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ortho-Palladated α-phenylalkylamines for enantiomeric purity determination of monodentate P*-chiral phosphines

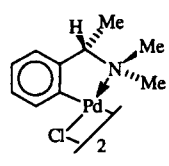
V. V. Dunina,[a,*] L. G. Kuz'mina,[b] M. Yu. Kazakova,[a] Yu. K. Grishin,[a] Yu. A. Veits[a] and E. I. Kazakova[c]

[a] Department of Chemistry, M. V. Lomonosov Moscow State University, 119899, V-234 Moscow, Russia
[b] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospect, 31, 117907 Moscow, Russia
[c] Department of Chemistry and Biology, Syktyvkar State University, 167005, Petrozavodskaya Street, 120, Syktyvkar, Komi Republik, Russia

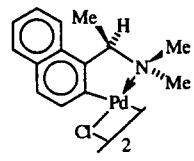
Abstract: Three *ortho*-palladated complexes were tested as chiral derivatizing agents for enantiomeric excess determination of monodentate P*-chiral phosphines by ^{31}P NMR analysis. The complexes containing a bulky substituent at the α-C*- **1e** or an N*-stereocentre **1d** are shown to be more efficient as compared to known N-achiral α-methyl substituted analogues. The structure and stereochemistry of the new dimeric complex (S_C)-**1e** was established by X-ray analysis. © 1997 Published by Elsevier Science Ltd

Introduction

The high efficiency of homochiral *ortho*-palladated α-arylethylamines in the resolution of mono- and bidentate ligands[1,2] is well recognized. The first examples of the use of these compounds for absolute configuration determination (as "reporter" complex[3]) and in asymmetric synthesis[4] have also evolved. The surprising thing is that their application for the enantiomeric purity determination of optically active substrates, obtained in other ways[5,4c] was limited until recently. To our knowledge, only three articles devoted to the testing of *ortho*-palladated complexes for the enantiomeric purities determination of diphosphines with **1a**,[6] functionalized monophosphines with **2**[7] or diamines with **1b,c**[8] by NMR analysis have been published.



(S_C)-**1a**



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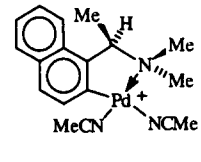
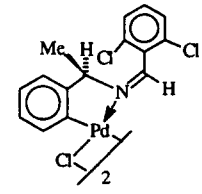


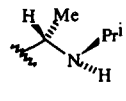
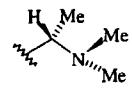
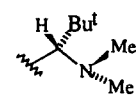
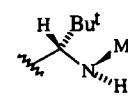
(R_C)-**1c**



(R_C)-**2**

Our investigations of enantiomeric discrimination during binding of the racemic phosphine *tert*-BuMePhP (**L**[1]) with a wide series of *ortho*-palladated α-arylalkylamines using ^{31}P NMR spectroscopy[9] have revealed a strong dependence of the diastereomeric peak separation (Δδ) on the palladacycle structure: Δδ(^{31}P) values range from 0.09 to 2.90 ppm at the low temperature (188 K).

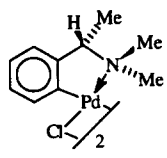
* Corresponding author. Fax: +7 (095) 932-88-46; Email: dunina@org.chem.msu.su

Side chain of palladacycle				
$\Delta\delta(^{31}P)$, ppm for L^1 adducts	0.09	0.89	1.49	2.90

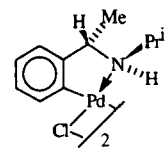
These data have stimulated us to elucidate the influence of cyclopalladated complexes (CPC) structure on their efficiency as chiral derivatizing agents (CDA) for enantiomeric purity determination.

Results and discussion

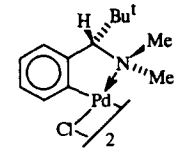
Three μ-chloro-bridged *ortho*-palladated complexes were tested as specific organometallic chiral derivatizing agents for the phosphine ligands: N-achiral dimer (S_C)-**1e**, bearing a bulky *tert*-Bu substituent at the α-C* stereocentre,[10] N*-chiral complex (S_CR_N)-**1d**, containing a rather bulky *iso*-Pr group at the asymmetric secondary nitrogen atom,[11] and their well known N-achiral α-Me-substituted analogue (S_C)-**1a**,[12] used as a reference point.



