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Enantioselective synthesis of platinum group metal complexes with the chiral PCP pincer ligand *R*,*R*-{C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$}. The crystal structure of *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$}

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Abstract

The novel PCP chiral ligand *R*,*R*-{C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$} and its platinum metal complexes have been easily synthesized in enantiomeric pure form. The palladium compound *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} has been characterized by X-ray crystal structure analysis thus confirming the absolute configuration of the complexated ligand. Preliminary catalytic experiments with the iridium and palladium complexes *R*,*R*-IrH_4{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} and *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} in the dehydrogenation of cycloalkanes and in the hydrosilylation of styrene, allylic alkylation and Heck coupling reactions, respectively have been carried out. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chiral phosphines; Asymmetric catalysis; PCP pincer complexes

1. Introduction

Among the most popular ligands used today in asymmetric synthesis, chiral phosphines occupy an important place [1]. These compounds have probed to be very efficient ligands in different catalytic processes and outstanding enantiomeric yields have continued the increasing interest for the synthesis of these ligands and its complexes [2]. The iridium PCP pincer complexes IrH_2{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$} [3] and PdCl{C_6H_3-2,6-($OPPr^i_2$)$_2$} [4] have been found to be highly efficient and robust catalysts for the dehydrogenation of alkanes [3a,3b,3c,3d,3e,3f], ethers and alkyl arenes [3c], amines [3g], alcohols [3h] and in the Heck reaction [4], respectively. Following our continuous interest in the design and screening of highly reactive and thermally stable organometallic species for organic transformations, we have turned our efforts to the design and synthesis of the chiral counterparts of the PCP pincer ligand in IrH_2{C_6H_3-2,6-($CH_2PBu^t_2$)$_2$}. First attempts for the introduction of chiral motifs in similar ligands have been carried out before by Venanzi and coworkers [5] for the synthesis of the chiral ligand {C_6H_4-2,6-(CH_3C*$HPPh_2$)$_2$}, however the synthetic method probed to be very difficult and tedious. Further efforts by the same group [6] led them to the synthesis of the chiral ligand 1*S*,2*S*-{C_6H_4-2,6-({2,3-*O*-$(CH_3)_2$C-2,3-O*C**HCH$_2$O}-1-*C**H$(PPh_2)_2$}; the platinum complex of this specie was tested in the enantioselective aldol reaction of methyl isocyanoacetate and aldehydes with good enantiomeric yields (65%). A more convenient approach by Zhang and coworkers [7] resulted in the efficient synthesis of the chiral compound 1*R*,1*R*-{C_6H_4-2,6-(CH_3C*$HPPh_2$)$_2$}. The palladium and platinum complexes were synthesized and the X-ray crystal structure analysis of both species obtained, the palladium complex was examined in the allylic alkylation [7a] couplings and aldol reactions [7b] of methyl isocyanoacetate with enantiomeric yields similar to those obtained by Venanzi. Also by Zhang and coworkers [8], the compounds *R*,*R*-{C_6H_4-2,6-[CH_2CH_2P*Ph(*o*-An)]$_2$} and *R*,*R*-{C_5H_3N-2,6-[CH_2CH_2P*Ph(*o*-An)]$_2$} were synthesized and applied in the asymmetric allylic alkylation [8a] and hydrosilylation [8b] reactions with

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modest enantiomeric yields. In this case the active species were assumed to be chelated complexes with the PCP or PNP compounds behaving as bidentated or tridentated ligands, respectively. As noted above by exception of Zhang's compounds the chiral information has been located on the α-benzylic positions. It has been suggested that in order to achieve high enantiomeric yields the chiral information must be located in a closer proximity to the metal center [9]. Based on these observations we have synthesized the *R,R*-{C_6H_4-2,6-(CH_2P*PhBu^t)$_2$} ligand and its platinum group metal complexes in enantio-pure form; preliminary catalytic results are also reported herein.

