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Synthesis and Resolution of 2,2'-bis-diphenylphosphino [3,3']biindolyl ; a New Atropisomeric Ligand for Transition Metal Catalysis

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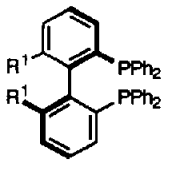
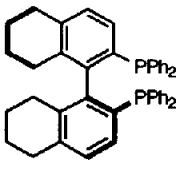
Abstract. A synthesis of the title ligand is described in which the key step is the dilithiation of 1,1'-bis(dimethylaminomethyl)-3,3'-biindolyl and electrophilic trapping with $ClPPh_2$. Concomitant N-deprotection and resolution with bis[(R)-dimethyl(1-(1-naphthyl) ethylaminato-C^2,N)palladium chloride] led to selective recovery of the S-enantiomer. The N-dimethylaminomethyl-substituted biindolyl, but not the parent compound, showed strongly second-order behaviour for ^{13}C NMR peaks in the region of the phosphorus atom due to a desymmetrising ^{13}C-induced isotope shift of the ^{31}P resonance.

The demonstration of high enantioselectivity in numerous catalytic reactions of complexes of 1,1'-bis(diphenylphosphino)binaphthyl (BINAP)[1] has encouraged the synthesis of several related ligands, including compounds **1** -**3** shown below,[2] all of which have led to examples of effective catalytic asymmetric synthesis. Among factors known to be important in controlling the outcome of homogeneous catalysis, the bite angle of chelating ligands[3] and the electronic character of substituents at phosphorus[4] have borne recent emphasis. For these reasons we were interested in defining how the replacement of the binaphthyl backbone of BINAP by a heterocyclic analogue would affect its catalytic chemistry. A recent report of the successful synthesis of the bithienyl **4** by Sannicolò, Cesarotti and co-workers and the high effectiveness of its Ru complex in the asymmetric hydrogenation of β-ketoesters[5] prompts us to record our own efforts in the 3,3'-biindolyl series.[6]



1a R^1 = F
1b R^1 = OMe



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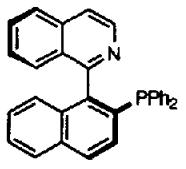

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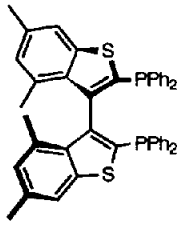

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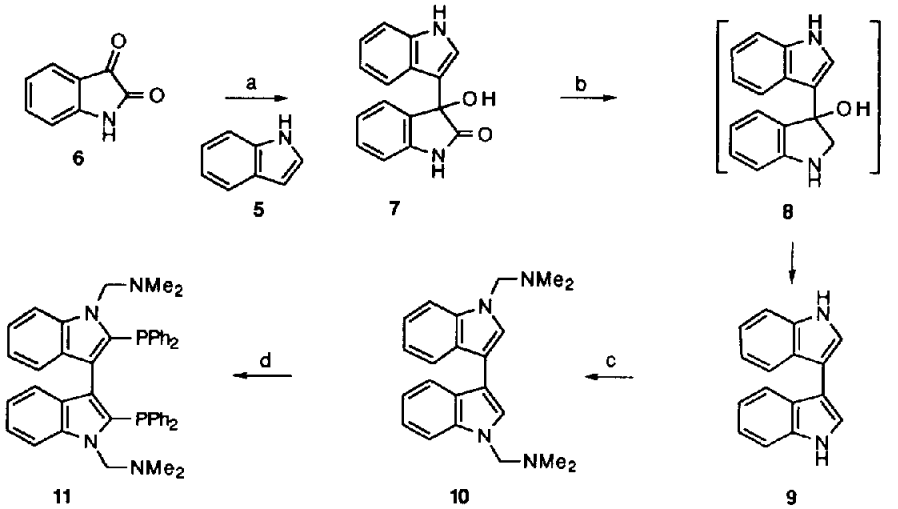
Our first goal was the 3,3'-biindolyl derived ligand **11** which was prepared as outlined in **Scheme 1**. Because of the enhanced acidity of C-H adjacent to the heteroatom in 5-ring heterocycles,[7] the synthetic strategy is straightforward, although in practice some modification had to be made to ensure that the lithiation step proceeded satisfactorily.