(S_C)-**1a**

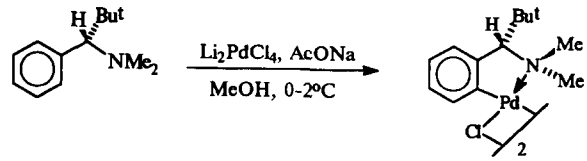


(S_CR_N)-**1d**



(S_C)-**1e**

The new dimer (S_C)-**1e** was obtained by direct *ortho*-palladation of N,N-dimethyl-(*S*)-α-phenylneopentylamine under mild conditions. The homochiral state of this complex was confirmed by means of ^1H NMR spectra of its adduct with (*S*)-α-methylbenzylamine, generated *in situ*.[10]



(*S*)-HL (S_C)-**1e**

To elucidate the absolute configuration of the new dimer (S_C)-**1e** the X-ray crystal structural determination was carried out (Flack's *x* parameter −0.057, esd 0.069). The structure and stereochemistry of this complex is shown in Figure 1. Full structural details have been deposited with the Cambridge Crystallographic Data Centre.

In common with most of the recorded X-ray structures of μ-chloro-bridged dimeric *ortho*-palladated amines[13–15] or related dimers of C,N-type,[16] complex (S_C)-**1e** reveals the expected *trans*-relationship between two nitrogen and two carbon donor atoms. It consists of two independent halves; the central four-membered cycle $\{Pd_2(\mu\text{-}Cl)_2\}$ is bent along the Cl(1)···Cl(2) axis by 7.1° as compared to 16.3° for (S_CR_N)-**1d** dimer,[15] 0° (**3a,b**) or 12.7° (**3c**) in the case of *ortho*-palladated α-unsubstituted benzylamines **3a–c**.[13] Both palladium atoms are in a nearly square-planar co-ordination with a very slight tetrahedral distortion 3.7–4.8°[17] compared to 6.5–12.4° for **1d**[15] or 2.7–5.9° for **3a–c**.[13]

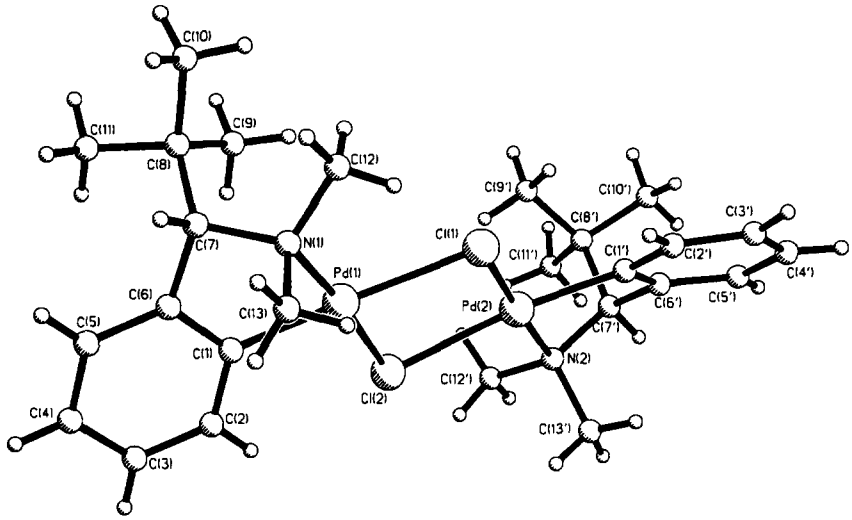
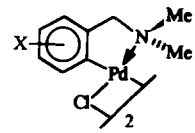


Figure 1. X-Ray structure of dimer (S_C)-**1e**. $C_{26}H_{40}Cl_2N_2Pd_2$, M 664.36, orthorhombic space group $P2_12_12_1$, a 10.640(3), b 12.126(4), c 22.496(7)A, V 2902(2) A^3, Z 4, D_x 1.520 g cm^{-3}, Mo–K_α radiation, l 0.71073 A, μ(Mo–K_α) 14.39 cm^{-1}; 293 K; the final R and R_w values are 0.0349 and 0.0694, respectively, for 2836 independent reflections corrected for absorption by Ψ-scan curve.