2. Experimental

2.1. General

All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. Solvents were degassed and dried using standard procedures. The following were purchased and used without further purification, Cl_2PPh, α,α-1,3-dibromoxylene, (−)-sparteine, $BH_3{\cdot}SMe_2$, $HBF_4{\cdot}Et_2O$ and *n*-BuLi (Aldrich Chemical Co.). The complexes [Ir(μ-Cl)(COE)$_2$]$_2$ [10] (COE = cyclooctene), [$PdCl_2$(COD)] [11] (COD = 1,5-cyclooctadiene) were synthesized by the literature methods. The ^{1}H-NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent as internal standard ($CDCl_3$, δ 7.26 or C_6D_6 δ 7.16). ^{13}C- and ^{31}P-NMR spectra were recorded with complete proton decoupling and are reported in ppm downfield of TMS with solvent as internal standard ($CDCl_3$, δ 77.0 or C_6D_6 δ 128.4) and external 85% H_3PO_4, respectively. GC analyses were carried out in a HP 5890A flame ionization detector (FID) and HP 5890 SERIES II with an 5971A mass selective detector gas chromatographs, and an HP-1 capillary column (25.0 m) from Hewlett Packard or a SPB^{TM}-1 capillary column (30.0 m) from SUPELCO®. Optical rotations were measured at 25 °C on a JASCO-DIP-370 Digital Polarimeter with a sodium lamp and reported as follows: $[\alpha]_\lambda^{T\ °C}$ (*c* g/100 ml of solvent). The ee values were determined by analytical high performance liquid chromatography (HPLC) on a IBM LC/9533 ternary liquid chromatograph with a variable wavelength detector, using a Daicel CHIRALPAK® AD column (250 × 4.6 mm).

2.2. Synthesis of $HPPhBu^tBH_3$ (*1*)

Phosphine **1** was synthesized using a modification of the procedure reported in the literature [12]. In a 100 ml Schlenk flask equipped with a magnetic stirring bar, were placed 5.0 g (3.9 ml, 27.93 mmol) of dichlorophenylphosphine and 10 ml of dry THF under Ar. The flask was cooled to −78 °C, and a solution of *tert*-butylmagnesium chloride (20.54 ml of 1.36 M THF solution) was added with stirring by syringe during 1 h. After addition, the cooling bath was removed and stirring was continued at room temperature (r.t.) for 1 h. The flask was then immersed in an ice bath and a THF solution of $LiAlH_4$ (27.94 ml of 1 M THF solution) and neat BH_3–SMe_2 (2.84 ml, 30.0 mmol) were added consecutively by syringe and the solution stirred for and additional 1 h. The reaction mixture was carefully poured into a mixture of concd. HCl (15 ml), ice (ca. 30 g) and CH_2Cl_2 (20 ml). The organic layer was separated and the aq. phase was extracted with CH_2Cl_2 (2 × 5 ml). The combined extracts were dried over $MgSO_4$ and concentrated in vacuum. NMR spectroscopy showed the product to be better than 98% pure and it was used in further steps without further purification. Yield: 3.5 g, 70%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 0.1–1.0 (q, br, 3H, PBH_3), 1.2 (d, J = 14.8 Hz, 9H, PC(CH_3)$_3$), 4.64 and 5.55 (dq, J = 363.6 Hz, 1H, P*H*), 7.4–7.7 (m, 5H, *Ar*); ^{31}P-NMR (161.90 MHz, $CDCl_3$, δ ppm): 31.00 (q, J = 91.65 Hz, 1P); ^{13}C-NMR (100.6 MHz, $CDCl_3$, δ ppm): 26.41 (d, J = 2.82 Hz, PC(CH_3)$_3$), 28.33 (d, J = 32.69 Hz, PC(CH_3)$_3$), 124.51–133.92 (m, *Ar*). Anal. Calc. for $C_{10}H_{18}BP$ (180): C, 66.71; H, 10.08. Found: C, 66.67; H, 9.97%.

2.3. Synthesis of *R,R*-{C_6H_4-2,6-(CH_2P*$PhBu^tBH_3$)$_2$} (*2*)

A Schlenk flask equipped with a magnetic stirring bar was charged with ether (100 ml), (−)-sparteine [13] (5.0 ml, 21.67 mmol), and *tert*-butylphenylphosphine-borane (**1**) (3.0 g, 16.67 mmol). The solution was cooled to −78 °C and *n*-butyllithium (10.42 ml, 1.6 M in C_6H_{14}) was added. The solution was allowed to warm to r.t., whereupon a thick suspension of white precipitate was formed. After the reaction mixture had stirred for 1 h at r.t., it was again cooled to −78 °C and α,α-1,3-dibromoxylene (2.2 g, 8.33 mmol) was added as a solution in THF (15 ml). The solution was allowed to slowly warm to r.t. (overnight, ca. 20 h). The reaction mixture was washed with 5% aq. H_2SO_4 (35 ml) and the aq. phase was extracted with ether of CH_2Cl_2 (3 × 15 ml). The combined organic phases were washed with water (15 ml), brine (15 ml), dried ($MgSO_4$) and filtered through a short plug of celite. The solution was concentrated under vacuum to yield a white solid. Yield: 3.66 g, 95%. $[\alpha]_D^{25}$ = +115.4° (*c* = 1.0, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 0.1–1.0 (q, br, 6H, PBH_3), 1.11 (d, J = 13.5 Hz, 18H, PC(CH_3)$_3$), 3.24–3.44 (m, 4H, PCH_2Ar), 6.90–7.90 (m, 14H, *Ar*); ^{31}P-NMR (161.90 MHz, $CDCl_3$, δ ppm): 33.28 (d, J = 55.47 Hz, 2P); ^{13}C-NMR (100.6 MHz, $CDCl_3$, δ ppm): 25.67 (s,