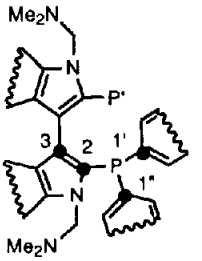


Scheme 1 (**a**): EtOH, cat. $HNMe_2$, 85% (**b**): $NaBH_4$, $BF_3{\cdot}OEt_2$, glyme, 58% (**c**): xs. $H_2C{=}NMe_2{}^+Cl^-$,thf ; NEt_3, 69% (**d**): 2.1 eq. n-BuLi, thf, Ph_2PCl, 51%.

Various syntheses have been described for the required 3,3'-biindolyl **9**.[8] We started with a procedure reported by Bergman[8a] because scaling up seemed simple, and neither difficultly obtainable starting materials[8c] nor toxic heavy metals[8d] were required. The precursor **7** was readily obtained by the reaction of indole **5** with isatin **6** in the presence of small amounts of dimethylamine. However, all attempts to reduce compound **7** with $LiAlH_4$ in dioxane as described by Bergman failed and intractable, deep purple coloured products were obtained. Although the nature of the products formed was not elucidated it seems possible that in the reduction of **7** an indoline was first produced which failed to aromatize later. It is known, however, that reduction of oxindoles or isatins to indoles with $LiAlH_4$ may cause problems which can be circumvented by the use of $BH_3{\cdot}$thf as reducing agent.[9] Reducing **7** with $BH_3{\cdot}SMe_2$ in glyme gave **9** in 44-55% yield, but it was found later that generating the B_2H_6 directly in the reaction mixture from $NaBH_4$ and $BF_3{\cdot}Et_2O$ afforded **9** in an improved yield of 58%. Interestingly, this procedure is very similar to another reported by Bergman for the synthesis of 3,3'-biindolyl.[8b]

Direct dilithiation of the 2,2'-positions in **9** is not feasible due to the acidic protons on nitrogen. This problem could be circumvented by N,N-dialkylation of **9**, but lithiation of the 1,1'-dialkyl-3,3'-biindole obtained was expected to be difficult, as the comparable N-methyl pyrrole can be effectively lithiated only by the Lochman-Schlosser base system. On the other hand, numerous auxiliary groups are known which being attached to the nitrogen facilitate lithiation in the indole 2-position.[9,10,11] The N,N-dimethylaminomethyl

group[10] was chosen for the following reasons: compared with N-arylsulfonamido groups no solubility problems were anticipated, and the basicity of the group could eventually offer a potential handle for the resolution of **11** with enantiomerically pure acids. Reaction of compound **9** with excess N,N-dimethylimmonium chloride (Eschenmoser's salt) and subsequent treatment with NEt_3 afforded **10** in a clean reaction.[12] After double lithiation of **10** and trapping with $ClPPh_2$ the racemic ligand **11** was obtained in 51% yield as a white crystalline solid. It was noted that the ^{13}C NMR spectrum showed unexpected complexity for signals in the vicinity of the phosphorus nuclei. There are precedents by which an induced isotope shift can create magnetic inequivalence;[13] for the present case, the chemical shifts of phosphorus nuclei adjacent to ^{13}C are different to those of the equivalent nuclei adjacent to ^{12}C, and there is a significant PP coupling. This gives the relevant ^{13}C signal the appearance of the X nucleus in an ABX spin pattern. The pattern for each of the affected signals was simulated using gNMR,[14] and the results are gathered in **Table 1**. Note that the spectrum is that of superimposed separate isotopomers of the diphosphine, each with a single ^{13}C at the site of observation. The existence of this phenomenon and the clear diastereotopicity of ortho and meta carbons of the PPh_2 groups, indicate that enantiomers of the ligand do not interconvert on the NMR timescale. In accord with this, the enantiomers can be separated to baseline by chiral HPLC.

