-cyclopalladated complex **25** derived from enantiopure *N,N*-dimethyl-α-methylbenzylamine. In contrast, resolution with this chiral entertainer was achieved in the case of the phosphepine derivatives **8a** and **8b**, which both produced readily resolvable complexes. With both ligands, a single crystallization of the equimolar diastereomeric mixture resulted in exclusive separation of the less soluble product. Both the complexes are configurationally stable and no interconversion between diastereoisomers of **20a** (R = Me) and **20b** (R = Ph) (see Figure 1) was observed even after warming in toluene for 3 h at 100 °C. The crystal structure of the less soluble isomer of complex **20b** reveals the *S* configuration of the ligand and a modest tetrahedral distortion of the palladium geometry with bond angles and lengths in the normal range. The enantiopure (−)-(*S*)-phenylphosphepine can easily be recovered from complex **20b** by treatment with diphenylphosphinoethane[17] and does not show any loss of optical activity in solution.

### 2.4 Applications to Enantioselective Catalysis

Pt(II) and Rh(I) complexes of binaphthophospholes and binaphthophosphepines are the precursors of efficient chiral catalysts to be used in enantioselective processes.

The chiral platinum complexes **29** and **30** in the presence of 2 mol of $SnCl_2$ display remarkable catalytic activity in the hydroformylation of styrene at a fairly high substrate-to-metal ratio (1750:1). The related complex **28** is much less efficient. Based on NMR evidence[16], it is assumed that hydroformylation is preceded by insertion of tin into the platinum–chloride bond, with formation of thrichlorostannyl platinum complexes.

The most significant results recorded in these experiments are collected in Table 3. The catalytic systems originating from **29** and **30** are quite active, and almost quantitative conversions of styrene could be attained in a reasonable time with a satisfactory chemoselectivity even at temperatures as low as 32 °C. The most interesting feature of these catalysts is that they favour the formation of the branched aldehyde with a regioselectivity that is unprecedentedly high (80–85%) for platinum catalysts[30].

These remarkable aspects are contrasted by the unsatisfactory enantioselectivity of the reaction (up to 45% e.e.). This arises from the conformational lability of the BNP

Table 3. Hydroformylation of styrene in the presence of $PtCl_2$[bis(binaphthophosphole)] + $SnCl_2$ catalysts (substrate/Pt, 1750:1; Pt/$SnCl_2$, 1:2; solvent: toluene; $p(CO) = p(H_2) = 40$ atm)

| Run | Catalyst | Time (h) | Temp.(°C) | Conv.(%) | RCHO[a] | Branched[b] | e.e. (%)[c] |
|---|---|---|---|---|---|---|---|
| 1 | **28** + $SnCl_2$ | 24 | 90 | 6 | 48 | 72 | – |
| 2 | **29** + $SnCl_2$ | 20 | 85 | 97 | 64 | 63 | 20 |
| 3 | **29** + $SnCl_2$ | 20 | 58 | 50 | 74 | 68 | 44 |
| 4 | **29** + $SnCl_2$ | 40 | 38 | 22 | 73 | 66 | 39 |
| 5 | **29** + $SnCl_2$ | 380[d] | 32 | 77 | 78 | 63 | 43 |
| 6 | **30** + $SnCl_2$ | 22 | 58 | 45 | 76 | 68 | 17 |
| 7 | **30** + $SnCl_2$ | 22 | 34 | 10 | 71 | 65 | 18 |
| 8 | **30** + $SnCl_2$ | 93[d] | 32 | 97 | 73 | 78 | 24 |
| 9 | **30** + $SnCl_2$ | 70[e] | 32 | 89 | 68 | 80 | 24 |
| 10 | **30** + $SnCl_2$ | 70[f] | 32 | 95 | 55 | 85 | 20 |

[a] Aldehydes/(aldehydes + ethylbenzene) × 100. – [b] Branched aldehyde/(branched + normal aldehydes) × 100. – [c] The predominant enantiomer always had *S* configuration. – [d] 55 atm $H_2$ + 40 atm CO. – [e] 80 atm $H_2$ + 40 atm CO. – [f] 100 atm $H_2$ + 20 atm CO.

framework which, during the catalytic runs, gives rise to a mixture of different catalytic species, each one endowed with a peculiar stereodifferentiating ability. Notably, a reversal of the stereoselection with respect to the corresponding diphenylphosphino derivative DIOP is observed when the bis(BNP) derivative **6** is used as chiral ligand.

The enantiopure binaphthophosphepine (−)-(S)-**8b** is also an effective chiral ligand for the asymmetric hydroformylation of styrene in the presence of rhodium complexes[17]. The reaction at 60 °C under standard conditions (benzene; substrate/P/Rh, 500:4:1, $CO/H_2$, 1:1, 50 bars) is completely chemoselective towards aldehydes and affords 96% conversion in 3 h (Table 4).

Table 4. Hydroformylation of styrene in the presence of (−)-(*S*)-phenylbinaphthophosphepine (**8b**) and $Rh(acac)(CO)_2$ as catalyst precursor (substrate/P/Rh, 500:4:1; solvent: benzene; $p(CO) = p(H_2) = 25$ atm)

| Run | Ligand | Temp.(°C) | Conv. (%) | RCHO[a] | Branched[b] | e.e.(%)[c] |
|---|---|---|---|---|---|---|
| 1 | **8b** | 60 | 96 | 99 | 93 | 12 |
| 2 | **8b** | 30 | 64 | 99 | 95 | 20 |
| 3 | $PPh_3$ | 60 | 95 | 90 | 85 | – |

[a] Aldehydes/(aldehydes + ethylbenzene) × 100. – [b] Branched aldehyde/(branched + normal aldehydes) × 100. – [c] The predominant enantiomer always had *R* configuration.

The branched isomer accounts for 93% of the product and shows 12% e.e. of the *R* enantiomer. Decreasing the reaction temperature to 30 °C has a positive effect both on the regio- and enantioselectivities, which improve to 95% and 20%, respectively. A comparison with the analogous triphenylphosphane-based catalyst shows that the one derived from *P*-phenylbinaphthophosphepine displays the same catalytic activity and is slightly more regioselective (93% vs. 85%).

The enantioselectivities are low, as is expected for a monodentate chiral ligand[30]. It is worth stressing, however, that 20% is one of the highest values so far obtained in Rh-catalysed hydroformylation with a monodentate ligand as a chiral auxiliary.

### 3. Concluding Remarks

The chemistry summarized above shows that binaphthophospholes and binaphthophosphepines are easily accessible compounds which are useful non-transferable ligands for the preparation of various transition-metal complexes. They can be exploited as homogeneous catalysts in several asymmetric processes. Although thus far the stereoselectivities are far from satisfactory, these ligands seem to hold the promise of a more successful future when either bidentate binaphthophosphepine derivatives will become available or the conformational stability of binaphthophospholes will be improved through suitable modification of the diaryl framework.

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