Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 10, pp. 2597-2610, 1995

0957-4166/95 $9.50+0.00

0957-4166(95)00341-X

Synthesis and Chemistry of a New P-N Chelating Ligand; (*R*) and (*S*)-6-(2'-Diphenylphosphino-1'-naphthyl)phenanthridine

Jean-Marc Valk, Timothy D. W. Claridge and John M. Brown*

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QY, U.K.

David Hibbs and Michael B. Hursthouse

School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, U.K.

Abstract. A synthesis of the title phosphinamine (PHENAP) is described, following previously established methodology. Resolution *via* the C,N-palladocycle derived from (*R*)-N,N-dimethyl-α-methyl-1-naphthylamine led to two crystallographically defined complexes with the (*R,S*)-form posessing a chelated ligand and the (*R,R*)-form open with only the phosphine coordinated. Palladium allyl complexes of the ligand were strikingly different from those of the corresponding isoquinoline ligand QUINAP, and the differences could be rationalised by recourse to molecular models, with the additional fused arene ring of PHENAP playing a critical part in defining the coordination sphere through its steric pressure. A brief appraisal of Pd-catalysed allylic alkylation reactions was performed with the new ligand.

Introduction.

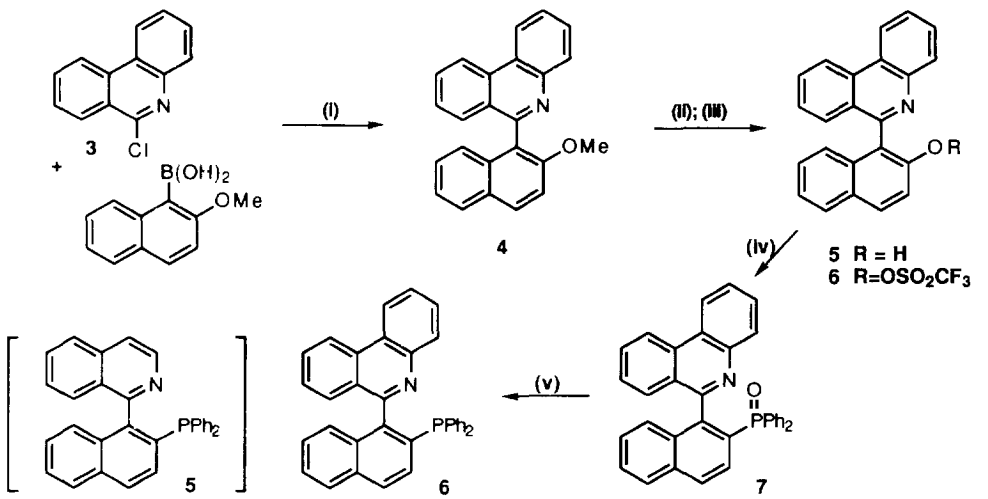
We previously reported the synthesis and resolution of the heterotopic P-N ligand 1-(2'-diphenylphosphino-1'-naphthyl)isoquinoline **1** (QUINAP)[1] which proved to be effective in Rh-catalysed hydroboration[2] and in Pd-catalysed allylic alkylation.[3] Examination of molecular models based on the X-ray crystal structures of its complexes led to a suggestion that the steric effect of 3-H of the isoquinoline played an important role in determining the high enantiomeric excesses observed in the latter reaction. This encouraged the synthesis of analogous compounds in which this region of the ligand is systematically varied; one of the simplest is the arene-fused analogue **2**, which could in principle be prepared by similar methodology to its parent **1** .

Results and Discussion

Ligand synthesis :The synthesis of compound **2** was carried out uneventfully according to the protocols of **Scheme 1**, in which manner over 15 grams of the racemic ligand were prepared. 6-Chlorophenanthridine **3** was prepared by minor modifications of procedures in the older literature.[4] The Suzuki coupling of **3** with 2-methoxy-1-naphthaleneboronic acid proceeded smoothly under the previously described conditions giving compound **4** in 89% yield; the crude material was pure enough to be used directly in the next step, although a

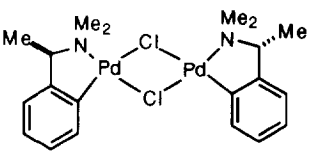
Dedicated to the memory of Professor Hidemasa Takaya, deceased on 5 October 1995

small sample was recrystallised from CH_2Cl_2 for analytical and spectroscopic characterisation. This was in turn demethylated[5] with BBr_3 giving phenol **5** in 81% crude yield which was converted into the triflate **6** in 72% yield with the standard reagents. Phosphinylation was carried out as described in the synthesis of QUINAP; in this case the competing reduction to the 2-H product was unimportant and the phosphine oxide **7** was formed in 88% yield. $HSiCl_3$ reduction of the oxide gave the racemic ligand **2** in 81% yield as a white powder.



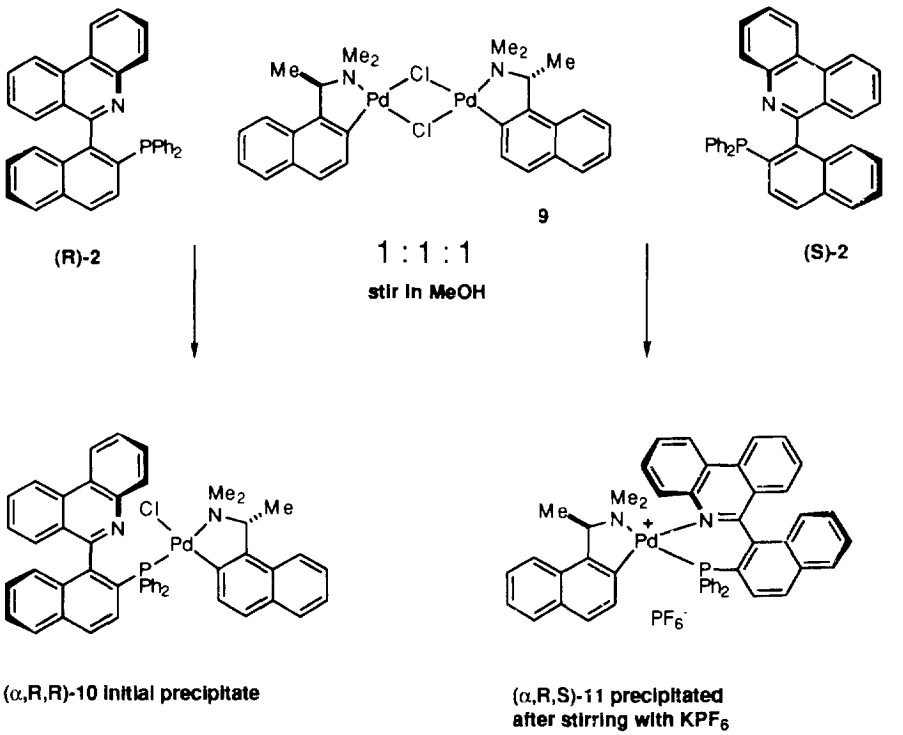
Reagents : (i) 3 mol% $Pd(PPh_3)_4$, Na_2CO_3, DME, reflux 12 h., 89% (ii) BBr_3, CH_2Cl_2, 12 h., 81% (iii) Tf_2O, DMAP, CH_2Cl_2, 1h., 72% (iv) [$Pd(OAc)_2$, dppp, (2 mol%)], $Ph_2P(H)O$, $NaHCO_3$, DMSO, 80°C, 20h, 88% (v) $HSiCl_3$, NEt_3, C_7H_8, reflux 2.5 h., 81%

Scheme 1



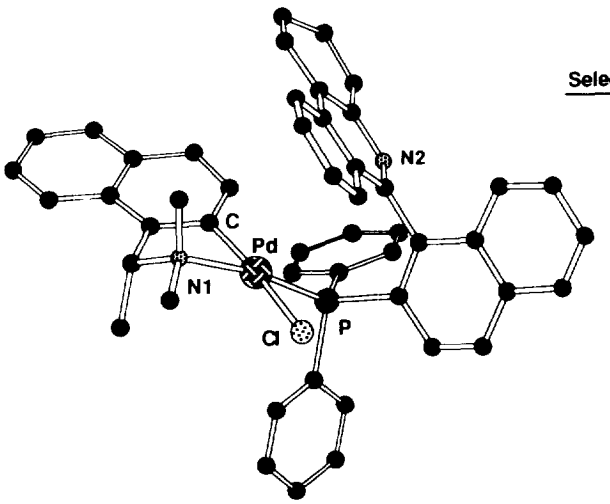
(*R*)-**8**

Resolution : A standard method for the resolution of chelating ligands has been the formation and separation of diastereomeric complexes by displacement of the chloride bridge in dimer **8** or its 1-naphthyl analogue. The latter proved to be extremely effective for QUINAP but the former was not, giving a crystalline quasiracemate. This was explained in terms of conformational flexibility of the palladocycle unit of complexes derived from **8**; the side-chain C-methyl group in the 1-naphthyl analogue is locked in an axial position, with enforced rigidity in its ligated complexes.[6] Under the conditions previously applied, the new ligand **2** behaved rather differently (**Scheme 2**). Mixing di-μ-chloro-bis[(*R*)-(α,N,N-trimethyl-1-aminomethylnaphthyl)palladium] **9** and ligand **2** in 1:2 molar ratio in MeOH at ambient temperature led to the precipitation of a white powder after 30 min. This was filtered off after stirring overnight, and the residual solution treated with KPF_6 leading to the precipitation of a second off-white solid.