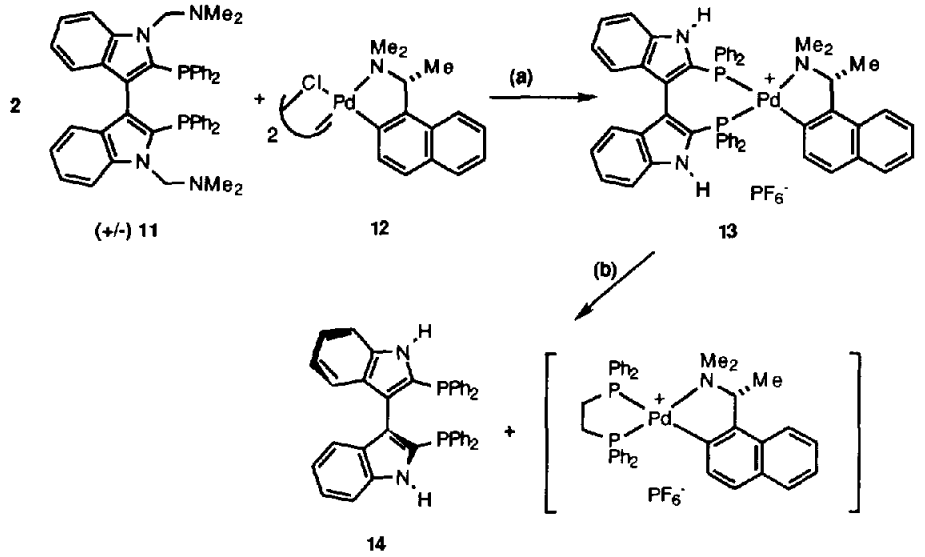


Atom Number	δ_C / ppm	J_{CP} / Hz	$J_{CP'}$ / Hz	δ_P-$\delta_{P'}$ / Hz[a]	$J_{PP'}$ / Hz
2	132.0	33.0	-1.5	5.5	8.2
3	124.5	37.5	5.5	0.7	8.2
1'	136.5	13.5	-1.0	2.5	8.2
1"	134.9	11.8	-2.0	2.1	8.2

Table 1. Simulated ^{13}C NMR data for 2,2'-bisdiphenylphosphino-1,1'bis-dimethylaminomethyl-3,3'-biindolyl in $CDCl_3$; in each case an excellent overlay with the experimental signal was obtained. [a] at 100 MHz.

For the resolution of biaryl-derived ligands, we had found that the chloropalladium complex derived from *R*- or *S*-dimethyl-1'-(1-naphthyl)ethylamine gave consistently satisfactory results. In the course of this earlier work, we proposed that the origin of its effectiveness lay in the conformational lock induced by the 8-H of the naphthalene, which forces the C-methyl group into an axial conformation in the 5-membered metallocycle. The corresponding phenylethylamine is much more flexible and its C-methyl group has access to both axial and equatorial conformations.[15] This explanation is now accepted by Wild,[16] who had earlier observed and proposed an alternative rationalisation of the axial C-Me preference.[17] When the diphosphine **11** was reacted

with an equivalent of the palladium complex **12** (based on monomer) and exposed to aqueous methanolic KPF_6, a yellow precipitate was obtained which was recrystallised from $CHCl_3$ to give X-ray quality crystals. Cursory inspection of the ^1H NMR of this material demonstrated loss of the distinctive signals of the Me_2NCH_2- groups, possibly because the conditions of anion-exchange are sufficiently acidic to promote cleavage. The gross structure **13** is suggested for the Pd-complex (**Scheme 2**) and this was confirmed by the X-ray analysis.



