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New chiral diphosphites derived from substituted 9,10-dihydroanthracene. Applications in asymmetric catalytic processes

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ABSTRACT

Two novel diphosphite ligands derived from 9,10-dihydroanthracene originating from a 1,3-diol chiral fragment, have been prepared in high yields from readily available starting materials. Rhodium and palladium catalytic systems containing these new P-donor ligands led to 51% and 90% ee in asymmetric hydroformylation and allylic alkylation processes, respectively.

1. Introduction

The preparation of new chiral ligands suitable for a wide range of metal-catalyzed reactions, is one of the major challenges in asymmetric catalysis.[1] During the last decade considerable attention has been devoted to phosphites as appropriate ligands for catalytic purposes. One of the major advantages of phosphites is their feasible synthesis and higher stability than phosphines, especially under aerobic conditions. Phosphites are less electron rich than phosphines, providing high activity in several catalytic reactions.[2,3] In 1992, Babin and Whiteker at Union Carbide developed an outstanding C_2-symmetrical diphosphite derived from (2*R*,4*R*)-pentanediol, (*R*,*R*)-Chiraphite, leading to excellent enantioselectivities (up to 90% ee) in the hydroformylation of styrene.[4] Later, van Leeuwen et al. reported the synthesis of diphosphite ligands derived from Chiraphite and also derived from carbohydrates, such as 1,2-*O*-isopropyliden-α-D-xylofuranose derivatives **I** (Fig. 1).[5] In styrene asymmetric hydroformylation, the catalytic system Rh/**I** provides excellent regioselectivity for the branched aldehyde with an enantioselectivity up to 53% (*S*).[5d] We have also reported the synthesis of diphosphites derived from 1,2-*O*-isopropyliden-α-D-ribofuranose (**II**, Fig. 1) and 6-deoxy-1,2-*O*-isopropyliden-α-D-glucofuranose (**III** and **IV**, Fig. 1).[6a,b] The use of the catalytic system Rh/**II** in the enantioselective hydroformylation of styrene gives mainly the branched aldehyde with an ee up to 53% (*R*).[6a] The asymmetric induction could be improved with ligands **III** and **IV** adding a new stereocentre in the 1,3-diol moiety, leading to 93% (*S*) and 89% (*R*) for the branched regioisomer, respectively.[6b,c] In relation to the Pd-allylic substitution, the 1,3-diphosphite ligands **I** and **II** have also been successfully applied in alkylation and amination reactions. In particular, the diphosphite ligands **I** and **II** give ee's of up to 90% and 95%, respectively, for the Pd-allylic alkylation of *rac*-1,3-diphenyl-acetoxypropen-1-ene.[7] Most recently, we have found an outstanding Pd-C_2-symmetrical 1,2-diphosphite system **V** reaching the highest activity reported for allylic alkylation (22,000 h^{-1}) and allylic amination (400 h^{-1}) together with excellent enantioselectivities (ee >98%).[8a] However, this C_2-symmetric ligand gives moderate enantiomeric excess in the Rh-catalyzed hydroformylation of styrene (ee = 41(*S*)).[8b]

Recently, Lemaire and co-workers have reported the synthesis of the 1,3-diphosphites derived from (*S*,*R*)-1,3-butanediol, containing only one stereocentre in the 1,3-diol backbone **VI** (Fig. 1).[9] These diphosphites give high regioselectivities (up to 99%) in the Rh-asymmetric hydroformylation of styrene, but give low to moderate enantioselectivities [up to 45% (*S*)].

In order to obtain information about the plausible cooperative effect between neighbouring carbon stereocentres in the three-sp^3 carbon spaced diol fragment compared with the reported systems (Chiraphite and **VI**, Fig. 2), we planned the synthesis of new 1,3-diphosphites derived from diols containing an N-heterocycle bonded to a 9,10-dihydroanthracene backbone. In our case, only one phosphite moiety is directly bonded to a stereogenic carbon, but an additional stereogenic carbon in the 3-carbon spaced backbone between the two phosphite groups is present, bonded to a bulky N-amide or -amine fragment.