Scheme 2.

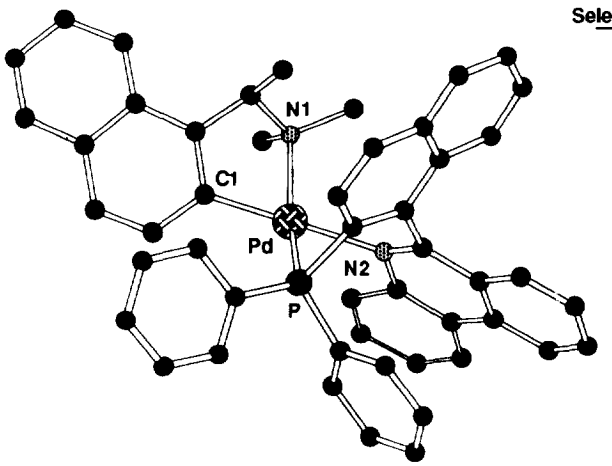
The two products were separately recrystallised from CH_2Cl_2/ Et_2O, and X-Ray crystal structures obtained. The first of these is complex **10** which is the (*α,R,R*)-diastereomer shown in **Figure 1**. The phenanthridine nitrogen remains uncoordinated, with the original covalent Pd-Cl intact. The second compound **11** is the (*α,R,S*)-diastereomer and had the expected chelate structure shown in **Figure 2**. As in previous examples, there is evidence of strain in the chelate ring, with the N-Pd vector displaced about 18° from the ring plane (ca. 24° in QUINAP complexes),[1,6] and the naphthalene C-P bent by 12°; the biaryl twist angle is 64°. In separate experiments where an excess of the ligand over resolving agent was employed, the (*α,R,S*) diastereomer was formed with a d.e. of 98%; this is also the more stable combination in the QUINAP series. As anticipated, the 3,4-ring fusion on the parent isoquinoline brings the 7-H of phenanthridine into close proximity to the metal, and leads to much closer ligand-ligand contacts. The importance of this interaction in defining the specificity of complexation will be addressed later.



Selected bond lengths (Å) and angles(°)

Pd-P	2.266(2)
Pd-N	2.150(5)
Pd-Cl	2.403(2)
Pd-C1	2.004(6)
P-Pd-N1	169.7(2)
P-Pd-Cl	87.3(1)
P-Pd-C1	98.7(2)
N1-Pd-Cl	94.2(2)
N1-Pd-C1	79.7(2)
Cl-Pd-C	173.8(2)

Figure 1. X-ray crystal structure of complex (*α,R,R*)-**10**. H-atoms have been omitted for clarity



Selected bond lengths (Å) and angles(°)

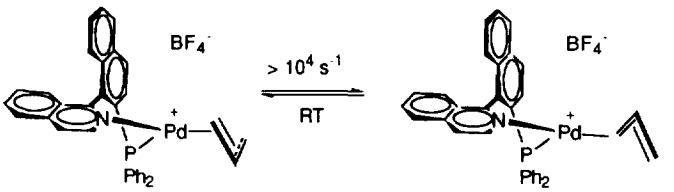
Pd-P	2.249(3)
Pd-N1	2.154(8)
Pd-N2	2.163(7)
Pd-C1	1.975(9)
P-Pd-N1	155.7(2)
P-Pd-N2	81.5(2)
P-Pd-C1	96.6(3)
N1-Pd-N2	103.5(3)
N1-Pd-C1	80.2(3)
N2-Pd-C1	174.8(3)

Figure 2. X-ray crystal structure of complex (*α,R,S*)-**11**. H-atoms and PF_6^- counterion have been omitted for clarity.

Decomplexation to remove the resolving agent proved to be straightforward, using 1,2-bis-diphenylphosphinoethane in CH_2Cl_2 followed by separation on a short silica column. In this way the (*R*)-enantiomer of **2**, $[\alpha]_D^{25}$ = +168.8 (c = 0.994, $CHCl_3$), was prepared in pure form from complex **10**. The (*S*)-enantiomer of **2**, $[\alpha]_D^{25}$ = -167.9 (c = 0.976, $CHCl_3$), was formed in pure form from complex **11** only after a second cycle of complexation / decomplexation.

Palladium allyl complexes obtained from ligand 2 : The high enantiomer excesses obtained in catalytic allylic alkylation with heterotopic P-N ligands has its origins in a regiospecific exometallic nucleophilic attack *trans*-

to phosphorus. In addition, it is the preferred allyl diastereomer which sustains the catalytic cycle, and the enantioselectivity exceeds the diastereoselectivity of catalysis.[3,7,8] Hence the recognition of η^3-allyl diastereomers by a coordinated ligand plays a critical role in asymmetric catalysis. It was previously reported that the simple Pd-QUINAP allyl **12** exhibited a highly dynamic ^{1}H NMR spectroscopy at ambient temperature, whilst below 220K both diastereomers could be observed in close to 1:1 ratio.



12

In contrast a sharp spectrum was obtained at ambient temperature from the PHENAP analogue **13**, with two diastereomers in 6:1 ratio. The allyl signals were fully assigned, based on the presumption that P-coupled protons were *trans*-to phosphorus. An EXSY spectrum reinforced the assignments through the patterns of spin-saturation and in addition revealed an specific exchange pathway linking the two diastereomers **13a** and **13b**, **Figure 3**.

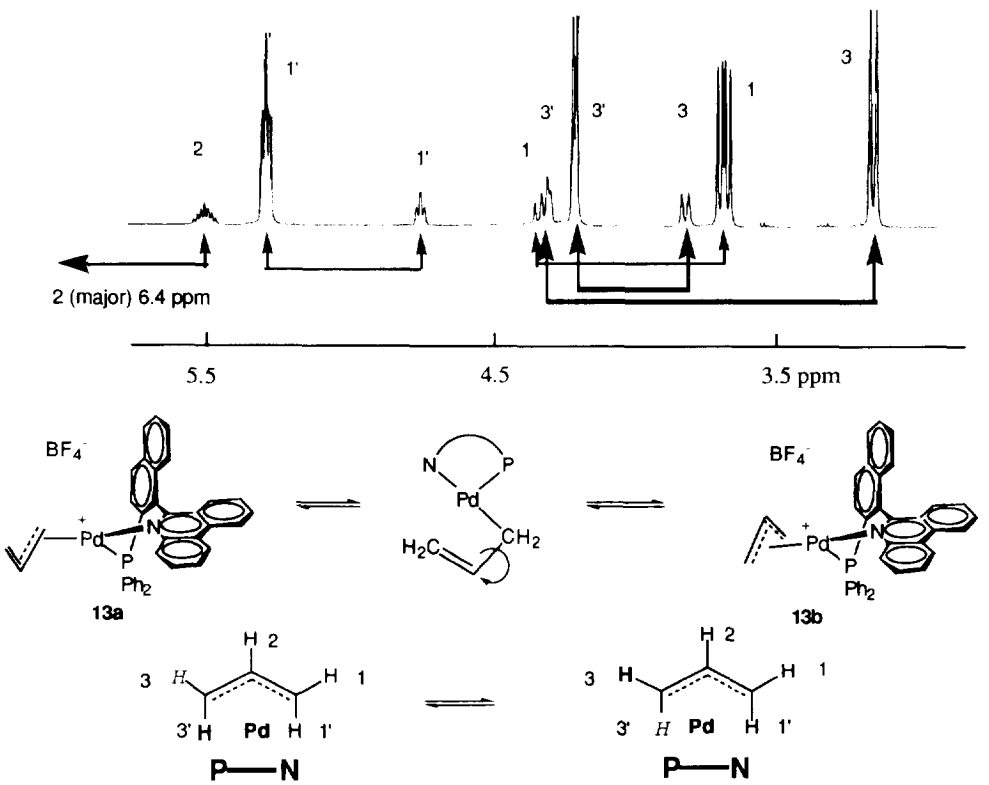
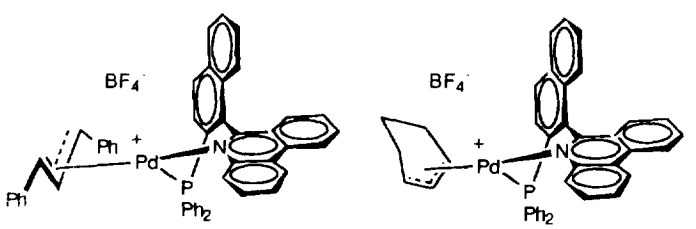