X = o-MeO (3a), m-MeO (3b), p-MeO (3c)

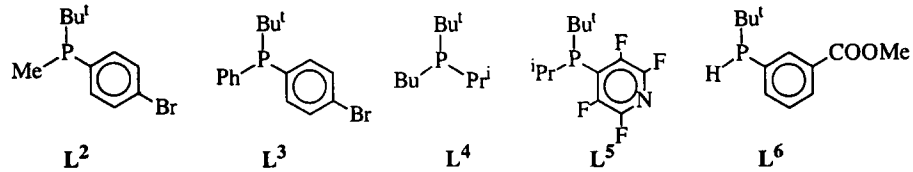
Both five-membered palladacycles adopt the usual twisted envelope-like conformation: the deviations of nitrogen atoms from the mean planes {PdCCC} being −0.727 and 0.655 Å; intrachelate torsion angle about the aromatic carbon–carbon bond being 3.0–13.3°, and the sum of intrachelate torsion angles[18] being 134.5–135.5° as compared to 99–122° for the complexes **1d**, **3a–c**.

The most important feature of this complex is the bulky *tert*-Bu substituent (and one of NMe groups, *trans*-positioned, as well) adopts a nearly axial position[19]: the angle between the C–CMe_3 bond and the normal to the mean coordination plane {$PdC(1)NCl_2$} equal to 6.8–4.4°, and the C(8)–C(7)–N–C(13) torsion angle between α-*tert*-Bu substituent and the axial NMe group is 160.9–162.3°. Probably, the λ(S)-conformation of palladacycle observed is a result of the need to avoid steric interactions present in the alternative δ(S)-form: for example, between *tert*-Bu and the neighbouring aromatic C(5)H proton and/or NMe groups. However, this conformation can be also stabilized at some extent due to a slight agostic interaction (*tert*-Bu)H· · ·Pd: in the dimer (S_C)-**1e** structure, the distances Pd· · ·H 2.92–2.91 Å were found to be less than the sum of Van der Waals radii of these atoms of 3.1 Å.[20] To note, this contact is a little shorter in the case of mononuclear adducts of the same complex with pyridine[21] and phosphine ligands:[22] 2.74 and 2.84–2.94 Å, respectively.

The absolute configuration of the N*-chiral dimer (S_CR_N)-**1d**, and λ(S_C)-conformation of its palladacycle were confirmed by X-ray data previously;[15] in this case a weak agostic interaction between the NPr^i group and the palladium centre with an H· · ·Pd distance of 2.84–2.92 Å was found as well.

To impose a lower limit on the ability of these complexes to determine spectroscopically enantiomeric purity, we decided in favour of simple monodentate phosphine ligands since these racemic substrates are the most difficult for enantiomer recognition due to their rotameric mobility in

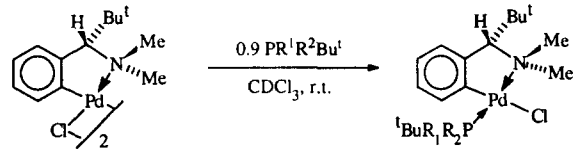
the coordinated state. A series of P*-chiral tertiary and secondary phosphines ($\mathbf{L^2}$–$\mathbf{L^6}$) of the general type *tert*-BuPR^{1}R^2 was used (see below); it includes only strictly monodentate ligands without any additional functional groups capable of intramolecular coordination with the metal centre.[23]



$\mathbf{L^2}$ $\mathbf{L^3}$ $\mathbf{L^4}$ $\mathbf{L^5}$ $\mathbf{L^6}$

The new racemic tertiary phosphines $\mathbf{L^2}$–$\mathbf{L^4}$ were synthesized by alkylation or arylation of chlorophosphines *tert*-Bu(R^1)PCl with organolithium reagent R^{2}Li following the known general method.[24] The *meta*-functionalized secondary phosphine $\mathbf{L^6}$ was prepared by the cross-coupling of silated phosphine *tert*-Bu(Me$_3$Si)PH with the appropriate arylbromide catalyzed by Pd(0) complex under conditions described previously[25] with a slight modification. The synthesis of phosphine $\mathbf{L^5}$ will be published shortly.[26]

The methodology of enantiomeric purity determination was developed on the racemic phosphines. It includes the complexation of the phosphine with a slight excess of homochiral CPC (Pd/P* ratio≈1.1) in 0.125 M $CDCl_3$ solution at room temperature under anaerobic conditions *in situ* in an NMR tube directly. An excess of derivatizing agent is required to guarantee the binding of both enantiomers. The reaction mixture formed contains two diastereomers of monophosphine adduct **4** of (S_C,S_P)- and (S_C,R_P)-configuration and a small excess of starting dimer **1**.