PC(CH_3)$_3$), 26.85 (d, $J = 29.68$ Hz, PCH_2Ar, δ ppm): 29.88 (d, $J = 29.68$ Hz, PC(CH$_3$)$_3$), 126.00–134.00 (m, *Ar*). Anal. Calc. for $C_{28}H_{42}B_2P_2$ (462.2): C, 72.76; H, 9.16. Found: C, 72.66; H, 9.19%.

2.4. Synthesis of *R,R*-{(C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$} (**3**)

A Schlenk flask equipped with a magnetic stirring bar was charged with **2** (1.0 g, 2.16 mmol) and CH_2Cl_2 (20 ml). The solution was cooled to −5 °C and tetrafluoroboric acid diethyl ether complex (3.75 ml, 21.63 mmol) was added dropwise by syringe. The solution was allowed to slowly warm to r.t. (overnight, ca. 20 h). The reaction mixture is then diluted with Et_2O (40 ml) and added to a degassed, saturated aq. solution of $NaHCO_3$ (110 ml). The resulting biphasic mixture was stirred vigorously under Ar for 10 min, after this time the organic layer was separated and the aq. phase extracted with ether (2 × 20 ml). The combined organic phases were washed with water (2 × 20 ml), brine (20 ml), dried ($MgSO_4$) and filtered through a short plug of celite. The solution was concentrated under vacuum to yield a viscous colorless oil. Yield: 921 mg, 98%. $[\alpha]_D^{25} = +196.0°$ ($c = 1.0$, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 0.91 (d, $J = 11.6$ Hz, 18H, PC(CH_3)$_3$), 2.92 (dd, $J = 14$, 2 Hz, 2H, PCH(H)Ar), 3.07 (dd, $J = 14$, 2.8 Hz, 2H, PCH(H)Ar), 6.91–7.52 (m, 14H, *Ar*); ^{31}P-NMR (161.90 MHz, $CDCl_3$, δ ppm): 9.44 (s, 2P); ^{13}C-NMR (100.6 MHz, $CDCl_3$, δ ppm): 27.58 (d, $J = 13.38$ Hz, PC(CH_3)$_3$), 29.11 (d, $J = 20.12$ Hz, PCH_2Ar), 29.46 (d, $J = 15.39$ Hz, PC(CH$_3$)$_3$), 127.00–139.40 (m, *Ar*). Anal. Calc. for $C_{28}H_{36}P_2$ (434.5): C, 77.39; H, 8.35. Found: C, 77.32; H, 8.29%.

2.5. Synthesis of *R,R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**4**)

To a $C_6H_5CH_3$ solution of the ligand *R,R*-[C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$] (**3**) (0.5 g, 1.15 mmol) was added under stirring a suspension of [$PdCl_2$(COD)] (0.33 mg, 1.15 mmol) in $C_6H_5CH_3$ (50 ml). The resulting mixture was set to reflux for 5 h, after this period the solvent was evaporated under vacuum to yield the title complex as white powder in good yield (650 mg, 98%). $[\alpha]_D^{25} = -96.44°$ ($c = 1.0$, CH_2Cl_2); ^{1}H-NMR (400.00 MHz, $CDCl_3$, δ ppm): 1.24 (vt, $J = 7.6$ Hz, 18H, PC(CH_3)$_3$), 3.27 (m, 4H, PCH_2Ar), 6.90–8.24 (m, 13H, arom.); ^{31}P-NMR (161.90 MHz, $CDCl_3$, δ ppm): 52.27 (s, 2P); ^{13}C-NMR (100.6 MHz, $CDCl_3$, δ ppm): 26.72 (s, PC(CH_3)$_3$), 32.96 (vt, $J = 11.32$ Hz, PCH_2Ar), 35.43 (vt, $J = 12.12$ Hz, PC(CH$_3$)$_3$), 124.60–160.00 (m, *Ar*). Anal. Calc. for $C_{28}H_{35}ClP_2Pd$ (575.4): C, 58.45; H, 6.13. Found: C, 58.42; H, 6.09%.