Figure3. Proton NMR spectrum of the allyl region of complex **13** in $CDCl_3$. The interconversion pathwa between the diastereomers is revealed by the ^{1}H EXSY spectrum, and the exchange-linked protons are denoted by arrows.

This path leads to conservation of geometry at the allylic terminus *trans* to phosphorus concurrent with its inversion *trans* to nitrogen in each exchange event. This is simply explained by the mechanism shown which follows that concurrently proposed by Pregosin, Togni and co-workers[9] and by Helmchen and co-workers.[10] This pathway implies that only one σ-allyl intermediate is easily accessible, in which the Pd-C bond is *trans* to nitrogen rather than to phosphorus. We defer judgment on whether the process requires nucleophilic attack by solvent or counterion, the nucleophile occupying the formally vacant coordination site, but note that the corresponding $CF_3SO_3^-$ salt shows the onset of dynamic broadening in its ^1H NMR at ambient temperature. The formal allyl rotation mechanism which has been shown by Backvall's group to involve ligand dissociation and return in specific cases, is not important on the timescale of the EXSY accumulation.[11] This or a related process must contribute to the corresponding QUINAP η^3-allyl dynamics,[3] since the high temperature limit has all the E- and Z-terminal allyl protons equivalent. The discrimination between the diastereomers **13a** and **13b** is likely to arise from the intrusion of the phenanthridine C-ring into the coordination sphere. Inspection of molecular models based on the X-ray structure of complex **11** indicates that one of the two is sterically favoured. This is reinforced by the observation that in the X-ray structure of an η^3-palladium allyl with a related P-N ligand, the allyl has twisted substantially with respect to the coordination plane so that one C-C bond is almost coplanar with Pd-P. At this stage the stereochemical assignment of the isomers **13** is tentative. The ^1H NMR spectrum of the corresponding diphenylallyl complex **14** showed two diastereomers in ratio 10 :1 ($CDCl_3$) or 20:1 (CD_2Cl_2) but specific information on assignments and interconversion was not easily derived.



14 diastereomers **15**

η^3-Cyclohexenyl complexes of palladium have been studied previously,[12] and in the case of QUINAP two diastereomers were formed in 1:1 ratio.[3] It has now been shown through an EXSY experiment that these interconvert readily on the NMR timescale. Complex **15** shows dramatically different behaviour, in that only a single diastereomer with clear separation of key NMR signals was obtained (**Figure 4**).

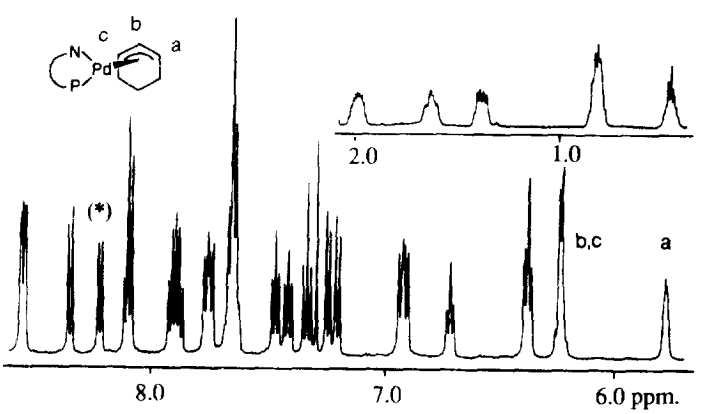


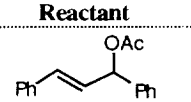
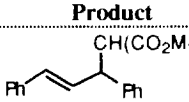
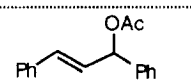
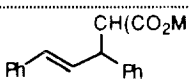
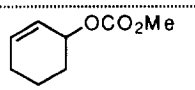
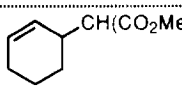
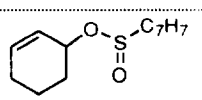
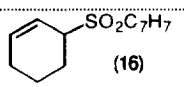
Figure 4. ^1H NMR spectrum of complex **15** in $CDCl_3$ demonstrating the diastereomeric homogeneity. In CD_2Cl_2, the allylic protons are separated; **a** (*trans* to N) has a strong nOe to an ortho-PPh_2 proton and both **b** and **c** have strong nOe's to the 4-proton of the phenanthridine(*).

We assign the configuration shown to this on the basis of molecular models; in the alternative diastereomer severe non-bonded interactions involving 4-H of the phenanthridine must occur.

Catalytic allylic alkylation reactions : A limited number of experiments have been carried out to compare the efficiencies of the two P-N ligands in catalytic allylic alkylation, and these are recorded in **Table 1**. The most interesting feature is that the PHENAP complex (which exhibits higher diastereoselectivity on complexation) gives a slightly reduced e.e. in the reaction of 1,3-diphenylallyl acetate under the previously optimised conditions,[3] but was the more enantioselective under the base-free conditions introduced by Trost.[13] It is these latter conditions which have been adopted to great effect by Pfaltz, Helmchen and their respective co-workers.[14]

Despite the high level of recognition in the cyclohexenyl complex **15**, there was no observed allylic alkylation of cyclohex-3-en-1-yl acetate under standard conditions. With the more reactive carbonate, and under quite forcing conditions, the desired product was formed in 84% yield as a racemate. This tends to imply that there are alternative pathways accessible which bypass the specificity of η^3-allyl formation. The intramolecular palladium-catalysed rearrangement of allylsulfinates to allyl sulfones has been observed previously,[15] and this was considered to be a means of bypassing steric constraints on reactivity. The cyclohexenyl sulfinate was prepared as a mixture of diastereomers and reacted with the catalyst in the presence of a small quantity of sodium dimethyl malonate as primer. No reaction was apparent at ambient temperature, but it was complete in a few minutes at 60°C giving enantiomerically enriched sulfone **16**, albeit in moderate e.e.. There are stereochemical complexities in the experiment including the possibility of kinetic resolution and diastereomer selection in the reactant, and Pd-catalysed racemisation of the product. There were indications that the e.e. diminished somewhat as reaction proceeded. Nonetheless, the observed e.e. was very similar for QUINAP and PHENAP catalysts, despite the gross differences in complexation of the cyclohexenyl fragment.

Table 1. Catalytic allylic alkylations with PHENAP - palladium complexes.

Reactant	Product	E.e. (yield)
		**95** (65%, 0.6 mmoles)[a] [**98**]
		**94** (67%, 0.6 mmoles)[b] [**76**]
		**0** (84%) [**67**][c]
	 **(16)**	**ca. 25** (>85%)[d]

Reactions were carried out with 1-2 mol% catalyst under previously described conditions, typically employing compex **13** as the catalyst; in the diphenylallyl series (*R*)-**2** derived catalyst gives rise to S-product. [a]Carried out in CH_3CN in the presence of 15-crown-5 at 0°C. [b]Carried out by the BSA method at 20°C in CH_2Cl_2. [c]E.e.s in square brackets are those obtained with ligand **1**, ref 3. [d]5 mol% catalyst.