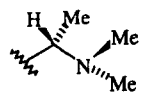
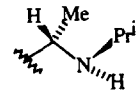
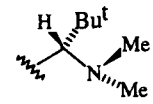
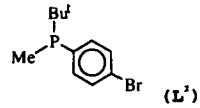
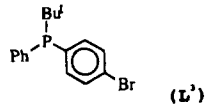
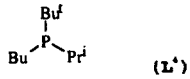
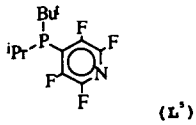
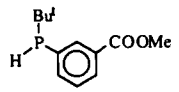
(S_C)-**1e** ($S_C S_P$)-**4e** + ($S_C R_P$)-**4e**

As the method of the control for the diastereomeric composition of these mixtures we have choosen $^{31}P\{^1H\}$ NMR spectroscopy (at room temperature) due to the simplicity of the spectra: two singlets for the two diastereomers **4** in the 1:1 ratio were observed in all systems investigated (see the experimental section). To identify these signals unambiguously we have performed the resolution of two diastereomers **4e**, containing $\mathbf{L^3}$ phosphine as an example. Their configurations were established by X-ray structure determination.[22]

The magnitude of the diastereomeric peak separation, $\Delta\delta=\delta(S_CS_P)-\delta(S_CR_P)$ seems to be the most important parameter to characterize the efficiency of *ortho*-palladated complexes as the CDA.[27] The $\Delta\delta$ values (ppm) obtained for the systems **1a**, **d**, **e**/$\mathbf{L^2}$–$\mathbf{L^6}$ are given in Table 1.

From the data presented it is evident that N*-chiral dimer (S_CR_N)-**1d** and α-*tert*-Bu substituted reagent (S_C)-**1e** reveal some advantages as compared to the known complex (S_C)-**1a**: the signal resolution is improved by a factor of 2–5 in the terms of $\Delta\delta$ values. The range of $\Delta\delta$ values observed for the simple monodentate phosphines $\mathbf{L^2}$–$\mathbf{L^6}$ with the use of (S_C)-**1e** as CDA ($\Delta\delta$ 0.28–5.36 ppm) is quite comparable with the data obtained previously for the chelated diphosphines (including P*-chiral *Dipamp*) using (S_C)-**1a** reagent ($\Delta\delta$ 0.1–3.1 ppm[6]) or for the functionalized monophosphines[23] capable of "hemi-chelation" with (R_C)-**2** reagent ($\Delta\delta$ 0.4–8.5 ppm[7]). Except for one case (**1e**/$\mathbf{L^5}$ system), the chemical shift nonequivalence ($\Delta\delta$) observed roughly correlates with the bulkiness of phosphine ligands determined in terms of Tolman's angles θ,[28] which varied from 148° ($\mathbf{L^2}$) up to 175° ($\mathbf{L^5}$) in the ligands $\mathbf{L^2}$–$\mathbf{L^5}$ series.

Table 1. The magnitudes of diastereomeric peak separation (Δδ, ppm) obtained for the systems **1a, d, e**/L^2–L^6

Side chain of CDA palladacycle :			
	(S_C)-**1a**	(S_CR_N)-**1d**	(S_C)-**1e**
 (L^2)	0.052	0.390	0.281
 (L^3)	0.289	0.437	0.654
 (L^4)	0.505	1.077	2.567
 (L^5)	1.521	2.520	2.510
 (L^6)	1.507	2.342	5.355

Conclusion

The method of enantiomeric purity determination and the reagents described satisfy all general requirements for CDA:[27] (i) the derivatizing agents **1a,d,e** are easily available in an enantiopure state; (ii) the stable diastereomers **4a,d,e** form *in situ* instantly and completely under mild conditions and without any racemization or kinetic resolution; (iii) the use of a CDA excess does not result in any spectral complications due to the choice of ^{31}P NMR control; (iv) the methodology used does not require the isolation of diastereomeric complexes **4a,d,e** before ^{31}P NMR spectra measurement; (v) an enantiomeric purity of the phosphine tested can be improved by recrystallization or chromatographic purification of the same sample;[29] (vi) in the case of monodentate phosphines, the valuable enantiopure P-ligand can be recovered from its adduct with CDA by a known method,[30] which (vii) allows regeneration of CDA as the dimer, suitable for further use.

