Chiral Aryl Diphosphites: a New Class of Ligands for Hydrocyanation Catalysis

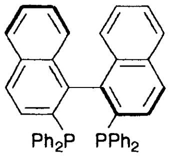
Michael J. Baker and Paul G. Pringle*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

The new diphosphite **1** derived from *R*-2,2′-binaphthol and its nickel(0) complex are described; optical yields for the hydrocyanation of norbornene are 38%.

Enantioselective catalysis using transition metal complexes of chiral chelating diphosphines is one of the most elegant applications of coordination chemistry.[1] The large range of chiral diphosphines which is now commercially available is a reflection of the widespread interest in these ligands. Chelating aryl diphosphite complexes have recently been shown to be excellent catalysts for hydrocyanation[2] and hydroformylation[3] and we were therefore interested in the potential of chiral aryl phosphite complexes as asymmetric catalysts for these C–C bond-forming reactions. We reasoned that the diphosphite **1**, derived from the readily available,[4] optically active *R*-2,2′-binaphthol, would be of particular interest because two very successful chiral ligands have been **2** (binap)[1,5] and the related diphosphinite **3** (binapo)[6] both of which are based on the chiral 2,2′-binaphthyl moiety. Recently a rhodium complex of a chiral alkyl diphosphite was reported[7] but the optical yields obtained for enantioselective hydrogenation were disappointing [2–10% enantiomeric excess (e.e.)].

White, crystalline ligand **1** was readily made from PCl_3 and *R*-2,2′-binaphthol in the presence of Et_3N (see Scheme 1).



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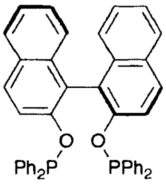

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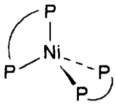
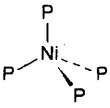


4 P P = ligand **1**



5 P = ligand **6**

The nickel(0) complex **4** was prepared by treatment of $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) with ligand **1** in toluene.†

The effectiveness of the nickel(0) complex **4** as an hydrocyanation catalyst was tested by treatment of norbornene with acetone cyanohydrin in the presence of **4**. The product, *exo*-2-norbornane carbonitrile, was converted to the corresponding carboxylic acid and the optical yields determined by

Table 1 Results for asymmetric hydrocyanation of norbornene[a]

Catalyst	*T*/°C	*t*/h	Yield(%)[b]	E.e.[c]	Ref.
4	150	18	70	28*R*	
4	120	40	42	33*R*	
4 + BPh_3[d]	100	40	58	38*R*	
5[e]	150	18	16	10*S*	
$[Ni(R,R\text{-diop})_2]$,[e,f]	80	18	20	5*R*	10
$[Pd(S,S\text{-diop})_2]$[e,f]	80	18	94	13*R*	10, 11
$[Pd(R\text{-binap})_2]$[e]	120	18	6	40*R*	11

[a] *Reaction conditions*: a 10 cm^3 stainless steel bomb was charged with norbornene (4.5 g, 48 mmol), $Me_2CO{\cdot}HCN$ (2.2 cm^3, 24 mmol), catalyst (0.068 mmol) and then sealed and heated at the temperatures shown for the time shown. [b] Isolated yield of distilled *exo*-2-norbornane carbonitrile. [c] Determined (±1%) by the optical rotation ($[\alpha]_D^{20}$, *c* = 1, EtOH) of the derived *exo*-2-norbornane carboxylic acid[8] or from the ^1H NMR spectrum of the *S*-methylmandelate ester of *exo*-2-norbornane carboxylic acid.[9] [d] 5 equiv. (0.34 mmol) of BPh_3 added. [e] These reactions are carried out in the presence of large amounts (*ca.* 8 equiv.) of ligand. [f] diop = 3,4-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane.