Acknowledgments : We thank the European Community for support (to JMV) under HCM Network contract CRT 920067, and to Johnson-Matthey for the loan of palladium salts. Mrs E. McGuinness was very helpful in the obtention of high-field NMR spectra. Full details of X-ray structures (data collection and refinement, crystal data, atomic coordinates and thermal parameters) may be obtained from the Cambridge Crystallographic Data Centre.

Experimental.

Standard procedures, general methods and resources may be obtained from recent related papers (e.g. ref 3)

6-[1-(2-methoxynaphthyl)]phenanthridine 4

6-Chlorophenanthridine (20.1g, 94 mmol) and $Pd(PPh_3)_4$ (3.26g, 2.82 mmol) were stirred at room temperature in dry DME for 10 min. to give an orange solution. To this was added 2-methoxy-1-boronic acid (19.0g, 94 mmol) in the minimum amount of ethanol (100 ml.) and 94 ml. of a 2M solution of Na_2CO_3 in water. The resulting yellow solution was heated at reflux overnight. After cooling to room temperature the solid was filtered off and thoroughly washed with CH_2Cl_2. The solution was washed with saturated brine (2 x 100 ml.), dried with $MgSO_4$. and concentrated. The solid residue was washed with Et_2O (2 x 50 ml.) and dried *in vacuo* giving white 6-[1-(2-methoxynaphthyl)]phenanthridine (28.0g, 84 mmol, 89%, m.p. 231°C). The product was pure enough to be used in subsequent reactions; a sample was recrystallised from CH_2Cl_2 for characterisation. (Found: C, 86.00; H, 5.25; N, 4.11, $C_{24}H_{17}NO$ requires: C, 85.97; H, 5.07; N, 4.18). δH ($CDCl_3$, 500 MHz) 8.76 (d, 1 H, J = 8.3 Hz), 8.72 (dd, 1 H, J_1 = 0.7 Hz, J_2 = 8.0 Hz), 8.34 (dd, 1 H, J_1 = 0.8 Hz, J_2 = 8.0 Hz), 8.07 (d, 1 H, J = 9.1 Hz), 7.92 (d, 1 H, J = 8.2 Hz), 7.85 (t, 1 H, J = 7.4 Hz), 7.82 (dt, 1 H, J_d = 1.3 Hz, J_t = 7.8 Hz), 7.76 (dt, 1 H, J_d = 1.2 Hz, J_t = 7.5 Hz), 7.63 (d, 1 H, J = 8.1 Hz), 7.51 - 7.48 (m, 2 H), 7.37 (t, 1 H, J = 7.5 Hz), 7.27 (t, 1 H, J = 7.4 Hz), 7.22 (d, 1 H, J = 8.3 Hz), 3.81 (s, 3 H, OMe)..δC ($CDCl_3$, 125.72 MHz) 159.0, 154.9, 144.2, 133.7, 132.9, 130.6, 130.5 (2 C), 129.2, 128.6, 128.4, 127.9, 127.3, 126.9, 126.8, 124.8, 124.0, 123.7, 122.1, 122.0, 113.5, 56.6 (CH_3). GC/MS (EI) m/z 335 (88%, M^+), 334 (100%, $[M-H]^{+\cdot}$), 319 (53%, $[M-O]^{+\cdot}$), 303 (21%, $[M-MeOH]^{+\cdot}$).

6-[1-(2-hydroxynaphthyl)]phenanthridine 5

BBr_3 (171 ml. of a 0.1 M solution in CH_2Cl_2) was added dropwise to a solution of 6-[1-(2-methoxynaphthyl)]phenanthridine (28.7g, 85.5 mmol) in CH_2Cl_2 (350 ml.), upon which the solution turned dark. The reaction was slightly exothermic. The resulting mixture was stirred overnight, quenched with 180 ml. of H_2O, and stirred for another 15 minutes. The solid was filtered off, the water layer neutralised with NaOH, and extracted with CH_2Cl_2 (2 x 300 ml.). The CH_2Cl_2 extracts were stirred with 10% HCl, and the resulting solid filtered off. The collected solids were stirred with 500 ml. CH_2Cl_2 and 71 ml. 2M Na_2CO_3. At first a clear two-layer system was obtained from which eventually a solid precipitated. This solid was filtered off, and extensively extracted with CH_2Cl_2 (800 ml., which was re-used in the process, *effectively* approx. 3 L of CH_2Cl_2 was used). The CH_2Cl_2 extracts were dried on $MgSO_4$, and concentrated *in vacuo*, yielding (22.2g 81%, mp. 255 - 258°C.) of crude product, slightly contaminated with an unknown compound, which could be removed by crystallisation from CH_2Cl_2. δH ($CDCl_3$, 500 MHz) 8.73 (d, 1 H, J = 8.3 Hz), 8.66 (m, 1 H), 8.10 - 8.08 (m, 1 H), 7.90 - 7.87 (m, 3 H), 7.77 - 7.71 (m, 3 H), 7.50 (dt, 1 H, J = 0.9, 7.6 Hz), 7.34 (dt, 1 H, J_d = 1.3, 7.4 Hz), 7.30 (d, 1 H, J = 8.9 Hz), 7.23 (dt, 1 H, J_d = 1.2, 7.5 Hz), 7.19 (d, 1 H, J = 8.2 Hz). δC ($CDCl_3$, 125.72 MHz) 158.9 (CO), 153.6, 142.9, 133.7, 133.6, 131.5, 131.1, 129.6, 129.1, 129.1, 128.9, 128.2, 127.7, 127.4, 126.6, 126.3, 125.0, 124.1, 123.4, 122.3, 122.2, 120.0, 118.3. MS (EI) m/z 321 ($M^{+\cdot}$), 320 ($[M-H]^{+\cdot}$), 291 ($[M-CH_2O]^{+\cdot}$)

6-[1-(2-hydroxynaphthyl)]phenanthridine trifluoromethanesulfonate 6

Trifluoromethanesulfonic anhydride (20g, 70.9 mmol) was added dropwise to a solution of 6-[1-(2-hydroxynaphthyl)]phenanthridine (20.3g, 63.3 mmol) and 4-(dimethylamino)pyridine (23.4g) in 330 ml. of

CH_2Cl_2. The resulting mixture was stirred overnight (although the reaction is complete after 1h), and subsequently washed with hydrochloric acid (1M, 3 x 330 ml.), H_2O (2 x 330 ml.), and brine (330 ml.). After drying on $MgSO_4$ the solvent was removed *in vacuo*. To the residue was added 40 ml. of toluene, and the resulting mixture heated close to the boiling point. At this point a clear yellow solution over an oily brown precipitate was obtained. The oil was discarded, and the solution concentrated, yielding product (20.6g, 72%, mp. 152.5 - 153.0°), which was recrystallised from toluene. δH ($CDCl_3$, 500 MHz) 8.77 (d, 1 H, J = 8.4 Hz), 8.73 (dd, 1 H, J = 1.4, 8.1 Hz), 8.27 (dd, 1 H, J = 1.2, 8.0 Hz), 8.14 (d, 1 H, J = 9.1 Hz), 8.01 (d, 1 H, J = 8.2 Hz), 7.88 (m, 1 H), 7.83 (dt, 1 H, J = 1.5, 7.5 Hz), 7.79 (dt, 1 H, J = 1.4, 7.6 Hz), 7.66 (d, 1 H, J = 9.1 Hz), 7.57 (m, 1 H), 7.54 - 7.52 (m, 2 H), 7.39 - 7.38 (m, 2 H). δC (125.72 MHz) 155.3, 145.6 , 144.3, 133.6 , 133.5 , 133.0 , 131.7, 131.6, 131.0, 129.9, 129.5, 128.7, 128.5, 128.4, 128.2, 128.0, 127.6, 127.0, 126.6, 122.7, 122.6, 120.0. MS (CI) m/z 454 ($[M+1]^{+\cdot}$, 100), 320 ($[M\text{-}HTf+1]^+$, 49).