The advantage of new CDA **1d,e** over the known dimer **1a** is a higher ability for the spectral discrimination between two enantiomeric forms of the simple monodentate phosphines; a high diastereomeric signal resolution offers the opportunity to measure the ^{31}P NMR spectra at room temperature. The new dimers **1d,e** exhibit higher solubility in organic solvents that seems to be a useful practical property.

To note, this approach is especially valuable for the secondary phosphines known for their high sensitivity to racemization (or epimerization) in the free state.[31]

Experimental

General

NMR spectra were recorded (unless indicated otherwise) on a Varian VXR-400 instrument at 400 and 161.9 MHz for ^1H and ^{31}P nuclei, respectively. The measurements were carried out at ambient temperature in $CDCl_3$ solutions (unless indicated otherwise). The proton chemical shifts are reported in parts per million relative to TMS as internal standard; the ^{31}P chemical shifts are given with respect to H_3PO_4 as an external reference. Specific rotations were measured on a VNIEKI-Prodmash AI-EPO polarimeter in a 0.25 dm cell at 20°C in $CHCl_3$ solutions. CD spectrum of (S_C)-**1e** was recorded on a spectropolarimeter "JASCO J-720" at 240–500 nm in $CHCl_3$ solution at the Centre for Sophisticated Instrument Facilities, Spectropolarymetry Division (FIMIS).

All manipulations involving free phosphines were carried out under an argon atmosphere using Shlenck technique. The solvents were generally dried over the appropriate drying agent,[32] distilled under argon and degassed just prior to use. Deuterated chloroform was purchased from Aldrich and deoxygenated. Starting chlorophosphines ^{t}Bu(Me)PCl,[33] ^{t}Bu(Ph)PCl,[34] ^{t}Bu(^{i}Pr)PCl,[35] and silylated secondary phosphine ^{t}Bu(Me_3Si)PH[36] were obtained as described. The resolution of α-phenylneopentyl amine was carried out according to the known method[37] with certain modifications;[10] N,N-dimethyl-(*S*)-α-phenylneopentylamine was prepared from the related primary amine (98.2% ee) according to that described for the racemic ligand.[38] $(+)_D$-Di-μ-chlorobis{(S_C)-2-[(1-dimethylamino)ethyl]phenyl-C,N}dipalladium(II), (S_C)-**1a**[12] and $(+)_D$-di-μ-chlorobis{(S_C,R_N)-2-[(1-isopropylamino)ethyl]phenyl-C,N}dipalladium(II), (S_CR_N)-**1d**[11] were prepared as reported previously.

$(+)_D$-Di-μ-chlorobis{(S_C)-2-(1-dimethylamino-2,2-dimethylpropyl)phenyl-C,N}dipalladium(II)

(S_C)-**1e** was obtained in the yield of 83% as reported.[10] The mixture of Li_2PdCl_4 (3.3 g, 13 mmol), (*S*)-N,N-dimethyl-α-phenylneopentylamine (2.48 g, 13 mmol) and NaOAc (1.69 g, 20.6 mmol) in anhydrous MeOH (100 mL) was stirred at 2°C for 8 h under argon. The dimer precipitated was filtered, washed with MeOH and extracted with $CHCl_3$; concentration *in vacuo* and addition of hexane allowed isolation of 3.465 g of dimer (S_C)-**1e**. After storage of the first methanol mother liquor in the presence of an excess of NaOAc (0.323 g, 3.9 mmol) at −2°C for 4 days an additional portion of dimer (0.496 g) was isolated by column chromatography (Silpearl, *h* 14 cm, *d* 2.5 cm) using benzene as an eluent. The combined portions of crude complex were recrystallized from a chloroform–hexane mixture and dried *in vacuo* to give homochiral dimer (S_C)-**1e** as light-yellow crystals in overall 83% yield (3.459 g): m.p. 185–188°C (dec.); $[\alpha]_D^{20}$ +255 (c 0.4, $CHCl_3$); R_f 0.91 (Silufol, benzene/acetone 5:1). CD spectra (c 0.01, $CHCl_3$, $[\theta]_{max}$ and λ_{max}, nm): −2666 (383), 4166 (352), −11770 (318), 820 (287), −3700 (282), 83900 (246).

