

0957-4166(95)00341-X

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

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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 possessing 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 hydroboration² 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 demethylated⁵ with BBr₃ 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. HSiCl₃ reduction of the oxide gave the racemic ligand 2 in 81% yield as a white powder.



Reagents : (i) 3 mol% Pd(PPh₃)₄, Na₂CO₃, DME, reflux 12 h., 89% (ii) BBr₃, CH₂Cl₂, 12 h., 81% (iii) Tf₂O, DMAP, CH₂Cl₂, 1h., 72% (iv) [Pd(OAc)₂, dppp, (2 mol%)], Ph₂P(H)O, NaHCO₃, DMSO, 80°C, 20h, 88% (v) HSiCl₃, NEt₃, C₇H₈, reflux 2.5 h., 81%

Scheme 1



Resolution : A standard method for the resolution of chelating ligands has been the formation and separation of diastereometric 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-1aminomethylnaphthyl)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 KPF₆ leading to the precipitation of a second off-white solid.



The two products were separately recrystallised from CH₂Cl₂/ Et₂O, 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.



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



Figure 2. X-ray crystal structure of complex (α , R, S)-11. H-atoms and PF₆ counterion have been omitted for clarity.

Decomplexation to remove the resolving agent proved to be straightforward, using 1,2-bisdiphenylphosphinoethane in CH₂Cl₂ followed by separation on a short silica column. In this way the (*R*)enantiomer of 2, $[\alpha]_D^{25} = +168.8$ (c = 0.994, CHCl₃), was prepared in pure form from complex 10. The (*S*)enantiomer of 2, $[\alpha]_D^{25} = -167.9$ (c = 0.976, CHCl₃), 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.^{3,78} 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 ¹H NMR spectroscopy at ambient temperature, whilst below 220K both diastereomers could be observed in close to 1:1 ratio.



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.



Figure 3. Proton NMR spectrum of the allyl region of complex 13 in $CDCl_3$. The interconversion pathware between the diastereomers is revealed by the ¹H 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-workers⁹ and by Helmchen and coworkers.¹⁰ This pathway implies that only one o-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 n^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 (CDCl₃) or 20:1 (CD₂Cl₂) but specific information on assignments and interconversion was not easily derived.



 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 CDCl₃ demonstrating the diastereometric homogeneity. In CD₂Cl₂, the allylic protons are separated; **a** (*trans* to N) has a strong nOe to an ortho-PPh₂ 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 coworkers.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.

| Reactant | Product | E.e. (yield) |
|----------------------|---|--|
| | CH(CO ₂ Me) ₂ | 95 (65%, 0.6 mmoles) ^a [98] |
| | CH(CO ₂ Me) ₂ | 94 (67%, 0.6 mmoles) ^b [76] |
| OCO ₂ Me | CH(CO ₂ Me) ₂ | 0 (84%) [67]° |
| °s ^{-C} 7H7 | SO ₂ C ₇ H ₇ (16) | ca. 25 (>85%) ^d |

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

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. ^aCarried out in CH₃CN in the presence of 15-crown-5 at 0°C. ^bCarried out by the BSA method at 20°C in CH₂Cl₂. ^cE.e.s in square brackets are those obtained with ligand 1, ref 3. ^d5 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(PPh3)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 Na₂CO₃ in water. The resulting vellow solution was heated at reflux overnight. After cooling to room temperature the solid was filtered off and thoroughly washed with CH₂Cl₂. The solution was washed with saturated brine (2 x 100 ml.), dried with MgSO4. and concentrated. The solid residue was washed with Et₂O (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 CH₂Cl₂ for characterisation. (Found: C, 86.00; H, 5.25; N, 4.11, C₂₄H₁₇NO requires: C, 85.97; H, 5.07; N, 4.18). δH $(CDCl_{3}, 500 \text{ MHz}) 8.76 \text{ (d, 1 H, J} = 8.3 \text{ Hz}), 8.72 \text{ (d, 1 H, J} = 0.7 \text{ Hz}, J_{2} = 8.0 \text{ Hz}), 8.34 \text{ (d, 1 H, J} = 0.8 \text{ Hz})$ Hz, J₂ = 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 (CDCl₃, 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 (CH₃). GC/MS (EI) m/z 335 (88%, M⁺), 334 (100%, [M-H]+.), 319 (53%, [M-O]+.), 303 (21%, [M-MeOH]+.).