6-[1-{2-diphenylphosphinyl)naphthyl}]phenanthridine 7

DMSO (430 ml.) was placed in a three necked flask, and Ar was bubbled through for 20 min. To this was added 6-[1-(2-hydroxynaphthyl)]phenanthridine trifluoromethanesulfonate (20.6g, 45.5 mmol), $PPh_2(O)H$ (42.9g, 212 mmol), dppp (2.19g, 5.3 mmol), $Pd(OAc)_2$ (1.19g, 5.1 mmol), and $NaHCO_3$ (26.8g, 320 mmol). The mixture was heated at 80°C for 20h, added to CH_2Cl_2 (1L), and washed subsequently with H_2O (2 x 1L), saturated Na_2CO_3 (1L), H_2O (2 x 1L) and saturated brine (1L). After drying on $MgSO_4$, and removal of the solvent *in vacuo*, a red/brown oil was obtained to which 80 ml. of toluene was added, and cooled to -18°C. After warming to room temperature, the precipitated solid was filtered off, washed with toluene (100 ml.) and Et_2O (100 ml.), and dried, giving product (20.2g. 88%, mp. 270 - 275°C). (Found: C, 82.87 H, 4.98; N, 2.76, $C_{35}H_{24}NOP$ requires: C, 83.15; H, 4.78; N, 2.77). The product could be further purified by crystallisation from toluene. δH ($CDCl_3$, 500 MHz) 8.47 - 8.45 (m, 1 H), 8.43 (d, 1 H, J = 8.4 Hz), 8.31 (dd, 1 H, J_{PH} = 8.7 Hz, J_2 = 10.9 Hz), 8.16 (dd, 1 H, J_{PH} = 1.7 Hz, J_2 = 8.7 Hz), 8.08 - 7.99 (m, 2 H, with P-coupling), 7.97 - 7.93 (m, 2 H), 7.72 - 7.68 (m, 3 H), 7.56 (dt, 1 H, J_1 = 0.8 Hz, J_2 = 7.5 Hz), 7.52 (dtt, 1 H, J_{PH} = 1.5 Hz, J_2 = 1.6 Hz, J_3 = 7.4 Hz), 7.46 (dt, 2 H, J_{PH} = 2.8 Hz, J_t = 7.5 Hz), 7.36 (dt, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_1 = 1.2 Hz, J_2 = 8.1 Hz), 7.25 (dt, 1 H, J_d = 1.1 Hz, J_t = 7.7 Hz), 7.08 (d, 1 H, J = 8.6 Hz), 6.90 (ddd, 2 H, J_1 = 1.1 Hz, J_2 = 8.1 Hz, J_{PH} = 12.5 Hz), 6.76 (ddt, 1 H, J_1 = 1.0 Hz, J_{PH} = 1.4 Hz, J_2 = 7.5 Hz), 6.41 (dt, 2 H, J_{PH} = 3.0 Hz, J_1 = 7.8 Hz). δC ($CDCl_3$, 125.72 MHz) 159.69, 159.66, 143.7, 141.6, 141.55, 135.3, 133.4, 133.2, 133.1, 132.8, 132.7, 132.6, 132.5, 132.4, 132.1, 131.6, 131.4, 131.3, 130.9, 130.6, 130.5, 130.5, 129.44, 129.35, 129.2, 129.1, 128.6, 128.6, 128.4, 127.8, 127.61, 127.58, 127.49, 127.2, 127.1, 124.9, 122.2, 122.1. δP NMR ($CDCl_3$, 202.40 MHz) 32.0. MS (EI) m/z 505 ($M^{+\cdot}$), 428 ($[M\text{-}C_6H_5]^+$).

6-[1-(2-diphenylphosphinoyl)naphthyl)]phenanthridine 2

To a suspension of 6-[1-{2-diphenylphosphinoyl)naphthyl}]phenanthridine (20.2g, 40.0 mmol) in toluene (1600 ml.) was added $HSiCl_3$ (32.5 ml., 326 mmol) and NEt_3 (57.0 mmol), leading to the evolution of white fumes. The solution was refluxed for 2.5h and cooled with ice. To this was added carefully a 2M NaOH solution (1600 ml.). The layers were separated, and the water layer was extracted with CH_2Cl_2 (2 x 800 ml.). The organic layers were dried on $MgSO_4$, and concentrated *in vacuo*, giving, after Et_2O trituration, product (15.8g, 81%, mp. 105 - 107°C). An analytical sample was obtained by crystallisation from CH_2Cl_2. (Found: C, 85.79; H, 5.15; N, 2.80, $C_{35}H_{24}NP$ requires: C, 85.87; H, 4.94; N, 2.86).From the Et_2O wash-layers 1.6g of starting material could be recovered. δH ($CDCl_3$, 500 MHz) 8.74 (d, 1 H, J = 8.3 Hz), 8.71 (m, 1 H), 8.08 (m, 1 H), 7.97 (d, 1 H, J = 8.6 Hz), 7.94 (d, 1 H, J = 8.3 Hz), 7.81 (dt, 1 H, J_d = 1.2 Hz, J_t = 7.6 Hz), 7.78 - 7.72 (m, 2 H), 7.55 - 7.48 (m, 3 H, with P-coupling), 7.39 - 7.21 (m, 13H). δC NMR ($CDCl_3$, 125.72 MHz)161.34, 161.29, 144.6, 144.4, 144.0, 127.8, 127.7, 127.4, 137.3, 135.2, 135.1, 133.93, 133.85, 133.76, 133.69, 133.60, 132.8, 132.73, 132.67, 130.8, 130.6, 130.3, 128.94, 128.9, 128.8, 128.5, 128.44, 128.40, 128.35, 128.2, 127.4, 127.3, 127.1, 126.9, 124.3, 122.3, 122.3. δP ($CDCl_3$, 202.40 MHz) -12.4 ppm. MS (EI) m/z 489 ($M^{+\cdot}$), 412 ($[M\text{-}C_6H_5]^{+\cdot}$), 335 ($[M\text{-}2C_6H_5]^{+\cdot}$).

Resolution of 6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine

A mixture of 6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine (1.889g, 3.864 mmol) and di-μ-chloro-bis[(R)-(α,N,N-trimethyl-1-aminomethylnaphthyl)palladium] (1.313g, 1.932 mmol) in MeOH (200 ml..) was stirred at room temperature overnight. The reagents slowly dissolved, but after 30 min. a white solid precipitated from the solution. The solid was filtered off, washed with MeOH (5 ml..) and dried, giving complex **10**, (1.364g, 86%), as its chloride. The solution was concentrated to dryness. To the residue was added 25 ml.. of MeOH, and the mixture was stirred for 10 min. The solid was filtered off, washed with MeOH (15 ml..) which was dried, giving more complex **10**. To the filtrate was added KPF_6 (0.71g) in 60 ml. of H_2O. The mixture was stirred for 10 min., and the precipitated solid filtered off and washed with 300 ml. of Et_2O. The off-white solid was washed with toluene (2 x 25 ml. cold, 2 x 25 ml. hot, approx. 60°C). There remained pure complex **11** (1.540g. 85%) After removal of the toluene and titruration with pentane, a further 0.28g of a mixture of diastereomers was obtained.

Complex **10**, mp 241°C (dec.),.$[\alpha]_D^{25}$ = 233.6 (c = 1.01, $CHCl_3$), δH ($CDCl_3$, 500 MHz) 8.38 (t, 2 H, J = 7.3 Hz), 8.20 (dd, 2 H, J_2 = 7.6, 10.9 Hz), 8.13 (d, 1 H, J = 8.0 Hz), 8.10 (dd, 1 H, J_2 = 0.7, 8.0 Hz), 7.94 (d, 1 H, J = 8.1 Hz), 7.90 (d, 1 H, J = 8.6 Hz), 7.86 (dd, 1 H, J = 8.8, 11.6 Hz), 7.76 (dt, 2 H, J = 1.3, 7.6 Hz), 7.71 (m, 2 H), 7.61 (d, 1 H, J = 8.4 Hz), 7.59 - 7.54 (m, 3 H), 7.48 - 7.45 (m, 2 H), 7.34 - 7.31 (m, 2 H), 7.29 - 7.24 (m, 2 H), 7.17 (dt, 1 H, J = 1.1, 7.7 Hz), 6.95 (br,t, 1 H, J = 7.0 Hz), 6.91 (d, 1 H, J = 8.5 Hz), 6.69 (br,t, 1 H, J = 6.3 Hz), 6.23 (br,d, 1 H, 8.2 Hz), 5.60 (br,t, 1 H, J = 6.7 Hz), 4.16 (dq, 1 H, J = 6.1 Hz, CH), 2.93 (d, 3 H, J = 3.2 Hz, NCH_3), 2.15 (s, 3 H, NCH_3), 2.05 (d, 3 H, CCH_3). δC NMR ($CDCl_3$, 125.72 MHz) 160.39, 160.36, 149.6, 148.9, 144.3, 138.5, 138.4, 136.1, 136.0, 135.0, 135.8, 134.1, 133.4, 132.8, 131.9, 131.8, 131.3, 131.0, 130.62, 130.59, 130.0, 129.7, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 126.8, 126.7, 125.6, 124.9, 124.0, 123.9, 123.8, 123.5, 122.4, 121.6, 73.2 (CH), 51.0 (NCH_3), 48.9 (NCH_3), 23.9 (CCH_3).δP ($CDCl_3$, 101 MHz) 41.6 ppm. MS (Electrospray) m/z 793 ($[M\text{-}Cl]^{+\cdot}$ with Pd-isotope pattern).