^1H NMR ($CDCl_3$, δ, ppm; two sets of signals from *cis/trans* isomers): 1.411 and 1.406 (s, 9H, ^{t}Bu), 2.838 and 2.779 (s, 3H, NMe^{ax}), 2.857 and 2.852 (s, 3H, NMe^{eq}), 3.180 (c, 1H, α-CH), 7.123 and 7.174 (d, 1H, $^3J_{HH}$ 7.7 Hz, C^6H), 6.82–6.93 (m, 3H, C^3H–C^5H). Anal. Calc.: C, 47.01; H, 6.07; N, 4.22 for $C_{26}H_{40}Cl_2N_2Pd_2$. Found: C, 47.20; H, 6.16; N, 4.18.

Phosphines L^2–L^6 synthesis

tert-Butyl(phenyl)(4-bromophenyl)phosphine (L^3)

Solution of 1,4-dibromobenzene (5.4 g, 25 mmol) in anhydrous Thf (15 mL) was added drop by drop to a 1.97 M solution of BuLi (25 mmol) in anhydrous hexane (13 mL) under vigorous stirring at −70°C. Then a solution of ^{t}Bu(Ph)PCl (5 g, 25 mmol) in Thf (5 mL) was added for 10 min at −60°C. After heating the reaction mixture up to room temperature for 30 min, the LiCl precipitate was filtered and the mother liquor was concentrated *in vacuo* (10 mm Hg). Subsequent fractional distillation affords phosphine **L**^{3} in a 79% yield (6.3 g): b.p. 150–152°C (2 mm Hg).

^{31}P NMR spectrum was recorded on a Varian FT-80 spectrometer (32.2 MHz) in C_6D_6: δ 15.9 ppm (s). ^1H NMR ($CDCl_3$, δ, ppm): 1.186 (d, $^3J_{HP}$ 12.4 Hz, 9H, *tert*-Bu), 7.358 (m, 3H, *meta*- and *para*-H

of Ph group), 7.41–7.49 (m, 4H, 4-BrC_6H_4), 7.555 (m, 2H, *ortho*-H of Ph group). Anal. Calc.: C, 59.83; H, 5.65 for $C_{16}H_{18}BrP$. Found: C, 59.48; H, 5.59.

tert-Butyl(methyl)(4-bromophenyl)phosphine (L^2)

L^2 was prepared in a manner analogous to that of L^3, starting from ^{t}Bu(Me)PCl (5 g, 36 mmol) in a 81% yield (7.6 g): b.p. 114–115°C (2 mm Hg), m.p. 72°C. ^{31}P NMR ($CDCl_3$, δ, ppm): −10.722 (s). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.902 (d, $^3J_{HP}$ 12.1 Hz, 9H, *tert*-Bu), 1.236 (d, $^2J_{HP}$ 3.6 Hz, 3H, Me), 7.28 (dd, 2H, $^3J_{HP}$ 6.4 Hz, $^3J_{HH}$ 8.1 Hz, *ortho*-H of 4-BrC_6H_4 group), 7.43 (d, $^3J_{HH}$ 8.1 Hz, 2H, *meta*-H of 4-BrC_6H_4 group). Anal. Calc.: C, 50.99; H, 6.22 for $C_{11}H_{16}BrP$. Found: C, 50.97; H, 6.33.

tert-Butyl(isopropyl)butylphosphine (L^4)

A 1.97 M solution of BuLi (20 mmol) in anhydrous hexane was added drop-by-drop to solution of ^{t}Bu(^{i}Pr)PCl (3.33 g, 20 mmol) in anhydrous Et_2O (15 mL) under vigorous stirring at −50°C. After the reaction mixture was heated to room temperature and stirred for 30 min, the LiCl precipitate was removed by means of a centrifuge, and washed with pentane (5 mL); the combined organic layers were evaporated *in vacuo*. The crude product was finally distilled *in vacuo* to afford phosphine L^4 in 88% yield (3.3 g): b.p. 75–76°C (7 mm Hg). ^{31}P NMR ($CDCl_3$, δ, ppm): 15.962 (s). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.887 (t, $^3J_{HH}$ 7.0 Hz, 3H, *Me*CH_2), 1.041 (d, $^3J_{HP}$ 10.3 Hz, 9H, *tert*-Bu), 1.046 (dd, $^3J_{HP}$ 9.7 Hz, $^3J_{HH}$ 7.0 Hz, 3H, CH*Me*), 1.132 (dd, $^3J_{HP}$ 15.6 Hz, $^3J_{HH}$ 7.1 Hz, 3H, CH*Me*), 1.365 (m, 6H, $(CH_2)_3$), 1.713 (d.sept., $^2J_{HP}$ 4.5 Hz, $^3J_{HH}$ 7.1 Hz, 1H, C*H*Me_2). Anal. Calc.: C, 70.17; H, 13.38 for $C_{11}H_{25}P$. Found: C, 69.86; H, 13.22.