Scheme 2. (a) KPF_6, MeOH; (b) $Ph_2P(CH_2)_2PPh_2$, CH_2Cl_2

The X-ray structure demonstrates the presence of two independent cations,[18] one of which is shown in **Figure 1**. Furthermore, the absolute configuration of the complex is R,S- and the ligand recovered by treating with $Ph_2P(CH_2)_2PPh_2$ is S-**14**, $[\alpha]_D^{25}$ = - 81.9 (c 1, CH_2Cl_2). Future work will be directed to the application of ligand **14** and its close relatives in asymmetric catalysis.

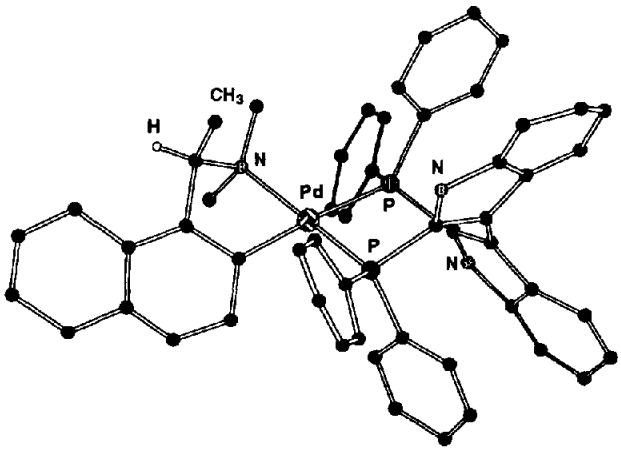


Figure 1. X-ray structure of one of the two independent molecules of complex α-R,S-**13**, with the PF_6^- counterion omitted for clarity.

Acknowledgments

We thank the EC for a Network support grant from the HCM Programme [CT-920067] which enabled UB to visit Oxford for June-Sept 1994. EPSRC provided studentship support to JML under the CASE scheme, and we thank Dr. Neil Cooley and Dr. Evert Ditzel (BP Chemicals) for their continued interest. Dr. Dai Hibbs and Professor M. D. Hursthouse (University of Wales, Cardiff) provided the preliminary X-ray data on complex **13** We thank Johnson-Matthey for the loan of Pd salts. The authors are indebted to Dr. Christine Fischer for the separation of the enantiomers of **11** by chiral HPLC.

Experimental

For general aspects see recent related papers, e.g. reference 2c.

3-Hydroxy-2-oxo-1,3-dihydro-1'H-3,3'-biindolyl 7. This compound was prepared in accordance with the procedure given by Bergman[8a]. Diethylamine used in the original procedure was replaced by an equal amount of a 40% aqueous solution of dimethylamine. Pink crystals (ex. MeOH), yield: 85%, mp.123°C (dec.). δ_H (d^6-acetone , 500 MHz): 5.33 (br s, 1H, OH), 6.95 (1H,"tr", ^3J = 7.5 Hz, H-5'), 7.007 (1H, d, ^3J = 7 Hz, H-7), 7.014 ("tr", 1H, ^3J = 7 Hz, H-5), 7.08 ("tr", 1H, ^3J = 7.6 Hz, H-6'), 7.21 (1H, d, ^3J = 2.6 Hz, H-2'), 7.29 ("tr", 1H, ^3J = 7.7 Hz, H-6), 7.38 (1H, d, ^3J = 7.4 Hz, H-7'), 7.39 (1H, d, ^3J = 8.4 Hz, H-4), 7.66 (1H, d, ^3J = 8 Hz, H-4'), 9.39 (br s, 1H, H-1), 10.19 (br s, 1H, H-1'). ^{13}C-NMR: δ_C 76.27 (C-3), 110.54 (C-7), 112.15 (C-7'), 116.90 (C-3'), 119.61 (C-5'),121.75 (C-4'), 122.23 (C-6'), 122.74 (C-5), 124.33 (C-2'), 125.81 (C-4), 126.31 (C-9'), 129.97 (C-6), 134.08 (C-9), 138.22 (C-8'), 142.62 (C-8), 179.05 (C-2).