Complex **11**, mp 228 - 231°C (dec), $[\alpha]_D^{25}$ = 262.1 (c = 0.88, $CHCl_3$), δH ($CDCl_3$, 500 MHz) 9.43 (d, 1 H, J = 8.1 Hz), 8.65 (d, 1 H, J = 7.6 Hz), 8.58 (d, 1 H, J = 8.4 Hz), 8.20 (d, 1 H, J = 8.4 Hz), 8.13 (d, 1 H, J = 8.3 Hz), 8.07 (dt, 1 H, J = 1.0, 7.7 Hz), 7.98 (t, 1 H, J = 7.3 Hz), 7.93 (dt, 1 H, J = 0.7, 7.7 Hz), 7.76 - 7.70 (m, 2 H), 7.76 (d, 1 H, J = 8.2 Hz), 7.55 (t, 1 H, J = 7.1 Hz), 7.51 - 7.38 (m, 4 H), 7.34 - 7.25 (m, 5 H), 7.19 (d, 1 H, J = 8.4 Hz)7.11 (d, 1 H, J = 8.2 Hz), 6.95 - 6.89 (m, 4 H), 6.73 (dd, 1 H, J = 6.0, 8.4 Hz), 6.66 (bt, 1 H, J = 6.2 Hz), 6.51 (bt, 1 H, J = 6.7 Hz), 4.30 (dq, 1 H, J = 5.9 Hz, CH), 2.89 (d, 3 H, J = 2.3 Hz, NCH_3), 2.33 (d, 3 H, J = 3.5 Hz, NCH_3, 1.24 (d, 3 H, CCH_3). δC NMR ($CDCl_3$, 125.72 MHz) 160.3, 150.6, 149.9, 141.8, 138.7, 137.1, 137.0, 136.2, 136.1, 134.4, 134.0, 133.7, 132.8, 132.3, 132.2, 132.2, 132.0, 131.8, 130.7, 130.3, 130.0, 129.43, 139.39, 129.3, 129.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.1, 126.9, 126.8, 126.5, 126.5, 126.2, 126.0, 125.6, 125.5, 125.3, 124.0, 123.9, 123.6, 123.5, 123.0, 122.1, 73.8 (CH), 53.0 (NCH_3), 48.1 (NCH_3), 23.0 CCH_3). δP ($CDCl_3$, 101.2 MHz)38.4, -54.1 (septet, J = 712 Hz, PF_6^-). MS (Electrospray) m/z 793 ($[M\text{-}PF_6]^{+\cdot}$, with Pd-isotope pattern).

X-Ray crystal structure determinations for complexes 10 and 11

Both compounds were recrystallised from CH_2Cl_2 / Et_2O. Collection and refinement details for structure **10** are recorded in **Table 2**, and for structure **11** in **Table 3**.

Table 2. Crystal data and structure refinement for complex **10**

Empirical formula	$C_{50}H_{45}Cl_3NPPd$
M_r	458.80
crys syst	monoclinic
crys size (mm)	0.18 x 0.14 x 0.14
space group	P21
a (Å) b (Å) c (Å)	10.227(3) 18.698 (3) 11.133 (4)
β (deg)	93.41 (4)
V(Å^3)	2125.1(10)
Z	2
D_c(g cm^{-3})	1.434
T (K)	150(2)
radiation; λ, Å	Mo-K_α; 0.71069
θ range for data collection	1.83 to 25.05 deg.
Index ranges	$-10 \le h \le 11, -15 \le k \le 16, -7 \le l \le 12$
No. of unique rflns	5717
Independent reflections	5336 [R(int) = 0.0547]
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	5333 / 1 / 517
Goodness of fit on F^2	1.068
Final R indices [I > 2σ(I)]	R1 = 0.0413 ωR2 = 0.1075
R indices (all data)	R1 = 0.0434 ωR2 = 0.1097
Absolute structure parameter	-0.02(3)
Largest diff. peak and hole	1.045 and -0.428 e Å^{-3}

Table 3. Crystal data and structure refinement for complex **11**

Empirical formula	$C_{49}H_{40}F_6N_2P_2Pd$
M_r	939.17
crys syst	monoclinic
crys size (mm)	0.24 x 0.019 x 0.023
space group	P21
a (Å),b (Å), c (Å)	115.796 (5),13.537 (3),19.688 (3)
β (deg)	92.27 (2)
V(Å^3)	4207 (2)
Z	4
D_c(g cm^{-3})	1.483
T (K)	293(2)
radiation; λ, Å	Mo-K_α; 0.71069
θ range for data collection	1.83 to 25.10 deg.
Index ranges	$-16 \le h \le 18, -12 \le k \le 16, -23 \le l \le 23$
No. of unique rflns	15278
Independent reflections	10381 [R(int) = 0.0581]
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	10380 / 91 / 1114
Goodness of fit on F^2	0.825
Final R indices [I > 2σ(I)]	R1 = 0.0448 ωR2 = 0.0937
R indices (all data)	R1 = 0.0608 ωR2 = 0.0971
Absolute structure parameter	-0.05(3)
Largest diff. peak and hole	0.943 and -0.534 e Å^{-3}

(-)6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine (S)-(-)-2 and $PdCl_2$ complex

Dppe (0.43g, 1.07 mmol) was added to a solution of {6-[1-(2-diphenylphosphinonaphthyl)]-phenanthridine}{(*R*)-(α,N,N-trimethyl-1-aminomethyl-2-naphthyl)}palladium hexafluorophosphate (1.0g, 1.07 mmol) in CH_2Cl_2 (100 ml.). After stirring for 30 min. the solution had turned from off-white to virtually colourless. The solution was concentrated to approx. 20 ml. Toluene (40 ml) was added, the solvent was removed *in vacuo* and again toluene (40 mL) was added. The solid (dppe-Pd complex) was filtered off. After removal of the solvent, the residue was taken up in 100 mL of CH_2Cl_2. The solution was filtered over a short silica column (approx. 3g), and concentrated to dryness, leaving (-)-**2** (0.617g, 94%, m.p. 105 - 107°C.) $[\alpha]_D^{25}$ = -154.7 (c = 0.984, $CHCl_3$); after repetition of the cycle : $[\alpha]_D^{25}$ = -167.9 (c = 0.976, $CHCl_3$). The recovered dppe-Pd complex was kept for recycling of the ligand by reaction with hydrazine in MeOH overnight.

A mixture of complex **11** (489 mg, 0.52 mmol) in CH_2Cl_2 (6 ml.), and concentrated HCl (6 ml.) was stirred for 2h at room temperature, after which time the organic solvent was removed *in vacuo*.The remaining water layer was extracted with CH_2Cl_2 (30 ml.), which was then washed with water (25 ml.), 10% HCl solution (25 ml.), water (25 ml.) and saturated brine (25 ml.). After drying on $MgSO_4$, and concentration *in vacuo*, 130 mg (0.20 mmol, 38%) of bright yellow/orange product of low solubility remained. Found: C, 62.32; H, 3.17; N, 2.11, $C_{35}H_{24}Cl_2NPPd$ requires: C, 63.04; H, 3.63; N, 2.10. δH ($CDCl_3$, 500 MHz) 10.55 (d, 1 H, J = 8.4 Hz), 8.44 (d, 1 H, J = 8.5 Hz), 8.39 (d, 1 H, J = 8.2 Hz), 8.20 (dd, 1 H, J_1 = 1.9 Hz, J_2 = 8.5 Hz), 8.09 (d, 1 H, J = 8.3 Hz), 8.04 (ddd, 1 H, J_1 = 1.3 Hz, J_2 = 7.8 Hz, J_3 = 7.8 Hz), 7.82 (ddd, 1 H, J_1 = 0.9 Hz, J_2 = 7.7 Hz, J_3 = 7.7 Hz), 7.77 (ddd, 1 H, J_1 = 1.0 Hz, J_2 = 7.7 Hz, J_3 = 7.7 Hz), 7.69 (ddd, 1 H, J_1 = 2.3 Hz, J_2 = 5.7 Hz, J_3 = 8.2 Hz), 7.62 - 7.56 (m, 3 H), 7.50 - 7.46 (m, 2 H), 7.44 (t, 1 H, J = 8.6 Hz), 7.40 - 7.38 (m, 2 H), 7.33 - 7.24 (unresolved m, 2 H?), 7.02 (d, 1 H, J = 8.4 Hz), 6.82 (t, 1 H, J = 7.9 Hz), 6.73 - 6.37 (b, 2 H). δP ($CDCl_3$, 101.2 MHz) 33.95. MS (Electrospray) m/z 630 ($[M-Cl]^{+\cdot}$) with Pd-isotope pattern.