tert-Butyl(isopropyl)(tetrafluoropyridyl-4)phosphine (L^5)

Synthesis of L^5 will be published shortly.[26] ^{31}P NMR ($CDCl_3$, δ, ppm): 16.34 (d, $^3J_{PF}$ 33.5 Hz).

tert-Butyl(3-methoxycarbonylphenyl)phosphine (L^6)

A mixture of ^{t}Bu(Me_3Si)PH (3.24 g, 20 mmol), methyl 3-bromobenzoate (3.87 g, 19 mmol) and $[Pd(MeCN)_2Cl_2]$ (0.05 g, 1 mol %) in benzene (10 mL) was heated in a sealed tube at 100°C for 8 h. After the evaporation *in vacuo* and distillation of the remainder, the secondary phosphine L^6 was obtained in 84% yield (3.6 g): b.p. 95–96°C (1 mm Hg). Lit. data:[25] b.p. 86–87°C (0.01 mm Hg). ^{31}P NMR (C_6D_6, δ, ppm): −7.04 (d, $^1J_{PH}$ 211 Hz). ^{1}H NMR (C_6D_6, δ, ppm): 1.151 (d, $^3J_{HP}$ 12.0 Hz, 9H, *tert*-Bu), 3.681 (s, 3H, MeO), 4.076 (d, $^1J_{HP}$ 208.1 Hz, 1H, P*H*); aromatic protons: 7.012 (dd, $^3J_{HH}$ 7.4 and 7.8 Hz, 1H, H^5), 7.403 (ddd, $^3J_{HP}$ 6.1 Hz, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.4 Hz, 1H, H^6), 8.055 (dd, $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.2 Hz, 1H, H^4), 8.390 (d, $^3J_{HP}$ 5.4 Hz, 1H, H^2).

Procedure of enantiomeric purity determination

A sample of racemic phosphine L^2 (0.0221 g, 0.0688 mmol) was weighed in an NMR tube under argon; then, the solution of dimer (S_CR_N)-**1d** (0.023 g, 0.0378 mmol) in deoxygenated $CDCl_3$ (0.55 mL) was added (Pd/L ratio≈1.1). After one hour storage the ^{31}P{^{1}H} NMR spectrum of the reaction mixture was recorded at room temperature. The data obtained for diastereomeric complexes **4a,d,e** are presented below ($CDCl_3$, δ, ppm; singlet, unless indicated otherwise).

4a (L=L^2): 35.849 and 35.797; **4a** (L=L^3): 58.508 and 58.219; **4a** (L=L^4): 70.657 and 70.152; **4a** (L=L^5): 65.802 and 64.281; **4a** (L=L^6): 54.580 (d, $^1J_{PH}$ 357 Hz) and 53.073 (d, $^1J_{PH}$ 362 Hz).

4d (L=L^2): 36.438 and 36.048; **4d** (L=L^3): 56.325 and 55.888; **4d** (L=L^4): 67.408 and 66.331; **4d** (L=L^5): 62.258 and 59.738; **4d** (L=L^6): 55.604 (d, $^1J_{PH}$ 369 Hz) and 53.262 (d, $^1J_{PH}$ 369 Hz).

4e (L=L^2): 34.051 and 33.770; **4e** (L=L^3): 56.740 and 56.086; **4e** (L=L^4): 53.799 and 51.232; **4e** (L=L^5): 67.599 and 65.089; **4e** (L= L^6): 55.489 (d, $^1J_{PH}$ 356 Hz) and 50.134 (d, $^1J_{PH}$ 357 Hz).

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