1H,1'H-[3,3']Biindolyl 9. A 1 L flask with efficient reflux condenser, dropping funnel and large magnetic stirring bar was charged with finely ground $NaBH_4$ (11.4 g., 0.3 mol), 28.0 g of **7** (0.1 mol) and 150 ml of 1,2-dimethoxyethane. Then a solution of BF_3•OEt_2 (57 g., 0.4 mol) in 50 ml of 1,2-dimethoxyethane is added by the dropping funnel. **[NB. This has to be done carefully, because the reaction is very exothermic.]** Where the BF_3•OEt_2 dropped into the mixture, an interesting colour change from deep blue to deep red was observed in the region of the drop, while the rest of the reaction mixture remained yellow. When about half of the BF_3•OEt_2 had been added, the reaction mixture became very viscous and thick lumps were formed which disappeared later. When the addition of BF_3•OEt_2 was completed, the mixture was stirred for another hour and then 6 N HCl (100 ml) was carefully added by dropping funnel. The obtained suspension was diluted with H_2O (600 ml) and the solid filtered off. The filter cake was washed with water, dried, and then redissolved in a minimum of hot thf (ca. 150 ml). This solution was filtered and after slow addition of CH_2Cl_2 (ca. 300 ml) to the filtrate compound **9** crystallised in fine plates. Yield: 13.45 g (58% based on **7**), mp. = 285-287°C. δ_H (DMSO d^6, 500 MHz): 7.09 (tr, 1, ^3J = 7.3 Hz, H-5); 7.17 (tr, 1, ^3J = 7.3 Hz, H-6); 7.48 (d, 1, ^3J = 8.0 Hz, H-7); 7.67 (d, 1, ^3J = 2.3 Hz, H-2); 7.82 (d, 1, ^3J = 8.0 Hz, H-4); 11.17 (br s, 1, H-1). δ_C : 109.97 (C-3); 111.77 (C-7); 119.02 (C-5); 119.80 (C-4); 121.41 (C-6); 122.04 (C-2); 126.30 (C-9); 136.61 (C-8).

1,1'-Bis(dimethylaminomethyl)[3,3']biindolyl 10. Under exclusion of moisture N,N-dimethylmethyleneimmonium chloride[12] (16 g., 172.4 mmol) was added to a solution of 1H,1'H-[3,3']biindolyl **9** (43.1 mmol) in thf (150 ml). The suspension obtained was stirred for 24 hours and then NEt_3 (17.4 g., 172 mmol) added. A slightly exothermic reaction took place and the mixture was stirred for further 2

h. After removal of the solvents on a rotary evaporator the residue was suspended in water (100 ml) and the product extracted twice with CH_2Cl_2 (100 ml each portion). The combined organic layers were dried ($MgSO_4$) and concentrated to a volume of ca. 30 ml. Petroleum ether (40-60) was carefully added until the solution became turbid. On standing for several h. compound **10** crystallised in chunky prisms, mp.127°C, (10.3 g., 69%). (Found: C, 76.10; H, 7.87; N 15.81; $C_{22}H_{26}N_4$ requires C, 76.27; H, 7.57; N, 16.17%) δ_H ($CDCl_3$, 400 MHz): 2.42 (s, 12H, $N(CH_3)_2$); 4.87 (s, 4H, NCH_2N); 7.22 (ddd, 2H, ^3J = 7.0 Hz, ^3J = 7.9Hz, ^4J = 1.0 Hz, H-5, H-5'); 7.32 (ddd, 2H, ^3J = 7.0 Hz, ^3J = 8.2 Hz, ^4J = 1.21 Hz, H-6, H-6'); 7.49 (s, 2H, H-2, H-2'); 7.56 (d, 2H, ^3J = 8.2 Hz, H-7, H-7'); 7.87 (d, 2H, ^3J = 7.9 Hz, H-4, H-4'). δ_C ($CDCl_3$, 100 MHz): 43.26 ($N(CH_3)_2$), 69.22 (NCH_2N), 110.30 (C-3, C-3'), 110.57 (C-7, C-7'), 120.06 (C-5, C-5'), 120.68 (C-4, C-4'), 122.55 (C-6, C-6'), 126.41 (C-2, C-2'), 127.84 (C-8, C-8'), 137.86 (C-9, C-9').