(+)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine (R)-(+)-2

In similar manner, but requiring only a single cycle of decomplexation, the (+)-enantiomer was prepared from complex **10** m.p. 105 - 106°C, $[\alpha]_D^{25}$ = +168.8 (c = 0.994, $CHCl_3$).

(+)-(η^3-allyl)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridinepalladium tetrafluoroborate 13

Preparation as **15**. Light yellow solid, mp 165 - 167°C (dec). $[\alpha]_D^{25}$ = 318.1 (c = 0.55, $CHCl_3$) δH (BF_4 salt, *minor diastereomer*, $CDCl_3$, 500 MHz) 8.68 (d, 1 H, J = 8.3 Hz), 8.07 (d, 1 H, J = 8.3 Hz), 7.92 (non-resolved m, 1 H), 7.13 (d, 1 H, J = 8.6 Hz), 7.03 (dd, 2 H, J_{HH} = 7.6 Hz, J_{PH} = 12.3 Hz), 5.59 - 5.54 (m, 1 H, allyl-H), 4.77 (m, 1 H, allyl-H, apparent triplet, $J_{PH} \approx J_{HH} \approx$7.6 Hz), 4.34 - 4.28 (m, 2 H, allyl-H and H), 3.79 (d, 1 H, J = 12.7 Hz, allyl-H). (*major diastereomer*, $CDCl_3$, 500 MHz) 8.55 (d, 1 H, J = 8.4 Hz), 8.51 (d, 1 H, J = 8.4 Hz), 8.37 (d, 1 H, J = 8.3 Hz), 8.23 (d, 1 H, J = 8.4 Hz), 8.15 (ddd, 1 H, J_1 = 1.1 Hz, J_2 = 7.7 Hz, J_3 = 7.7 Hz), 8.10 (d, 1 H, J = 8.3 Hz), 7.89 (ddd, 1 H, J_1 = 0.9 Hz, J_2 = 7.6 Hz, J_3 = 7.8 Hz), 7.86 (ddd, 1 H, J_1 = 1.0 Hz, J_2 = 7.6 Hz, J_3 = 8.1 Hz), 7.67 - 7.59 (m, 4 H), 7.48 (dd, 1 H, J_1 = 1.4 Hz, J_2 = 7.8 Hz), 7.45 (ddd, 1 H, J_1 = 1.3 Hz, J_2 = 8.4 Hz, J_{PH} = 12.3), 7.41 - 7.33 (m, with P-coupling, 3 H), 7.19 (d, 1 H, J = 8.6 Hz), 6.99 (d, 1 H, J = 8.3 Hz), 6.92 (dd, 1 H, J_{HH} = 7.5 Hz, J_{PH} = 12.3 Hz), 6.80 - 6.77 (m, 1 H), 6.49 (dt, 2 H, $J_{,PH}$ = 2.1 Hz, J = 7.8 Hz), 6.42 (m, 1 H, allyl-H), 5.34 (m, 1 H, allyl-H), 4.20 (d, 1 H, J = 6.9 Hz), 3.64 (dd, 1 H, J_{PH} = 9.3 Hz, J_2 = 14.1 Hz), 3.10 (d, 1 H, J = 11.9 Hz, allyl-H). Allyl protons assigned by means of spin saturation transfer experiments according to **Figure 3**. δC ($CDCl_3$, 125.72 MHz) 160.9, 142.6, 139.9, 134.4, 134.3, 133.7, 133.6, 133.0, 132.9, 132.7, 132.6, 132.5, 131.8, 131.5, 130.9, 130.2, 130.1, 129.4, 128.8, 128.7, 128.45, 128.39, 128.3, 127.3, 127.0, 126.6, 126.4, 126.2, 125.9, 125.6, 124.9, 124.6, 122.7, 122.1, 79.5, 79.2, 55.8, 34.5, 22.7, 14.4. δP NMR ($CDCl_3$, 202.40 MHz) 44.0 (minor diastereomer?), 34.5 (major diastereomer). MS (Electrospray) m/z 636 ($[M-BF_4]^{+\cdot}$)

(+)-(η³-1,3-diphenylallyl)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridinepalladium trifluoromethanesulfonate 14

Preparation as **15**. Orange solid, mp 192 - 202°C (dec, very amorphous before melting), $[\alpha]_D^{25}$ = 631.8 (c = 0.984, $CHCl_3$) δC (both diastereomers reported, but not individually assigned) ($CDCl_3$, 125.72 MHz) 160.41, 160.36, 159.50, 159.47, 141.04, 139.93, 139.81, 139.69, 138.57, 138.47, 137.02, 136.97, 135.76, 135.72, 134.45, 134.34, 134.14, 134.10, 134.05, 133.54, 133.45, 133.15, 133.03, 132.97, 132.61, 132.55, 132.10, 131.97, 131.83, 131.59, 131.52, 131.32, 131.01, 130.76, 130.54, 130.29, 130.01, 129.89, 129.85, 129.77, 129.71, 129.64, 129.57, 129.39, 129.32, 129.08, 128.88, 128.85, 128.72, 128.70, 128.54, 128.41, 128.37, 128.25, 128.18, 128.12, 127.70, 127.61, 127.52, 127.50, 127.25, 127.17, 126.93, 126.52, 126.40, 126.35, 126.27, 126.22, 126.04, 125.99, 125.80, 125.62, 125.55, 125.41, 125.20, 124.90, 124.63, 123.98, 123.66, 122.85, 122.78, 122.58, 122.37, 120.29, 117.74, 112.36, 110.44, 110.40, 100.69, 100.52, 91.81, 91.62, 84.71, 79.08, 79.05, 71.58, 71.54, 53.87. δP ($CDCl_3$, 202.40 MHz) 33.56 (minor diastereomer), 29.70 (major diastereomer) MS (Electrospray) m/z 788 ($[M\text{-}OTf]^+$.

***(+)-(η³-cyclohexenyl)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridinepalladium trifluoromethanesulfonate* 15**