Herein we report the synthesis of chiral diphosphite ligands **3** and **4** (Scheme 1) coming from the corresponding diol derivatives containing the 9,10-dihydroanthracene backbone (**1** and **2**, Scheme 1) and their coordination chemistry with palladium and rhodium precursors. These Pd and Rh catalytic systems have been tested in the enantioselective allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene and the hydroformylation of styrene.

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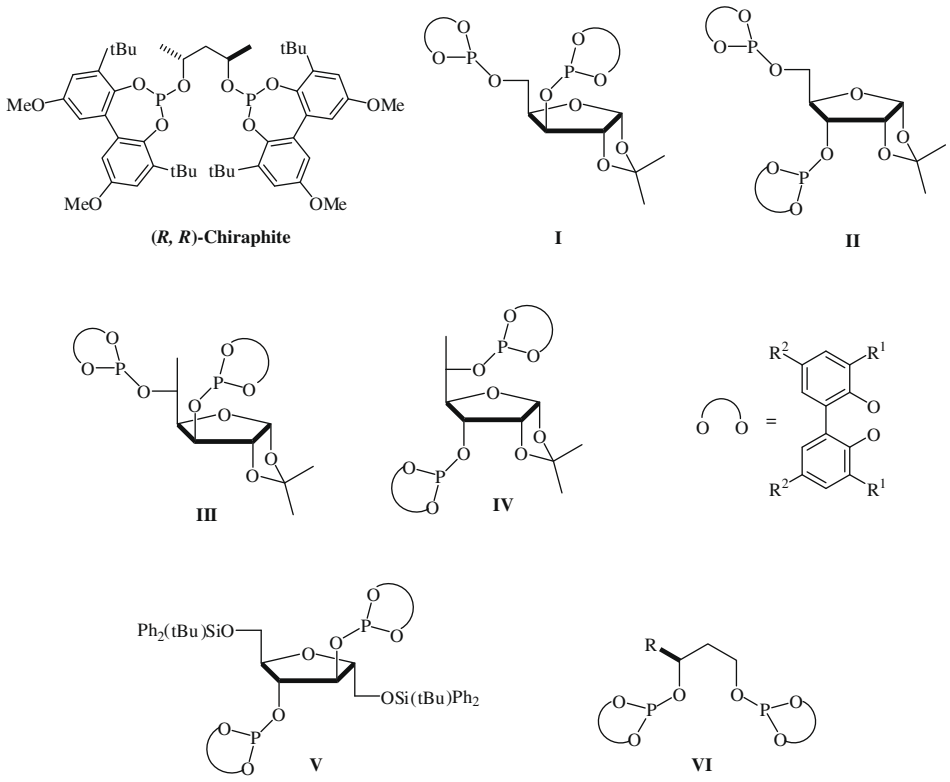


Figure 1. Chiral diphosphite ligands (Chiraphite and **I–VI**) originating from diol fragments.

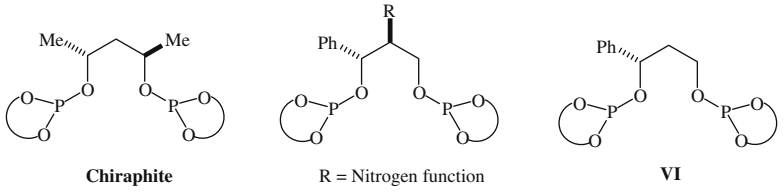
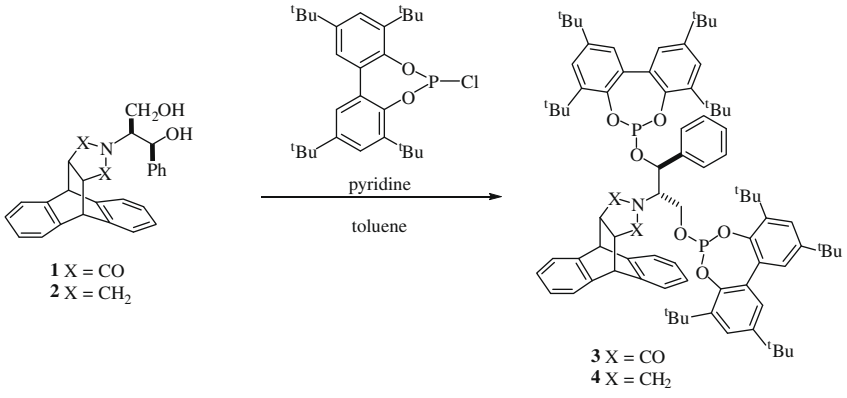


