Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 391–395

TETRAHEDRON: *ASYMMETRY*

2-Diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthalene (BINAPO), an axially chiral heterobidentate ligand for enantioselective catalysis

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Received 6 November 1997; accepted 8 January 1998

Abstract

Racemic 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthalene (BINAPO) **5** has been prepared in four steps from 1,1′-binaphthalene-2,2′-diol (BINOL) **1** and has been resolved with the aid of the C,N-cyclopalladated complex with N,N-dimethyl (S)-1-(1-naphthyl)ethylamine **6**. P,O-chelate binding to palladium occurs in solution and this is confirmed in the solid state by X-ray analysis. (S)-BINAPO is an immediate precursor of (S)-BINAP and is itself an effective chiral inducer for the Pd-catalyzed asymmetric hydrosilylation of styrene (over 70% e.e.).

In the course of a recent investigation aimed at the preparation of unsymmetrical binaphthalene-templated diphosphines,[1] we have developed an efficient methodology for appending one phosphino and one phosphinyl group onto the 2,2′-carbon atoms of the binaphthalene backbone. This new procedure provides an easy entry into axially chiral phosphine–phosphine oxide derivatives, an almost unprecedented class of products, and makes them available in substantial amounts. This prompted us to study some aspects of their coordination chemistry and to explore their potential as chiral inducers in enantioselective catalysis. Here we report the first results obtained with 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthalene (**5**; BINAPO),[2] the most accessible member of this novel family of axially chiral, potentially heterobidentate ligands.

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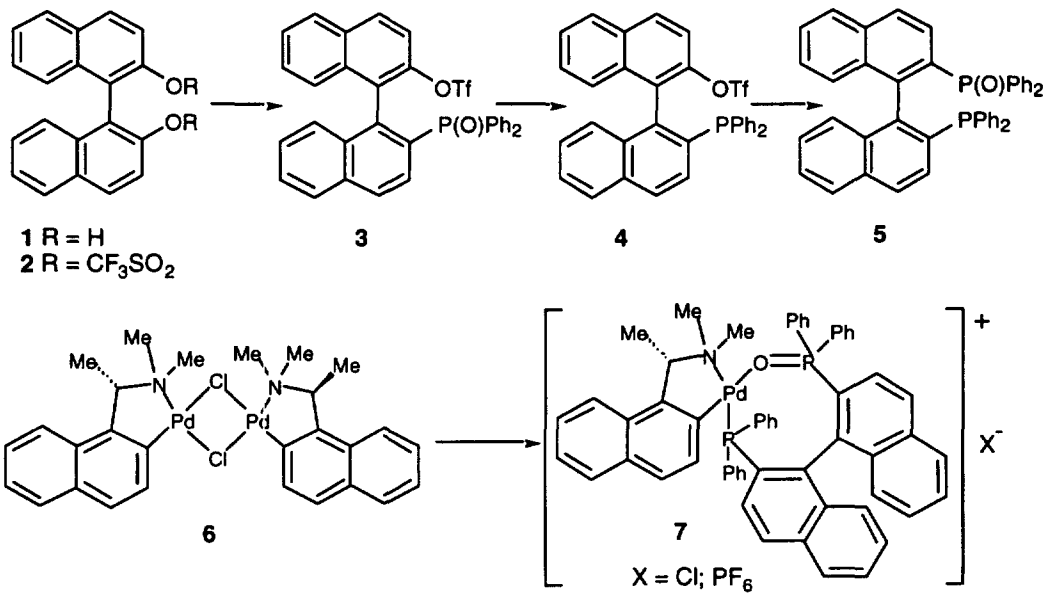
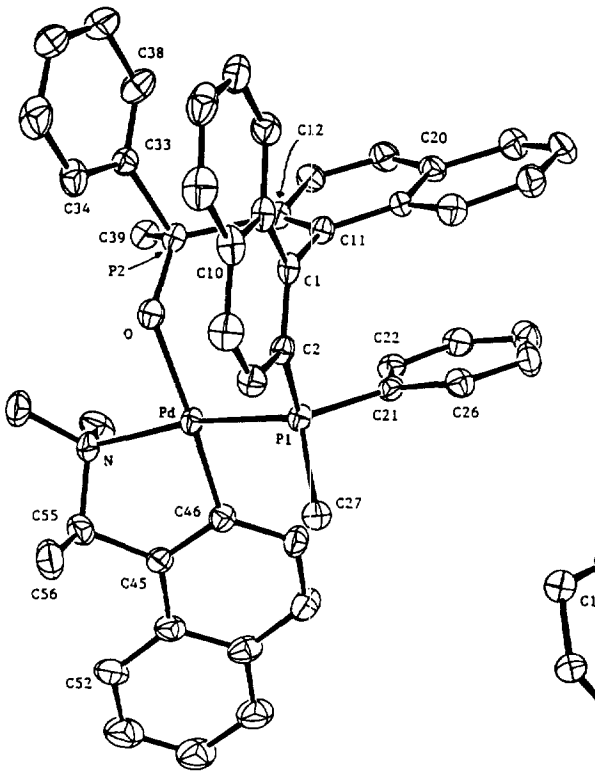
0957-4166/98/$19.00
PII: S0957-4166(98)00009-3