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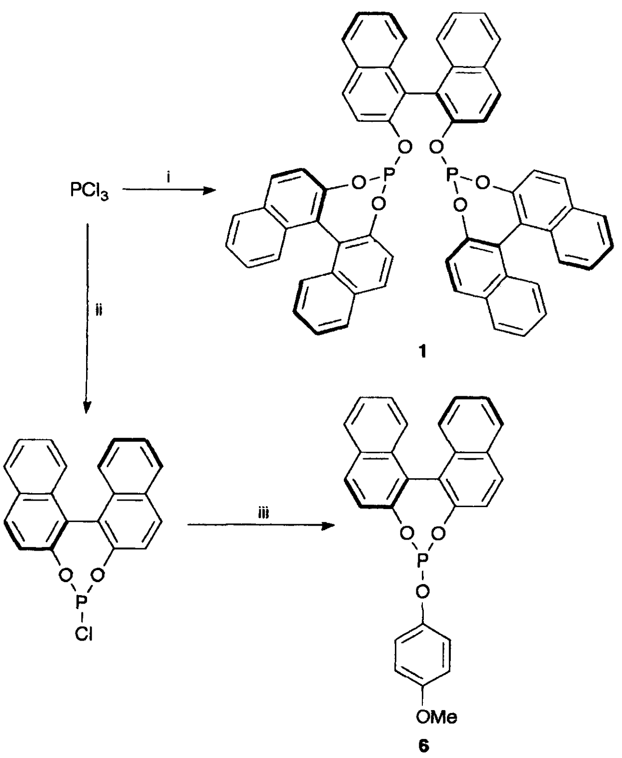
† All new compounds have been characterised by elemental analysis, $^{31}P\{^1H\}$ NMR spectroscopy (in $CDCl_3$) and specific optical rotations ($[\alpha]_D^{20}$, *c* = 1, THF, ±2%). *Selected data* for **1**: δ_P 144.6, $[\alpha]_D^{20}$ −192°; for **4**: δ_P 175.0, $[\alpha]_D^{20}$ +600°; for **5**: δ_P 161.8, $[\alpha]_D^{20}$ −230°; for **6**: δ_P 145.1, $[\alpha]_D^{20}$ +190°.



Scheme 1 All reactions were carried out in tetrahydrofuran (THF) at −40 °C using: i, 1.5 equiv. of *R*-2,2′-binaphthol and 3.0 equiv. of NEt_3; ii, 1.0 equiv. of *S*-2,2′-binaphthol and 2.0 equiv. of NEt_3; iii, 1.0 equiv. of *p*-$MeOC_6H_4OH$ and 1.0 equiv. of NEt_3

comparing the optical rotation with the literature value[8] for the (1*R*, 2*R*, 4*S*)-(−)-acid and confirming these values by integration of the ^1H NMR spectrum of the *S*-methylmandelate ester;[9] the results are presented in Table 1. The chemical yields are up to 70% and the optical yields (up to 38% e.e.) are as good or better than the best metal–phosphine systems for this reaction (see Table 1).[10,11] The optical yields are improved if the catalysis is performed at lower temperatures. It is known[12] that the rate of hydrocyanation is increased by Lewis acids and for our system, the addition of BPh_3 allows the use of lower temperatures (see Table 1).

In order to assess the importance of the chelate rings in **4** in determining the enantioselectivity of the hydrocyanation catalysis, the nickel(0) complex **5** of the chiral monophosphite **6** was synthesized (see Scheme 1). Complex **5** catalyses the hydrocyanation of norbornene but in much lower chemical and optical yields than the chelate **4** (see Table 1).

The stability of the new chiral aryl phosphite complex **4** is a considerable advantage over metal–phosphine and metal–monophosphite systems for asymmetric hydrocyanation: **4** is completely air stable and requires no additional ligand to stabilise it under the conditions used for the catalysis. Further work is required to improve optical yields but we have shown that aryl diphosphites are a new class of chiral ligands with considerable promise for enantioselective catalysis.

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