2.6. Synthesis of *R,R*-IrHCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**5**)

A mixture of [Ir(COE)$_2$(μ-Cl)]$_2$ (0.575 g, 0.575 mmol), *R,R*-[C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$] (**3**) (0.5 g, 1.15 mmol) and $C_6H_5CH_3$ (50 ml), was heated under reflux for 24 h. After this time the solvent is evaporated under vacuum and the solid residue taken off in C_5H_{12} (4 × 50 ml), the solution filtered through a short plug of celite and the solvent removed under vacuum to yield a microcrystalline dark-brown powder. Yield: 632 mg, 83%. $[\alpha]_D^{25} = +78.0°$ (C_6H_6, 1 M); ^{1}H-NMR (400.00 MHz, C_6D_6, δ ppm): −25.4 (t, $J = 11.2$ Hz, 1H, *Ir–H*), 1.15 (vt, $J = 6.4$ Hz, 18H, C(CH_3)$_3$), 3.57 (m, 4H, PCH_2Ar), 6.9–7.7 (m, 13H, *Ar*); ^{31}P-NMR (161.90 MHz, $CDCl_3$, δ ppm): 45.77 (s, 2P); ^{13}C-NMR (100.6 MHz, $CDCl_3$, δ ppm): 24.67 (s, PC(CH_3)$_3$), 32.90 (vt, $J = 11.21$ Hz, PCH_2Ar), 35.29 (vt, $J = 12.02$ Hz, PC(CH$_3$)$_3$), 121.7–152.6 (m, *Ar*). Anal. Calc. for $C_{28}H_{36}ClIrP_2$ (662.2): C, 50.78; H, 5.48. Found: C, 50.74; H, 5.46%.

2.7. Synthesis of *R,R*-IrH_4\{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**6**)

The title complex was synthesized using the method reported by Jensen and coworkers [3] by reacting the hydrochloride complex **5** (0.6 g, 0.906 mmol) with superhydride [$LiB(C_2H_5)_3H$] (0.91 ml, 1 M solution in THF) under a hydrogen atmosphere in C_5H_{12} (100 ml). Filtration through a short plug of celite and evaporation of the solvent under vacuum affords complex **6** as pale-orange powder. Yield: 0.548 g, 96%. $[\alpha]_D^{25} = -132.31°$ (C_6H_6, 1 M); ^{1}H-NMR (400.00 MHz, C_6D_6, δ ppm): −8.27 (t, $J = 10$, 4 Hz, 4H, *Ir–H*), 1.10–1.50 (vt, $J = 7.2$ Hz, 18H, C(CH_3)$_3$), 3.67 (dt, $J = 16.4$, 4.4 Hz, 2H, PCH(H)Ar), 3.87 (dt, $J = 16.8$, 3.8 Hz, 2H, PCH(H)Ar), 6.86–7.78 (m, 13H, *Ar*); ^{31}P-NMR (161.90 MHz, $CDCl_3$, δ ppm): 50.09 (s, 2P); ^{13}C-NMR (100.6 MHz, $CDCl_3$, δ ppm): 26.72 (s, PC(CH_3)$_3$), 32.96 (vt, $J = 11.32$ Hz, PCH_2Ar), 35.43 (vt, $J = 12.12$ Hz, PC(CH$_3$)$_3$), 127.00–160.00 (m, *Ar*). Anal. Calc. for $C_{28}H_{39}IrP_2$ (629.8): C, 53.4; H, 6.24. Found: C, 53.37; H, 6.24%.

2.8. General procedure for the hydrosilylation of styrene

Complex **4** (3 mg, 5.2×10^{-3} mmol) and styrene (1 ml, 8.7 mmol) were mixed in 4 ml of C_6H_6. The addition of trichlorosilane (1.1 ml, 10.9 mmol) started the reaction. The mixture was stirred for 24 h. The crude product was carefully poured into a suspension of KF (10 g, 0.17 mol) in 80 ml of MeOH, and stirred for 30 min. The solvent was removed in vacuo. The resulting solid was suspended in 100 ml of DMF, H_2O_2 (30% water solution, 10 ml) was added and the mixture heated for 1 h at 60–70 °C. The residue was isolated by aq.

workup and extraction and analyzed by GC–MS and HPLC. Yield: 97% of $PhCH(OH)CH_3$.