The preparation of **5** from racemic BINOL **1** has been accomplished according to a four step reaction path involving sequential substitution of the homotopic triflate groups of **2** by diphenylphosphine oxide.[3] Dissymmetrization of the substrate is achieved in the second step of the synthetic scheme where the first phosphorated substituent is introduced in the form of a diphenylphosphinyl group by means of palladium chemistry following a reported procedure.[4] For the second triflate group to be substituted, removal of the oxygen of the phosphinyl group of **3** is required ($HSiCl_3/Et_3N$; xylene; 120°; 12 h; 84% yield). The diphenylphosphino triflate **4** is then converted into BINAPO **5** by further reaction with diphenylphosphine oxide in the presence of Pd- or Ni-catalysts (DMF; 100°C; 10 h; 70% yield). Following this set of reactions, racemic **5** is obtained in over 45% overall yield. In the ^{31}P-NMR spectrum, compound **5** shows one singlet at −14.70 (sharp) and one at 27.69 ppm (fairly broad) due to the phosphino and phosphinyl groups, respectively.

Reaction of racemic **5** with the enantiopure chloride-bridged C,N-cyclopalladated complex **6**[5] affords an equimolar diastereomeric mixture of two mononuclear cationic complexes, which could be isolated in crystalline form after exchanging the chloride counterion with hexafluorophosphate.[6] In the ^{31}P-NMR spectrum of this mixture, the resonances of the phosphino and phosphinyl groups appear as singlets at 44.44, 43.41, 42.28 and 34.68 ppm. While the two peaks at lower field are quite sharp, some line broadening is apparent in the other two signals and this supports the attribution to the phosphinyl substituents. In comparison with the free ligand, all the ^{31}P-resonances are shifted downfield and this provides convincing evidence for the chelate coordination of BINAPO to the Pd-atom. As expected, this deshielding effect is larger for the P-centre of the phosphino group, which is directly bound to the metal ($\Delta\delta \approx 60$ ppm), and is less pronounced for that of the phosphinyl group, which is separated from the metal by the oxygen atom ($\Delta\delta$ 7–15 ppm). The structure of the complex can be confidently formulated as **7** since in these Pd-complexes the softer donor is expected to take up the position *trans* to the NMe_2 group.[7]

One single crystallization of this mixture from CH_2Cl_2–petroleum ether was sufficient to attain the selective separation of the less soluble diastereomer in pure form and in a crystalline shape suitable for X-ray structure determination. An ORTEP view and the most representative parameters of the structure are reported in Fig. 1.[8]



Selected bond lenghts and angles

Pd-P1	2.260(1)
Pd-O	2.146(4)
Pd-N	2.151(5)
Pd-C46	2.000(6)
P2-O	1.511(4)
P1-Pd-O	90.9(1)
P1-Pd-N	167.2(1)
P1-Pd-C46	93.5(2)
O-Pd-N	95.5(2)
O-Pd-C46	175.6(2)
N-Pd-C46	80.3(2)
Pd-O-P2	125.1(2)