A solution of (+)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine (100 mg, 0.205 mmol) and di-μ-dichloro-bis[(η³-cyclohexenyl)palladium] (46 mg, 0.103 mmol, 0.206 mmol Pd), was added to a suspension of AgOTf (53mg, 0.205 mmol) in CH_2Cl_2 (15 ml.). Gradually a milky suspension was obtained. After stirring for 3h at room temperature, the AgCl was filtered off, first through a filter paper, then over celite. The solvent was removed *in vacuo*, and the residue washed with Et_2O (2 x 20 ml.) leaving a light yellow powder, (162mg, 96%), mp 175 - 177°C (dec), $[\alpha]_D^{25}$ = 197.7 (c = 0.977, $CHCl_3$) δH ($CDCl_3$, 500 MHz) 8.52 (ddd, 2 coincident H, J ca. 1, 4, 8 Hz), 8.32 (dd, 1 H, J_1 = 0.7 Hz, J_2 = 8.3 Hz, phenanthridine-H4), 8.20 (d, 1 H, J = 8.3 Hz), 8.08 (dt, 1 J = 1.1, 6.9 Hz, phenanthridine-H3), 8.07 (d, 1 H, J = 6.9 Hz), 7.88 (apparent q of d, 2 H, J = 1.2, 8.4 Hz), 7.74 (ddd, J = 1.6, 9, 11.9 Hz, P-Ph(ortho)), 7.66 - 7.61 (m, 4 H), 7.46 (ddd, J = 1.0, 7.1 Hz, 8.2 Hz), 7.40 (ddd, J = 1.3, 7.0, 8.4 Hz), 7.32 (dd, 1 H, J = J"= 8.3 Hz), 7.24 (d, 1 H, J = 8.3 Hz), 7.19 (dd, 1 H, J = 0.5, 8.7 Hz), 6.92 (dd, 2 H, J = 7.2, 11.9 Hz, P-Ph"(ortho)), 6.72 (m, 1 H, J = ca. 7.6 Hz, P-Ph(para)), 6.39 (dt, 2 identical H, J = 2.1, 7.9 Hz, P-Ph(meta)), 6.26 - 6.25 (m, 2 H, allyl-H), 5.81 (brm, 1 H, allyl-H), 1.98 (m, 1 H,), 1.61 (m, 1 H), 1.36 (m, 1 H), 0.82 (m, 2 H), 0.45 (m, 1H) δC ($CDCl_3$, 125.72 MHz) 160.8, 138.8, 138.7, 134.5, 134.4, 133.6, 133.2, 133.2, 132.6, 132.5, 132.0, 132.0, 131.0, 130.5, 130.1, 130.0, 129.9, 129.5, 129.3, 128.9, 128.6, 128.5, 128.3, 128.2, 128.2, 127.6, 127.5, 126.4, 126.2, 125.8, 125.8, 125.5, 125.4, 125.3, 122.4, 122.3, 110.22, 110.18, 94.8 (allyl), 94.6 (allyl), 72.3 (allyl), 28.7, 28.09, 28.05, 11.8 (cyclohexenyl). δP ($CDCl_3$, 202.40 MHz) 32.1. MS (electrospray) m/z 676 ($M^{+\cdot}$ with Pd-isotope pattern).

Cyclohex-3-en-1-yl p-tolyl sulfone 16

Preparation of precursor :p-Toluenesulfinyl chloride[16] (1.78g, 10.2 mmol) was added dropwise to a solution of 2-cyclohexen-1-ol (1.0g, 10.2 mmol) and pyridine (0.8g, 10.2 mmol) in Et_2O (20 ml.) at 0°C. The mixture was stirred at room temperature for 2h, and then filtered and washed with HCl (2N, 20 ml.), water (20 ml.), $NaHCO_3$ solution (5%, 20 ml.), and water (20 ml.). After drying on $MgSO_4$ the solvent was removed *in vacuo* leaving 2-cyclohexen-1-yl p-toluenesulfinate as a colourless oil (2.26g, 94%). The ^1H NMR spectrum showed the product to be pure enough for further use. Attempts to purify further by distillation or column chromatography failed, leading to more contamination rather than to purification. δH (CD_3CN, 200 MHz) 7.60 (d, 2 H, J = 8.0 Hz, ArH), 7.39 (d, 2 H, J = 7.8 Hz, ArH), 6.02 - 5.81 (m, 1 H of each diastereomer), 5.77 (m, 1 H of other diastereomer), 4.80 (m, 1 H, C(O)), 2.41 (s, 3 H, CH_3), 2.10 - 1.77 (m, 4 H), 1.77 - 1.52 (m, 2 H). δC NMR (CD_3CN, 50.3 MHz) 144.2, 143.6, 134.1, 134.0, 130.6, 127.6, 127.3, 125.9, 118.3, 73.8 and 73.0 (CO), 31.0, 30.9, 25.3, 21.5, 19.3, 19.2. To a solution of sulfinate (320mg, 1.36 mmol) in CD_3CN (1.5 ml.) was added η³-allyl-(*R*)6-[1-(2-diphenylphosphinonaphthyl)]phenanthridinepalladium trifluoro methanesulfonate (53mg, 5 mol%, as solid), 15-crown-5 (15mg, 5%, in 0.5 ml. of CD_3CN) and sodio dimethyl malonate (10mg, 5%, as solid). Negligible reaction occurred at room temperature. At 60°C the reaction was complete within 25 min. The reaction mixture was purified by preparative tlc (pentane/Et_2O =

10/3, R_f = 0.3 - 0.4). Yield of cyclohex-3-en-1-yl p-tolyl sulfone,[17] 85 -100%. The e.e. was determined using Resolve-Al (AgFOD)-Yb(hfc)$_3$ as chiral shift reagent.[18]

References

1 Alcock, N. W.; Brown, J. M.; Hulmes, D. I., *Tetrahedron Asymmetry* , **1993**, *4*, 743.

2 Brown, J. M.; Hulmes, D. I.; Layzell, T. P., *J. Chem. Soc. Chem. Comm.*, **1993**, 1673.

3 Brown, J. M.; Hulmes, D. I.; Guiry, P. J., *Tetrahedron* , **1994**, *50*, 4493.

4 *2-Aminobiphenyl* : Scarborough, H.A. ;Waters, W.A.,*J. Chem. Soc.* **1927**, 91; *2-acetamidobiphenyl* : Morgan, G.T; Walls, L.P, *J. Chem. Soc.* **1931**, 2447; *6-methylphenanthridine* **[NB exothermic reaction, care!]** : Morgan, G.T; Walls, L.P, J. Chem. Soc. **1931**, 2447; *phenanthridinone* :Walls, L.P, *J. Chem. Soc.* **1935**, 1405; *6-chlorophenanthridine* : Ikehara, M.,*Chem. Pharm. Bull.*, **1954**, *2*, 111. Copies of modified procedures and spectroscopic characterisation of intermediates may be obtained from the authors.

5 Cickery, E.H.; Pahler, L.F; Eisenbraun, E.J., *J. Org. Chem.*, **1979**, *44*, 4444.

6 Alcock, N. W.; Hulmes, D. I.; Brown, J. M., *J. Chem. Soc. Chem. Comm.* , **1995**, 395.

7 MacKenzie, P. B.; Whelan, J.; Bosnich, B., *J. Am. Chem. Soc.* **1985**, *107*, 2046.

8 Sprinz, J.; Kiefer, M.; Helmchen, G.; Huttner, G.; Walter, O.; Zsolnai, L.; Reggelin, M., *Tetrahedron Lett.* , **1994**, *35*, 1523.

9 Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A., *J. Am. Chem. Soc.*, **1994**, *116*, 4067; Pregosin, P. S.; Salzmann, R.; Togni, A., *Organometallics*, **1995**, *14*, 842.

10 Sprinz, J.; Kiefer, M.; Helmchen, G.; Huttner, G.; Walter, O.; Zsolnai, L.; Reggelin, M. *Tetrahedron Lett.*, **1994**, *35*, 1523.

11 Gogoll, A.; Ornebro, J.; Grennberg, H.; Backvall, J. E., *J. Am. Chem. Soc* . ,**1994**, *116*, 3631.

12 Akermark, B.; Oslob, J. D.; Norrby, P. O., *Organometallics*, **1995**, *14*, 1688; Togni, A., Rihs, G.; Pregosin, P. S.; Ammann, C., *Helv. Chim.* Acta, **1990**, *73*, 723.

13 Trost, B. M.; Murphy, D. J., *Organometallics*, **1985**, *4*, 1143.

14 Von Matt, P.; Pfaltz, A., *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 566; Sprinz, J.; Helmchen, G. *Tetrahedron Letters* ,**1993**, *34*, 1769; Dawson, G. J.; Frost, C. G.; Williams, J., *Tetrahedron Lett.*, **1993**, *34*, 3149.

15 Eichelmann, H.; Gais, H. J., *Tetrahedron Asymmetry*, **1995**, *6*, 643; c.f. Pyne, S. G.; Dong, Z. M. *Tetrahedron Lett.*, **1995**, *36*, 3029; Gais, H. J.; Scommoda, M.; Lenz, D. *Tetrahedron Lett.*, **1994**, *35*, 7361.

16 Kurzer, F., *Org. Synth. Coll. Vol. III*, 937.

17 Knight, D. J.; Whitham, G. H.; Williams, J. G., *J. Chem. Soc., Perkin Trans.*,**1987**, *1*, 2149.

18 Parker, D., *Chem. Rev.*, **1991**, *91*, 1441; refs 111-118.

(*Received in UK* 24 *August* 1995)