2.9. General procedure for the allylic alkylation

To a solution of complex **4** (3 mg, 5.2×10^{-3} mmol) in CH_2Cl_2 (2 ml) silver triflate (2 mg, 7.7×10^{-3}) was added, the solution was stirred for 30 min. After this time the solution was filtered through a short plug of celite. Then (*E*)-3-acetoxi-1,3-diphenyl-1-propene (50.4 mg, 0.2 mmol), dimethylmalonate (68 μl, 0.6 mmol), BSA (148 μl, 0.6 mmol), and KOAc (1 mg) were added, and the resulting reaction mixture stirred at r.t. for 4 h. After this time the resulting reaction mixture was diluted with ether, washed with water and brine, and then dried over $MgSO_4$. The solvent was evaporated under vacuum to yield an oily residue, which slowly crystallizes. Yield: 100% of *rac*-$PhCH\{CH(CO_2Me)_2\}CH{=}CHPh$.

2.10. General procedure for the Heck reaction

To a solution of **4** (3 mg, 5.2×10^{-3} mmol) in C_6H_6 (3 ml) silver triflate (2 mg, 7.7×10^{-3}) was added, the solution was stirred for 30 min. After this time the solution was filtered through a short plug of celite. Then phenyl triflate (81 μl, 0.5 mmol), *N*,*N*-diisopropylethylamine (261 μl, 1.5 mmol), and 2,3-dihydrofuran (189 μl, 2.5 mmol) were added. The solution was stirred at 60 °C for 4 days under Ar. The reaction mixture was cooled, diluted with C_5H_{12} (200 ml) and filtered to remove solid materials. The solution was then washed with 0.1 N HCl and saturated with $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed under vacuum and the residue analyzed by GC–MS and HPLC. Yield: 100% of 2-phenyl-3,4-dihydrofuran.

2.11. General procedure for the catalytic dehydrogenation experiments [3a,3b,3c,3d,3e,3f]

A solution of cyclooctane (4.0 ml, 37.0 mmol) and the (*tert*-butylethylene) (2.0 ml, 1.6 mmol) were charged with **6** (5 mg, 0.008 mmol) in a sealed tube under Ar, the tube was fully immersed in an oil-bath for 2 h at 150 °C. The production of cyclooctene was quantified by GC.

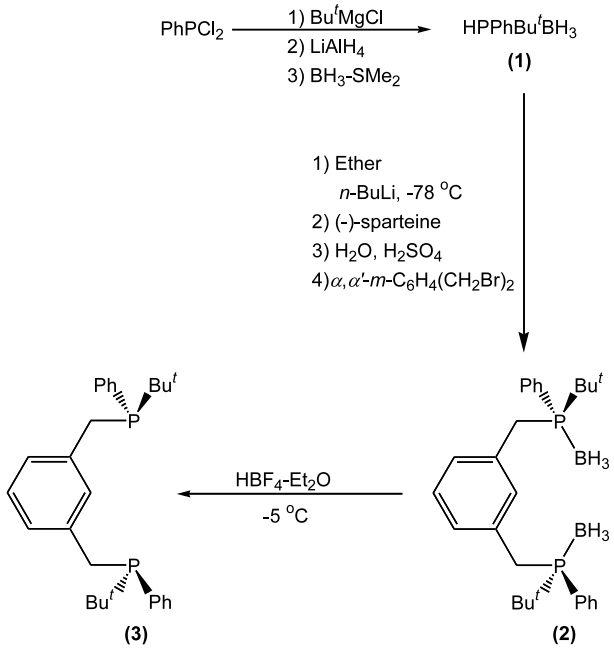
2.12. Single crystal X-ray structure determination *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**4**)

A crystalline colorless prism of *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$}, grown from a CH_2Cl_2–MeOH solvent system was glued to a glass fiber. A Siemens P3 diffractometer was used for unit cell measurements and for data collection using Mo–K_α radiation. Three check reflections, monitored every 100 reflections, showed no significant decay. The data were processed using the SHELXTL [14] program package, and an absorption correction was applied based upon ψ-scans of six reflections. Transmission coefficients ranged from 0.85 to 0.94. The diffractometer auto indexing routine indicated a hexagonal unit cell. The only systematic absence was OOOL, $L = 2n+1$. Since the crystal was known to be chiral, the space group was uniquely determined to be $P6_3$. Using SHELX-97, both Patterson and direct methods yielded the position of the Pd atom. The remaining atoms were located via a few cycles of least-square refinements and difference Fourier maps. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Three group thermal parameters were refined for hydrogen atoms, one each for phenyl, methylene and methyl protons. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [15] and anisotropic thermal parameters for all non-hydrogen atoms. The absolute configuration was determined via the Flack parameter [16], which refined to −0.03(6). The absolute configuration at the two P atoms is *R*,*R*.