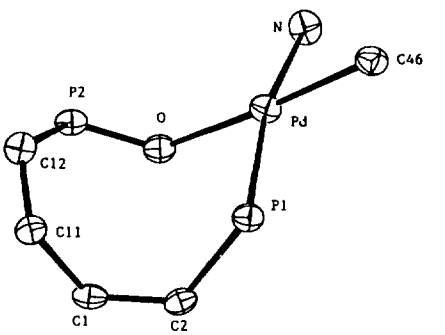


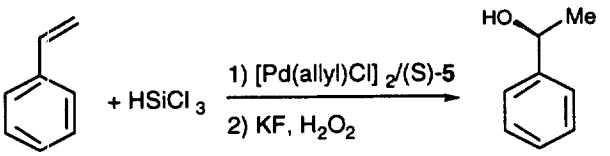
Fig. 1. (a) ORTEP view of the cation (less soluble diastereoisomer) of compound **7** (X=PF_6). For clarity the phenyl substituents at the phosphorus centres not involved in π-stacking are represented by a single carbon atom (C27 and C39). (b) Perspective view of the eight-membered chelate ring

The crystal contains discrete mononuclear units of **7** in which BINAPO (S configuration) acts as a bidentate ligand providing an eight-membered chelate ring with an irregular, partly boat-like conformation.[9] As anticipated, the harder oxygen atom occupies the coordinative position *trans* to the carbon. In the pentatomic metallacycle formed by N,N-dimethyl (S)-1-(1-naphthyl)ethylamine, the benzylic methyl group is located in an axial position. This feature is common to all the recorded X-ray structures of Pd-complexes derived from **6** and it is due to the necessity to avoid steric repulsion between the C(56) methyl and the hydrogen atom bound to the C(52) of the naphthylamine.[10] The Pd atom is in a butterfly-distorted square planar coordination, with the atoms Pd, P(1), O and C(46) strictly planar and the atoms Pd, N, O and C(46) also planar, whereas the dihedral angle between their best planes is 11.7(6)°. In the pentatomic metallacycle, the atoms Pd, C(46), C(45) and C(55) are essentially planar, whereas the nitrogen atom is displaced 0.75 Å out from this best plane. As usual, the naphthyl rings of the binaphthyl framework are significantly bent. They show a dihedral angle of 82.1(1)° between their average best planes which allows the opposing hydrogens at C(17) and C(27) to be located at a comfortable distance. These figures suggest that the chiral diaryl backbone is basically free from torsional strain. A significant π-stacking interaction involves one of the phenyl substituents on each P-atom and the phenyl ring which is more remote from the metal of each naphthyl group of the binaphthalene template. The dihedral angles between the best planes of the π-stacked aromatic rings are 13.1(5)° and 8.8(8)° for the interactions involving the naphthyl rings C(1)–C(10) and C(11)–C(20), respectively. The distances of the atoms C(33)–C(38) from the best plane of the C(1)–C(10) naphthyl ring are in the range 3.03(1)–3.63(1) Å

(average 3.32 Å); those of the atoms C(21)–C(26) from the best plane of C(11)–C(20) naphthyl are in the range 3.07(1)–3.47(1) Å (average 3.28 Å).