Figure 2. Design of new 1,3-diphosphite ligands.

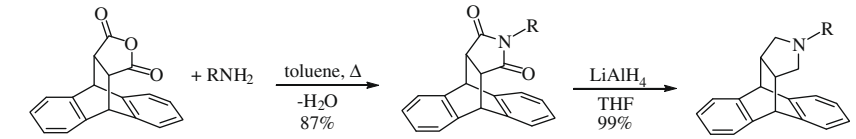


Scheme 1. Synthesis of **3** and **4** chiral diphosphites.

2. Results and discussion

Diphosphites **3** and **4** were synthesized from imide **1** and amine **2** diol precursors, respectively (Scheme 1). These diols were treated with the corresponding phosphorochloridite (prepared in situ by standard procedures)[10] to give the C_1-symmetry diphosphites **3** and **4** in good yields (80–86%).

Imide **1** was prepared by condensation of 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride with the primary amine, (2*S*,3*S*)-2-amino-1-phenyl-1,3-propandiol, in toluene at reflux (Scheme 2),[11] based on the methodology described in the literature.[12] The corresponding amine **2** was obtained by reduction of imide **1** using $LiAlH_4$ as reagent (Scheme 2).[13] The structure of **1** was determined by single-crystal X-ray diffraction at 160 K (Fig. 3).



Scheme 2. Synthesis of imide **1** and amine **2**.

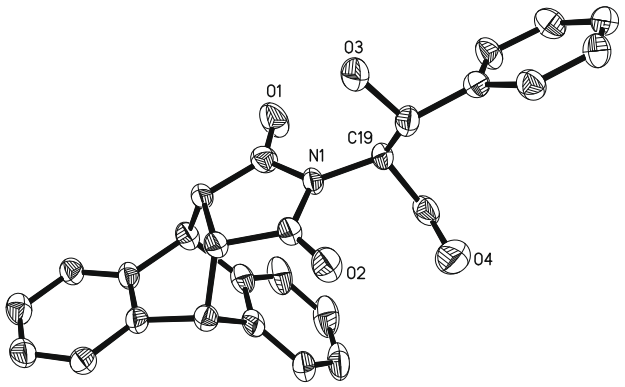
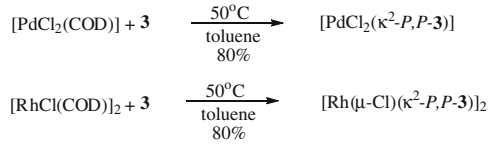


Figure 3. Molecular view in the solid state of imide **1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

A coordination chemistry study has been carried out with diphosphite **3**, using $[PdCl_2(COD)]$ and $[Rh(\mu\text{-}Cl)(COD)]_2$ as metallic precursors (Scheme 3).



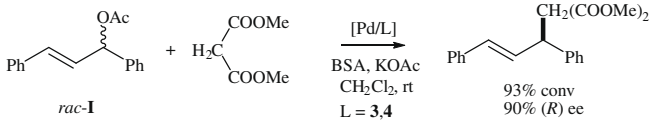
Scheme 3. Synthesis of Pd and Rh complexes containing ligand **3**.