3. Results and discussion

3.1. Synthesis of the ligand

The ligand *R*,*R*-{C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$} (**3**) has been synthesized in two easy steps according to Scheme 1. In the first step, phenyl *tert*-butylphenylphosphine-borane (**1**) is reacted with *n*-butyl lithium in the presence of (−)-sparteine to afford the lithium salt of the phosphine. This compound is further reacted at −78 °C with α,α-1,3-dibromoxylene to afford the borane

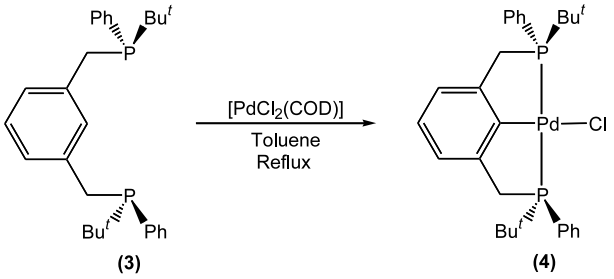


Scheme 1.

complex *R*,*R*-{C_6H_4-2,6-(CH_2P*$PhBu^tBH_3$)$_2$} (**2**) in good yield (95%). The bisborane intermediate **2** was isolated as a white powder, this compound is air stable allowing the purification to be carried out easily in aerobic conditions. The ^{1}H-NMR spectra of **2** exhibits the signals corresponding to the phenyl, *tert*-butyl and methylene groups in the ligand, in addition a set (quartet) of broad signals at 0.9 ppm corresponding to the presence of the borane protecting group is observed. The ^{31}P-NMR shows a single absorption at 33.28 ppm as a broad doublet, the broadness and multiplicity of both the quartet at high field in the ^{1}H and the doublet in the ^{31}P-NMR are due to quadrupolar effects and spin value ($s = 3/2$) of boron [17]. In the second step, deprotection of the pincer-borane compound **2** with $HBF_4 \cdot Et_2O$ [18] in dichloromethane affords the free ligand *R*,*R*-{C_6H_4-2,6-(CH_2P*$PhBu^t$)$_2$} (**3**) in pure enantiomeric form as colorless oil in almost quantitative yield (98%). The ^{1}H-NMR spectra of this compound is similar to that of the borane complex **2**, signals corresponding to the phenyl, *tert*-butyl and methylene groups were observed, absence of the broad quartet at high field accounts for complete deprotection of the borane adduct.

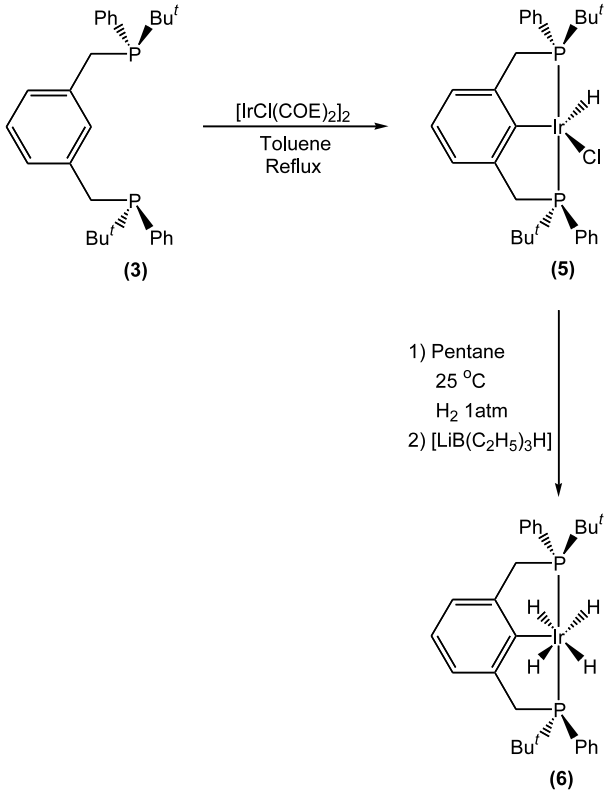
3.2. Synthesis of *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$}, *R*,*R*-IrHCl{C_6H_3-2,6(CH_2PPhBu^t)$_2$} and *R*,*R*-IrH_4{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$}