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

BBr₃ (171 ml. of a 0.1 M solution in CH₂Cl₂) was added dropwise to a solution of 6-[1-(2methoxynaphthyl)]phenanthridine (28.7g, 85.5 mmol) in CH₂Cl₂ (350 ml.), upon which the solution turned dark. The reaction was slightly exothermic. The resulting mixture was stirred overnight, quenched with 180 ml. of H₂O, and stirred for another 15 minutes. The solid was filtered off, the water layer neutralised with NaOH, and extracted with CH₂Cl₂ (2 x 300 ml.). The CH₂Cl₂ extracts were stirred with 10% HCl, and the resulting solid filtered off. The collected solids were stirred with 500 ml. CH₂Cl₂ and 71 ml. 2M Na₂CO₃. At first a clear two-layer system was obtained from which eventually a solid precipitated. This solid was filtered off, and extensively extracted with CH₂Cl₂ (800 ml., which was re-used in the process, effectively approx. 3 L of CH₂Cl₂ was used). The CH₂Cl₂ extracts were dried on MgSO₄, 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 CH₂Cl₂. δ H (CDCl₃, 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 (CDCl₃, 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+·), 320 ([M-H]+·), $291([M-CH_2O]^+)$

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

CH₂Cl₂. The resulting mixture was stirred overnight (although the reaction is complete after 1h), and subsequently washed with hydrochloric acid (1M, 3 x 330 ml.), H₂O (2 x 330 ml.), and brine (330 ml.). After drying on MgSO₄ 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. δ H (CDCl₃, 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). δ C (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]⁺, 100), 320 ([M-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), PPh₂(O)H (42.9g, 212 mmol), dppp (2.19g, 5.3 mmol), Pd(OAc)₂ (1.19g, 5.1 mmol), and NaHCO₂ (26.8g, 320 mmol), The mixture was heated at 80°C for 20h, added to CH₂Cl₂ (1L), and washed subsequently with H₂O (2 x 1L), saturated Na₂CO₃ (1L), H₂O (2 x 1L) and saturated brine (1L). After drying on MgSO₄, 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 Et₂O (100 ml.), and dried, giving product (20.2g, 88%, mp. 270 - 275°C). (Found: C, 82.87 H, 4.98; N, 2.76, C₃₅H₂₄NOP requires: C, 83.15; H, 4.78; N, 2.77). The product could be further purified by crystallisation from toluene. δH (CDCl₃, 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, J₂ = 10.9 Hz), 8.16 (dd, 1 H, J_{PH} = 1.7 Hz, J₂ = 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_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz, J_t = 7.5 Hz), 7.31 (dd, 1 H, J_{PH} = 0.9 Hz), 7. 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, $J \approx 8.6$ 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, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_{PH} = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_2 = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_1 = 1.0$ Hz, $J_2 = 1.4$ Hz, $J_2 = 7.5$ Hz), 6.41 (dt, 1 H, $J_2 = 1.4$ Hz, $J_2 = 1.4$ H 2 H, J_{PH} = 3.0 Hz, J_1 = 7.8 Hz). &C (CDCl₃, 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. SP NMR (CDCl₃, 202.40 MHz) 32.0. MS (EI) m/z 505 (M^{+,}), 428 ([M-C₆H₅]⁺).

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 HSiCl₃ (32.5 ml., 326 mmol) and NEt₃ (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 CH₂Cl₂ (2 x 800 ml.). The organic layers were dried on MgSO₄, and concentrated *in vacuo*, giving, after Et₂O trituration, product (15.8g, 81%, mp. 105 - 107°C). An analytical sample was obtained by crystallisation from CH₂Cl₂. (Found: C, 85.79; H, 5.15; N, 2.80, C₃₅H₂₄NP requires: C, 85.87; H, 4.94; N, 2.86).From the Et₂O wash-layers 1.6g of starting material could be recovered. δ H (CDCl₃, 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). δ C NMR (CDCl₃, 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. δ P (CDCl₃, 202.40 MHz) -12.4 ppm. MS (EI) m/z 489 (M^{+.}), 412 ([M-C₆H₅]^{+.}), 335 ([M-2C₆H₅]^{+.}).