1,1'-Bis-dimethylaminomethyl-2,2'-bis-diphenylphosphino[3,3']biindolyl 11. A 100 ml flask with magnetic stirrer bar was charged with compound **10** (2.0 g., 5.77 mmol) and flushed with argon. Then 15 ml. of anhydrous Et_2O was added and n-BuLi solution (2.5 M in hexanes, 7.13 g., 12.1 mmol, 5% excess) was added slowly via syringe to the slurry obtained. After stirring for 30 min, glyme was added slowly via a syringe until the slurry dissolved (ca. 2 ml required). After some minutes a precipitate was formed again and the mixture was stirred for a further hour. A solution of of $ClPPh_2$ (2.67 g., 12.1 mmol) in Et_2O (10 ml) was added over 10 min. A slightly exothermic reaction took place and the reaction mixture was then stirred for another h. After addition of 1 ml of MeOH the solvents were removed on a rotavapor and the residue redissolved in CH_2Cl_2 (20 ml.). This solution was washed twice with water and after drying (Na_2SO_4) most of the dichloromethane was removed until a light syrup remained. After addition of Et_2O (ca. 30 ml) the product began to crystallize as chunky crystals, (2.1 g., 51% based on **10**), mp.197-200°C.(Found: C, 77.20; H, 6.22; N 7.81; $C_{46}H_{44}N_4P_2$ requires C, 77.29; H, 6.20; N, 7.84%) δ_C ($CDCl_3$, 62.5 MHz): (see discussion) 41.20 (s, $N(CH_3)_2$); 68.43 (s, NCH_2N); 112.57 (s, C-7, C-7'); 119.83 (s, C-5, C-5'); 120.78 (ABX, C-4, C-4'); 123.36 (s, C-6, C-6'); 124.53 (ABX, C-3, C-3'); 127.48, 127.88 (2 s, Ph p-C); 127.86, 128.26 (2 ABX, Ph m-C); 130.49, 132.03 (2 ABX, C-3,C-3'; C-9,C-9'); 132.46, 132.58 (2 ABX, Ph o-C); 135.07, 136.61 (2 ABX, Ph ipso-C); 139.95 (s, C-8, C-8'). δ_P ($CDCl_3$): -30.3 ppm.

Resolution/Deprotection of (+/-) 1,1'-Bis-dimethylaminomethyl-2,2'-bis-diphenylphosphino [3,3']biindolyl 11; synthesis of R,S-13 : Racemic diphosphine **11** (143 mg, 0.2 mmol) and palladium dimer **12** (68 mg, 0.1 mmol) were dissolved in MeOH (5 ml) and the solution was stirred at room temperature for 2 h.. KPF_6 (50 mg, 0.26 mmol) in water (5 ml) was added whereupon a yellow precipitate formed. This was removed by filtration and dried in a vacuum dessicator to give the bisphosphine palladium complex (0.18 mmol, 195 mg. 85 %). Deprotection occurs *in situ* under the mild reaction conditions. δ_P (CD_2Cl_2, 101.3 MHz) 26.7, 2.6 (ABq, J_{PP} 39 Hz), 22.8, 1.8 (ABq, J_{PP} 39 Hz). Dissolution of the product in ice-cold $CHCl_3$ led to the rapid precipitation of a yellow powder which was recrystallised from chloroform to give yellow blocks of **13**. δ_H (CD_2Cl_2, 500 MHz): 8.16 (2H, m), 8.09 (1H, s, N-H), 8.03 (1H, s, N-H), 7.83 (2H, m), 7.75 (2H, br m), 7.70 (2H, d, J = 8.5 Hz), 7.64 (3H, m), 7.57 (1H, d, J = 8.1 Hz), 7.43 (1H, dt, J = 7.0, 1.2 Hz), 7.37 (2H, d, J = 7.9 Hz), 7.34-7.28 (4H, m), 7.25 (1H, d, J = 8.3 Hz), 7.20-7.12 (7H, m), 7.08 (2H, t, J = 6.9 Hz), 7.01 (2H, q, J = 6.9 Hz), 6.86 (1H, d, J = 8.6 Hz), 6.83 (2H, br m), 6.75 (1H, e), 2.10 (3H, s, N-Me); δ_P (CD_2Cl_2, 101.3 MHz) 23.5 (d, J = 39 Hz), 2.5 (d, J = 39 Hz), -143 (sept, J_{PF} = 135 Hz); $[\alpha]_D^{22}$ = -139 (c=0.1, CH_2Cl_2); m/z (electrospray) 903 (100 %; correct isotope pattern).