The palladium complex *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**4**) was synthesized (Scheme 2) by refluxing stoichiometric amounts of ligand *R*,*R*-{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**3**) and [$PdCl_2$(COD)] in toluene for 5 h. Evaporation of the solvent under vacuum affords compound **4** as a white powder in good yield (98%). Complex **4** is air and moisture stable, convenient characteristics that make this complex an excellent candidate for its screening in asymmetric catalysis. Compound **4** was characterized by multinuclear NMR. The ^{31}P-NMR of this complex exhibits a single absorption (δ 52.27 ppm) as expected for equivalent phosphorus nuclei.



Scheme 2.

Reaction of [Ir(μ-Cl)(COE)$_2$]$_2$ with two equivalents of the PCP pincer ligand **3** under reflux in toluene for 24 h yields the hydrochloride–iridium complex *R*,*R*-IrHCl{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**5**) as a deep red powder in good yield. The complex was characterized by multinuclear NMR. The ^{1}H-NMR spectra shows absorptions corresponding to the phenyl, *tert*-butyl and methylene groups in the molecule, additionally a triplet at high field due to the presence of the hydride is observed. The multiplicity is attributed to the coupling of the hydride with the two equivalent phosphorus nuclei. The ^{31}P-NMR shows a single sharp signal at 45.76 ppm accounting for equivalent mutually *trans* phosphorus centers. Treatment of a solution (pentane) of the hydrochloride complex **5** with an excess of superhydride [$LiB(C_2H_5)_3H$] in a hydrogen atmosphere (1 atm) at r.t. affords the tetrahydride complex *R*,*R*-IrH_4{C_6H_3-2,6-(CH_2P*$PhBu^t$)$_2$} (**6**) as light orange powder (Scheme 3). Characteristic signals for the hydrocarbon backbone and phosphorus substituents are observed in the ^{1}H-NMR spectra, the presence of hydrides was inferred by a triplet at −8.27 ppm with the proper integration. A single sharp signal was observed in the ^{31}P-NMR spectrum (50.09 ppm) which is in agreement with equivalent phosphorus nuclei.



Scheme 3.

3.3. Catalysis

For completeness, we have used **4** as a catalyst in the hydrosilylation of styrene, allylic alkylation (with $CH(CO_2Me)_2^-$ as nucleophile to afford $PhCH\{CH(CO_2Me)_2\}CH{=}CHPh$) and Heck coupling reactions with phenyl triflate and 2,3-dihydrofuran. However, neither of these reactions gave substantial ee's (6.5, 4.3 and 3.0%, respectively). This might be due to the similarity in size of both substituents at the phosphorus centers. Current efforts are focus in the synthesis of new series of PCP *P**-homochiral ligands in order to prove this theory.

As expected complex **6** is an efficient catalyst for the transfer dehydrogenation of cyclooctane to cyclooctene in the presence of *tert*-butylethylene at 200 °C, with turnover numbers similar to those observed for $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}$ [3a,3b,3c,3d,3e,3f].

Table 1
Crystal data and structure refinement for *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*PhBu^t)$_2$} (**4**)

Empirical formula	$C_{28}H_{35}ClP_2Pd$
Formula weight	575.35
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P6_3$
Unit cell dimensions	
a (Å)	20.575(12)
b (Å)	20.575(12)
c (Å)	11.709(7)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	4293(4)
Z	6
D_{calc} (g cm^{-3})	1.335
Absorption coefficient (mm^{-1})	0.867
F(000)	1776
Crystal size (mm)	0.15 × 0.15 × 0.50
θ range for data collection (°)	1.98–20.02
Index ranges	$-17 \le h \le 17$, $-17 \le k \le 17$, $-11 \le l \le 11$
Reflections collected	5951
Independent reflections	2684 [$R_{int} = 0.1235$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2536/3/297
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0499$, $wR_2 = 0.0807$ [b]
R indices (all data)	$R_1 = 0.0938$, $wR_2 = 0.0938$ [b]
Absolute structure parameter	−0.03(6)
Goodness-of-fit on F^2	0.927 [a]
Largest difference peak and hole (e Å^{-3})	0.701 and −0.528