Reaction of $[PdCl_2(COD)]$ with 1 equiv of **3** in toluene proceeds cleanly to give $[PdCl_2(\kappa^2\text{-}P,P\text{-}\mathbf{3})]$ in 80% yield (Scheme 3). This complex was fully characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopies. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ 101.01 and 98.97 ($^1J_{P-P}$ = 67 Hz), proving the bidentate coordination of the ligand to the palladium centre to form an eight-membered metallacycle. Concerning the ^1H and ^{13}C spectra, the signals corresponding to the atoms located in the 3-carbon spaced bridge between the two P atoms are the most shifted in relation to the free ligand. The methylene protons are observed as two doublet of doublets at 5.12 and 2.46 ppm (3.30 and 3.20 ppm for **3**) and the carbon at 62.0 ppm (59.6 ppm for **3**). The proton of the stereocentre C*H–O appears as a doublet of doublet at δ 5.65 (5.33 ppm for **3**) and that of the C*H–N at δ 4.27 (4.58 ppm for **3**) The ^{13}C chemical shifts for C*H–O and C*H–N appear at δ 77.8 and 52.0, respectively (71.6 and 57.6 ppm, respectively, for **3**).

The rhodium complex containing **3** was isolated by addition of 2 equiv of **3** to $[Rh(\mu\text{-}Cl)(COD)]_2$ in toluene, leading to the dimer $[Rh(\mu\text{-}Cl)(\kappa^2\text{-}P,P\text{-}\mathbf{3})]_2$ in 80% isolated yield (Scheme 3). Relevant spectroscopic data for this complex follow. The $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets of triplets at δ 132.5 and δ 134.5, due to the coupling constant between each phosphorus with the rhodium atom ($^1J_{P-Rh}$ = 320 Hz) and the coupling constant between inequivalent phosphorus atoms ($^2J_{P-P} + {}^4J_{P-P}$ = 43 Hz), showing a bidentate coordination of the diphosphite to the rhodium atom. This AA′XX′ spin system is also found in the complex $[IrCl(\kappa^2\text{-}P,P\text{-}L)]_2$ (L = diphosphines) where the $^2J_{P-P} + {}^4J_{P-P}$ is 38 Hz.[14] In the $^{103}Rh\{^{31}P\}$ NMR spectrum, only one signal at δ −7968 is observed indicating that the two rhodium atoms are equivalent.

2.1. Pd-catalyzed asymmetric allylic alkylation

The alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-**I**) with dimethyl malonate under basic conditions was evaluated using in situ catalyst generation by reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and L (L = **3**, **4**) (Scheme 4). These catalytic systems led to the expected alkylated product with a conversion of 93% after 15 min at room temperature and an enantiomeric excess of 90% (*R*). No different catalytic behaviour was observed between these two diphosphite ligands containing imide or amine group in the anthracene backbone, **3** and **4**, respectively. These results prove the P,P-bidentated coordination without influence of the nitrogen (imide or amine) on the metal centre. Palladium catalytic systems containing diols **1** and **2** were inactive.



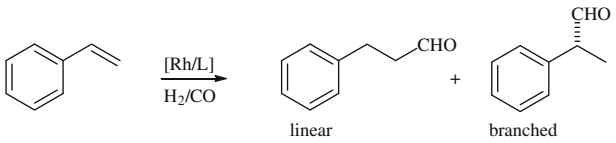
Scheme 4. Pd-catalyzed asymmetric allylic alkylation of *rac*-**I** using the chiral diphosphites **3** and **4**.

2.2. Rh-catalyzed asymmetric hydroformylation of styrene

Catalytic systems containing the chiral diphosphites **3** and **4** were also used in the rhodium-catalyzed asymmetric hydroformylation of styrene (Scheme 5).

The catalytic systems were formed in situ by addition of 1.1 equiv of the corresponding diphosphite to a toluene solution of $[Rh(acac)(CO)_2]$ (acac = acetylacetonate); the substrate was then added. The catalytic solution was introduced into the autoclave and pressurized under 25 bar of a CO/H_2 mixture (ratio 1:1) and heated at 40 °C during 15 h. The results are collected in Table 1.