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

A mixture of 6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine (1.889g, 3.864 mmol) and di- μ -chlorobis[(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 KPF₆ (0.71g) in 60 ml. of H₂O. The mixture was stirred for 10 min., and the precipitated solid filtered off and washed with 300 ml. of Et₂O. 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, CHCl₃), δ H (CDCl₃, 500 MHz) 8.38 (t, 2 H, J = 7.3 Hz), 8.20 (dd, 2 H, J₂ = 7.6, 10.9 Hz), 8.13 (d, 1 H, J = 8.0 Hz), 8.10 (dd, 1 H, J₂ = 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, NCH₃), 2.15 (s, 3 H, NCH₃), 2.05 (d, 3 H, CCH₃). δ C NMR (CDCl₃, 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 (NCH₃), 48.9 (NCH₃), 2.3.9 (CCH₃). δ P (CDCl₃, 101 MHz) 41.6 ppm. MS (Electrospray) m/z 793 ([M-Cl]^{+,} with Pd-isotope pattern).

Complex 11, mp 228 - 231°C (dec), $[\alpha]_D^{25} = 262.1$ (c = 0.88, CHCl₃), δ H (CDCl₃, 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), 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, NCH₃), 2.33 (d, 3 H, J = 3.5 Hz, NCH₃, 1.24 (d, 3 H, CCH₃). δ C NMR (CDCl₃, 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, 125.5, 125.3, 124.0, 123.9, 123.6, 123.5, 123.0, 122.1, 73.8 (CH), 53.0 (NCH₃), 48.1 (NCH₃), 23.0 CCH₃). δ P (CDCl₃, 101.2 MHz)38.4, -54.1 (septet, J = 712 Hz, PF₆⁻). MS (Electrospray) m/z 793 ([M-PF₆]⁺, 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. Crys | stal data and st | tructure refinement | for complex 1 | 0 |
|---------------|------------------|---------------------|---------------|---|
|---------------|------------------|---------------------|---------------|---|

| Empirical formula | C50 H45 Cl3 N P Pd 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) |
| B (deg) | 93.41 (4) |
| V(Å ³) | 2125.1(10) |
| Z | 2 |
| $D_c(g \text{ cm}^{-3})$ | 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 \leq h \leq 11,-15 \leq k \leq 16, -7 \leq l \leq 12 |
| No. of unique rflns | 5717 |
| Independent reflections | 5336 [R(int) = 0.0547] |
| Refinement method Data/restraints/parameters | Full matrix least-squares on F ² 5333 / 1 / 517 |
| Goodness of fit on F^2 | 1.068 |
| Final R indices [I > $2\sigma(I)$] | R1 = 0.0413 ω R2 = 0.1075 |
| R indices (all data) | R1 = 0.0434 ω R2 = 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 | C49 H40 F6 N2 P2 Pd |
|------------------------------------|--|
| Mr | 939.17 |
| crys syst | monoclinic |
| crys size (mm) | 0.24 x 0.019 x 0.023 |
| space group | P21 |
| a (A),b (A), c (A) | 115.796 (5),13.537 (3),19.688 (3) |
| β (deg) | 92.27 (2) |
| V(Å ³) | 4207 (2) |
| Z | 4 |
| $D_c(g \text{ cm}^{-3})$ | 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 | $-16 \le h \le 18, -12 \le k \le 16, -23 \le 1 \le 23$ |
| 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 $[I > 2\sigma(I)]$ | $R1 = 0.0448 \ \omega R2 = 0.0937$ |
| R indices (all data) | $R1 = 0.0608 \ \omega R2 = 0.0971$ |
| 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 PdCl₂ complex