[a] $S = [w(F_o)^2 - (F_c)^2)^2/(n-p)]^{1/2}$, where n, number of reflections and p, total number of parameters.
[b] $R_1 = |F_o - F_c|/|F_o|$, $wR_2 = [w((F_o)^2 - (F_c)^2)^2/w(F_o)^2]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for *R*,*R*-PdCl{C_6H_3-2,6(CH_2P*PhBu^t)$_2$} (**4**)

Bond distances	
Pd–C(1)	2.020(14)
Pd–P(1)	2.299(4)
Pd–P(2)	2.302(4)
Pd–Cl	2.385(4)
Bond angles	
C(1)–Pd–P(1)	82.2(4)
C(1)–Pd–P(2)	82.1(4)
P(1)–Pd–P(2)	163.60(13)
C(1)–Pd–Cl	178.7(4)
P(1)–Pd–Cl	96.50(14)
P(2)–Pd–Cl	99.28(13)

3.4. X-ray crystal structure of *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*PhBu^t)$_2$} (**4**)

Crystals suitable for X-ray structure analysis were obtained form a CH_2Cl_2–MeOH double layer solvent system as colorless prisms. The details of the structure determination are given in Table 1 and selected bond lengths and angles are listed in Table 2. A thermal ellipsoid drawing of **4** with atomic number scheme of the obtained structure is presented in Fig. 1. The palladium center is found in a distorted square planar geometry with angles of 163.60 and 178.7° for P(1)–Pd–P(2) and C(1)–Pd–Cl, respectively. Two chelated five-membered rings formed by Pd–P(2)–C(8)–C(6)–C(1) and Pd–P(1)–C(7)–C(2)–C(1) are present in the complex. These rings are quite strained due to constrains imposed by the atoms forming the two adjacent five-membered chelated rings. Part of this strain is released by formation of unequal P(1)–Pd–Cl (96.5°) and P(2)–Pd–Cl (99.28°) angles. In addition the methylene groups on C(7) and

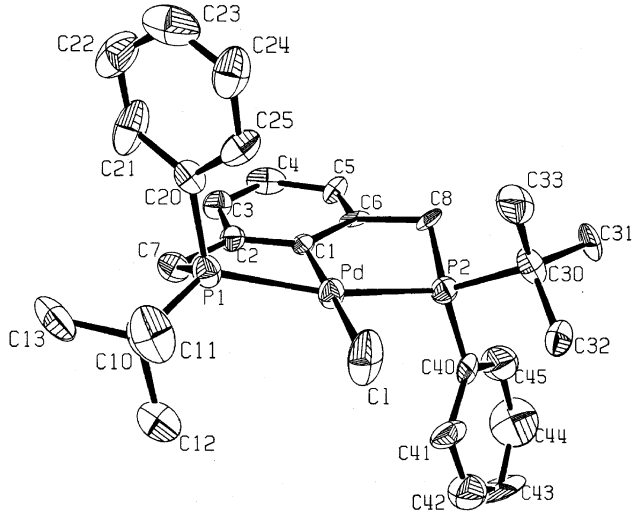


Fig. 1. Thermal ellipsoid (50% probability) drawing of *R*,*R*-PdCl{C_6H_3-2,6-(CH_2P*PhBu^t)$_2$} (**4**). Hydrogen atoms have been omitted for clarity.

C(8) located in the axial position of the puckered five-membered chelated rings result in a C_2-symmetry metal complex with the phenyl groups and *tert*-butyl groups on the phosphines being in pseudoaxial and -equatorial positions, respectively. Furthermore, while the pseudoaxial substituent on one side of the molecule is above the coordination plane, the corresponding substituent on the other side is below the coordination plane. This imposed asymmetric environment is expected to lead to high enantioselectivity in asymmetric catalysis. The absolute configuration of both stereocenters is determined to be *R* (based on refinement of the Flack parameter). In other respects, bond lengths and angles are similar to those observed in other PCP-complexes [3b,3h,4a].

4. Conclusions

Although the present system did not achieved the goal of being able to provide high enantioselective yields in the catalytic reactions studied, we believe that by careful tuning of both the steric and electronic properties of the R groups in the phosphorus donor centers we will have better possibilities to provide not only an efficient catalytic system but also a better understanding of the factors that govern the reactivity of these ligands.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 177277 for complex **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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