(S)-2,2'-bis-diphenylphosphino[3,3']biindolyl, S-14.

The palladium complex **13** (130 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (3 ml), *bis*-Diphenylphosphinoethane (52 mg, 0.13 mmol) was added as a solid, and the solution was stirred for one hour. Toluene (3 ml) was added and the solvents removed *in vacuo*. The residue was redissolved in toluene (5 ml) and the solid filtered off. The toluene was again removed *in vacuo* leaving an off-white solid which was dissolved in a little CH_2Cl_2 and filtered through a short silica column using CH_2Cl_2 as the eluent. Removal of the CH_2Cl_2 *in vacuo* gave a diphosphine **14** as a white solid (0.070 g., 94 %), m.p. = 146-8 °C. ^1H (500 MHz): δ_H ($CDCl_3$) 7.88 (2H, br s, N-H), 7.43 (2H, d, J = 8.0 Hz, H4), 7.34-7.21 (24H, m), 7.04 (2H, t, J = 7.5 Hz, H5); ^{13}C (125.6 MHz): δ_C ($CDCl_3$) 138.4 (C8), 137.0 (C2, J = 63.7 Hz), 133.0-132.8 (Co, Co', Cp, Cp'), 130.5 (Ci, Ci'), 129.7 (C9), 128.5-128.4 (Cm, Cm', J = 15.3 Hz), 123.3 (C5); 121.0 (C4), 120.7 (C3, J = 13 Hz), 119.7 (C6), 111.0 (C7); δp ($CDCl_3$) -31.9 ppm; $[\alpha]_D^{25}$ = -81.9 (c=1.01, CH_2Cl_2).

References

1. (a) Takaya H.; Akutagawa S.; Noyori R. *Org. Synth.* **1989**, *67*, 20. (b) Takaya H.; Mashima K.; Koyano K.; Yagi M.; Kumobayashi H.; Taketomi T.; Akutagawa S.; Noyori R. *J. Org. Chem.* **1986**,*51*, 629.
2. Ligand **1a**: Jendralla, H.; Li, C.-H.; Paulus, E. *Tetrahedron: Asymmetry* **1994**, *5*, 1297; Ligand **1b**: Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P.; Hansen, H.-J. *Helv. Chim. Acta* **1988**, *71*, 897. Ligand **2**: Zhang, X. Y.; Uemura, T.; Matsumura, K.; Sayo, N.; Kumobayashi, H.; Takaya, H.*Synlett* , **1994**, 501; Ligand **3**: Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* , **1994**, *50*, 4493; Brown, J. M.; Hulmes, D. I.; Layzell, T. P. *J. Chem. Soc. Chem. Comm.*, **1993**, 1673-1674.
3. Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A.; Powell, D. R. *J. Am. Chem. Soc* , **1992**, *114*, 10680; Yamamoto, K.; Momose, S.; Funahashi, M.; Ebata, S.; Ohmura, H.; Komatsu, H.; Miyazawa, M. *Chem. Lett.*, **1994**, 189.
4. Allen, J. V.; Bower, J. F.; Williams, J. *Tetrahedron Asymmetry*, **1994**, *5*, 1895; Casalnuovo, A. L.; Rajanbabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem Soc.*, **1994**, *116*, 9869; Legros, J. Y.; Fiaud, J. C. *Tetrahedron* , **1994**, *50*, 465; Rajanbabu, T. V.; Ayers, T. A. *Tetrahedron Lett.*, **1994**, *35*, 4295; Rajanbabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**,*116*, 4101; Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 931-933.
5. Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Antognazza, P.; Cesarotti, E. *J. Chem. Soc., Chem. Commun.* **1995**, 685.
6. Synthesis of ligands in this class was commenced during a visit to Oxford between June and September 1994 by Dr. Berens and continued in Rostock and Oxford subsequently. In addition to much of the work described in this paper, racemic 2,2-*bis*-(diphenylphosphino)-3,3'-di-(benzothiophenyl) was prepared in summer 1994 and subsequently resolved by the method described herein, On learning of the interest of the Milan group we discontinued work on the benzothiophen system; we are grateful to Professor E. Cesarotti for an exchange of information, June-Sept 1995
7. Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.*, **1983**, 620-621; Fraser, R. R.; Mansour, T. S.; Savard, S. *Can. J. Chem* **1985**, *63*, 3505-3509; Tupitsyn, I. F.; Popov, A. S.; Shibaev, A. Y. *Z. Obshch. Khimii* **1992**, *62*, 2319-2328.