Dppe (0.43g, 1.07 mmol) was added to a solution of $\{6-[1-(2-diphenylphosphinonaphthyl)]$ phenanthridine} $\{(R)-(\alpha,N,N-trimethyl-1-aminomethyl-2-naphthyl)\}$ palladium hexafluorophosphate (1.0g, 1.07 mmol) in CH₂Cl₂ (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 CH₂Cl₂. 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, CHCl₃); after repetition of the cycle : $[\alpha]_D^{25}$ = -167.9 (c = 0.976, CHCl₃). 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 CH₂Cl₂ (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 CH₂Cl₂ (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 MgSO₄, 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, C₃₅H₂₄Cl₂NPPd requires: C, 63.04; H, 3.63; N, 2.10. δ H (CDCl₃, 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, J₁ = 1.9 Hz, J₂ = 8.5 Hz), 8.09 (d, 1 H, J = 8.3 Hz), 8.04 (ddd, 1 H, J₁ = 1.3 Hz, J₂ = 7.7 Hz, J₃ = 7.7 Hz), 7.77 (ddd, 1 H, J₁ = 1.0 Hz, J₂ = 7.7 Hz, J₃ = 7.7 Hz), 7.69 (ddd, 1 H, J₁ = 2.3 Hz, J₂ = 5.7 Hz, J₃ = 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). δ P (CDCl₃, 101.2 MHz) 33.95. MS (Electrospray) m/z 630 ([M-Cl]⁺) 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, CHCl₃).

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

Preparation as 15. Light yellow solid, mp 165 - 167°C (dec). $[\alpha]_D^{25} = 318.1$ (c = 0.55, CHCl₃) δ H (BF₄ salt, minor diastereomer, CDCl₃, 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} ≈ J_{HH}≈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, CDCl₃, 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, J₁ = 0.9 Hz, J₂ = 7.6 Hz, J₃ = 7.8 Hz), 7.86 (ddd, 1 H, J₁ = 1.0 Hz, 1.3 Hz, J₂ = 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. &C (CDCl₃, 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. SP NMR (CDCl₃, 202.40 MHz) 44.0 (minor diastereomer?), 34.5 (major diastereomer). MS (Electrospray) $m/z 636 ([M-BF_{d}]^{+})$

(+)-(η^3 -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, CHCl₃) & C (both diastereomers reported, but not individually assigned) (CDCl₃, 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. & P (CDCl₃, 202.40 MHz) 33.56 (minor diastereomer), 29.70 (major diastereomer) MS (Electrospray) m/z 788 ([M-OTf]⁺.

(+)-(η^3 -cyclohexenyl)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridinepalladium trifluoromethanesulfonate 15

A solution of (+)-6-[1-(2-diphenylphosphinonaphthyl)]phenanthridine (100 mg, 0.205 mmol) and di-udichloro-bis[(n³-cyclohexenyl)palladium] (46 mg, 0.103 mmol, 0.206 mmol Pd), was added to a suspension of AgOTf (53mg, 0.205 mmol) in CH₂Cl₂ (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 $Et_2O(2 \times 20 \text{ ml})$ leaving a light vellow powder. (162mg, 96%), mp 175 - 177°C (dec), $[\alpha]_{D}^{25} = 197.7$ (c = 0.977, CHCl₃) δ H (CDCl₃, 500 MHz) 8.52 (ddd, 2 coincident H, J ca. 1, 4, 8 Hz), 8.32 (dd, 1 H, J₁ = 0.7 Hz, J₂ = 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 = 8.3 Hz), 7.19 (dd 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) & (CDCl₂, 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 (CDCl₃, 202.40 MHz) 32.1. MS (electrospray) m/z 676 (M⁺· with Pd-isotope pattern).

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

Preparation of precursor :p-Toluenesulfinyl chloride¹⁶ (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 Et₂O (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.), NaHCO₃ solution (5%, 20 ml.), and water (20 ml.). After drying on MgSO₄ 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 (CD₃CN, 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, CH₃), 2.10 - 1.77 (m, 4 H), 1.77 - 1.52 (m, 2 H). & NMR (CD3CN, 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 CD₃CN (1.5 added n^3 -allyl-(R)6-[1-(2-diphenylphosphinonaphthyl)]phenanthridinepalladium trifluoro ml.) was methanesulfonate (53mg, 5 mol%, as solid), 15-crown-5 (15mg, 5%, in 0.5 ml. of CD₃CN) 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/Et₂O = 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

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(Received in UK 24 August 1995)