From this complex, (S)-BINAPO **5** could be recovered in quantitative yield by treatment with a slight excess of ethylenediamine in the biphasic system $CHCl_3$–H_2O.[11] Its enantiomeric purity was determined by deoxygenation with trichlorosilane which afforded enantiopure (S)-BINAP in excellent yield. The same diphosphine can be obtained in a single step from complex **7** by reaction with $LiAlH_4$ (ether; 35°C; 3 h; 70% yield). This provides an alternative synthesis of enantiopure BINAP from racemic BINOL which adds to the other ones already available.[12]

(S)-BINAPO has been tested as a chiral inducer in the Pd-catalyzed asymmetric hydrosilylation of styrene. The reaction has been performed on the neat substrate at room temperature using $[Pd(allyl)Cl]_2$–(S)-BINAPO (1:2) as an in situ catalyst at a substrate to metal ratio 1000:1.[13] A quantitative conversion with complete regioselectivity for the branched isomer is attained in 70 h affording, after oxidative work-up, (S)-1-phenylethanol in 18% e.e. The e.e. increases up to 72% when the reaction is run using benzene as a solvent. This result is comparable with the one obtained on the same substrate with MOP[14] as the chiral inducer and encourages future applications of this new ligand to asymmetric catalysis.



Acknowledgements

Financial support from CNR, Rome 'Progetti Finalizzati' and M.U.R.S.T., Rome is gratefully acknowledged.

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6. Selected data for (S)-**5**: mp 230–233°C; $[\alpha]^{20}_D$ −92.2 (c=1.02, $CHCl_3$); IR (KBr): 1208 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 6.63 (d, *J*=8.1 Hz, Ar, 1H), 6.72 (dt, *J*=1.2, 6.6 Hz, Ar, 1H), 6.81–7.43 (series of m, Ar, 23H), 7.60 (m, Ar, 3H), 7.79 (d, *J*=8.1 Hz, Ar, 1H), 7.81 (d, *J*=8.4 Hz, Ar, 1H), 7.82 (d, *J*=7.8 Hz, Ar, 1H), 7.93 (dd, *J*=2.4, 8.4 Hz, Ar, 1H); ^{31}P-NMR ($CDCl_3$) δ: −14.70, 27.69. Anal. calcd. for $C_{44}H_{32}OP_2$: C, 82.74; H, 5.05. Found: C, 82.68; H, 5.16. Selected data for **7** (X=PF_6): (S,S_a)-**7** (less soluble complex): mp 210–215°C (dichloromethane–petroleum ether); $[\alpha]^{20}_D$ −311.6 (c=0.584, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ: 1.85 (d, *J*=6.6 Hz, 3H), 2.20 (d, *J*=6.2 Hz, 3H), 2.41 (d, *J*=3.2 Hz, 3H), 4.28 (m, 1H), 5.80 (d, *J*=8.4 Hz, 1H), 6.12 (dd, 1H), 6.53 (t, *J*=7.8 Hz, 1H), 6.72 (d, *J*=8.4 Hz, 1H), 6.85–8.12 (series of m, 34H); ^{31}P-NMR ($CDCl_3$) δ: 43.41, 42.28. Anal. calcd. for $C_{58}H_{48}F_6NOP_3Pd \cdot 0.5CH_2Cl_2$: C, 60.2; H, 4.32; N, 1.2. Found: C, 60.44; H, 4.48; N, 1.25. (S,R_a)-**7** (more soluble complex): mp 215–220°C; ^{1}H-NMR ($CDCl_3$) δ: 1.80 (d, *J*=6.6 Hz, 3H), 2.60 (d, *J*=6.4 Hz, 3H), 2.81 (d, *J*=3.0 Hz, 3H), 4.28 (m, 1H), 6.15–8.22 (series of m, 38H); ^{31}P-NMR ($CDCl_3$) δ: 44.44, 34.68.
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8. Crystal data for compound **7**: $C_{58}H_{43}F_6NOP_3Pd \cdot 0.5CH_2Cl_2$, M=1130.8, monoclinic, space group C2 (no. 5), a=21.161(3), b=12.111(2), c=21.437(3) Å, β=104 28(1)°, U=5324(2) Å^3, Z=4, D_c=1.411 g cm^{-3}, μ=5.4 cm^{-1}, F(000)=2308. Reflections measured=6667, unique=5685 with $I \geq 3\sigma(I)$, refined parameters=666. For the correct enantiomorph final R=0.040 and R_W=0.051; for the incorrect one R=0.044 and R_W=0.056. Full structural details have been deposited with the Cambridge Crystallographic Centre.
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