8. (a) Bergman, J. *Acta Chem. Scand.* **1971**, *25*, 1277. (b) Bergman, J.; Eklund, N. *Tetrahedron* **1980**, *6*, 1445. (c) Saleha, S.; Khan, N. H.; Siddiqui, A. A.; Kidwai, M. M. *Indian J. Chem.* **1978**, *16B*, 122. (d) Hino, T.; Tsuneoka, K.; Nakagawa, M.; Akaboshi, S. *Chem. Pharm. Bull.* **1969**, *17*, 550.
9. Sirowej, H.; Khan, S.A.; Plieninger, H. *Synthesis* **1972**, 84.
10. (a) Hlasla, D.J.; Bell, M. R. *Heterocycles* **1989**, *29*, 849; (b) Katritzky, A. R.; Lue, P.; Chen, Y.-X. *J. Org. Chem.* **1990**, *55*, 3688.
11. (a) Katritzky, A. R.; Akutagawa, K. *Tetrahedron Lett.* **1985**, *26*, 5935. (b) Hasan, I.; Marinelli, E. R.; Lin, L-C. C.; Fowler, W. F.; Levy, A. B. *J. Org. Chem.* **1981**, *46*, 157. (c) Edwards, M. P.; Doherty, A. M.; Ley, S. V.; Organ, H. M. *Tetrahedron* **1986**, *42*, 3723. (d) Somei, M.; Kobayashi, T. *Heterocycles* **1992**, *34*, 1295. (e) Gharpure, M.; Stoller, A.; Bellamy, F.; Firnau, G.; Snieckus, V. *Synthesis* **1991**, 1079. (f) Sundberg, R. J.; Russell, H. F. *J. Org. Chem.* **1973**, *38*, 3324.
12. Kinast, G.; Tietze, L.-F. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 239, see also Böhme, H.; Hartke, K. *Chem. Ber.* **1960**, *63*, 1305.
13. Lowe, G.; Potter, B. *J. Chem. Soc., Chem. Commun.*, **1984**, 877-879; Hansen, P. E. *Prog.Nucl. Mag. Res.* , **1988**, *20*, 207-255.
14. Programme gNMR for Apple Macintosh; IvorySoft®1994.
15. Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* ,**1993**, *4*, 743-756; Chooi, S.; Tan, M. K.; Leung, P. H.; Mok, K. F. *Inorg.Chem.*, **1994**, *33*, 3096-3103; Alcock, N.W.; Hulmes, D. I.; Brown, J. M. *J. Chem. Soc. Chem. Comm.*, **1995**, 395-397.
16. Pabel, M.; Willis, A. C.; Wild, S. B. *Tetrahedron : Asymmetry*, **1995**, *6*, 2369-74.
17. Leung, P. H.; Willis, A. C.; Wild, S. B. *Inorg. Chem.*, **1992**, *31*, 1406.
18. Hursthouse, M. D.; Hibbs, D., to be published.

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