Total chemoselectivity for the aldehydes formation was achieved for both catalytic systems. When the reaction was performed in the presence of ligand **3**, the conversion was 45% with a regioselectivity towards the branched product of 97% and an ee of 35% (entry 2). This moderate enantioselectivity is in the range of that generally found in the literature using 1,3-diphosphites ligands with only one phosphite function directly bonded to a stereogenic carbon.[9] When ligand **4** was employed, the enantioselectivity is clearly improved (ee = 51% (*R*)) although the conversion was lower than that observed for **3** (14%, entry 3), maintaining a high regioselectivity towards the branched product (97%). This moderate enantioselectivity is in the range of that generally found for 1,3-diphosphite ligands derived from 1,2-*O*-isopropyliden-α-D-xylofuranose.[5] The backbone hydroanthracene with an imide or amine function (**3** or **4**, respectively) could play a role in the



Scheme 5. Rh-catalyzed asymmetric hydroformylation of styrene using the chiral diphosphites **3** and **4**.

Table 1
Rh-catalyzed hydroformylation of styrene using ligands **3** and **4**[a]

Entry	L	T (°C)	% Conv.[b]	% Regioselectivity[c]	% ee[b]
1	—	80	99	53	—
2	**3**	40	45	97	35 (*R*)
3	**4**	40	14	97	51 (*R*)

[a] Substrate/Rh = 1000, styrene 1.3 mmol, Rh/L = 1/1.1, [Rh(acac)(CO)$_2$] = 0.0135 mmol, P = 25 bar, PCO/H$_2$ = 1, t = 15 h, 15 mL of toluene.
[b] % Conversion of styrene and ee determined by GC.
[c] % 2-Phenylpropanal.

asymmetric induction. The coordination of the nitrogen to the rhodium centre is certainly favoured in the case of ligand **4** containing an amine group. When diols **1** and **2** were used instead of chiral diphosphites, low regioselectivity was achieved (53% towards the branched regioisomer) without asymmetric induction, analogously to the ligand-free catalytic system (entry 1), proving that the rhodium does not interact with the diols.[5b]

3. Conclusions

In summary, new chiral 1,3-diphosphite ligands derived from 9,10-dihydroanthracene backbone were synthesized, and their coordination chemistry was studied for rhodium and palladium complexes. These diphosphite ligands were tested in palladium-catalyzed asymmetric allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-propene and in rhodium-catalyzed asymmetric hydroformylation of styrene. The corresponding alkylated product was obtained in excellent conversion and enantioselectivity of up to 90% ee. The best asymmetric induction in enantioselective styrene hydroformylation was found with the chiral diphosphite **4,** giving an ee up to 51%; for both systems, high regioselectivity was obtained towards the branched aldehyde (up to 97%). These new diphosphite ligands provided comparable selectivities to those previously reported using the ligand derived from 1,2-*O*-isopropyliden-α-D-xylofuranose in the Pd-allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene and in Rh-asymmetric hydroformylation of styrene.

4. Experimental

4.1. General methods

All compounds were prepared under a purified nitrogen or argon atmosphere using standard Schlenk and vacuum-line techniques. The organic solvents were purified by standard procedures and distilled under nitrogen. NMR spectra for **1**, **2** and complexes were recorded on Bruker Avance 300 and 500 MHz (^{1}H, ^{13}C and ^{31}P, standard SiMe$_4$); For **3** and **4** NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to SiMe$_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard and the spectra are recorded at 298 K. All NMR spectral assignments were determined by COSY and HSQC spectra. IR spectra were recorded on a FTIR Perkin Elmer 1600 series. Elemental analyses for **1** and **2** and complexes were carried out in a Perkin Elmer 2400 series II microanalyzer; for **3** and **4**, elemental analyses were performed on a Carlo Erba EA-1108 instrument. The electro-spray (positive) analyses were performed in a LC TOF Waters instrument. Enantiomeric excesses for the allylic alkylation were determined by HPLC on a Hewlett-Packard 1050 Series chromatograph (Chiralcel-OD chiral column) with a UV detector. Hydroformylation reactions were carried out in a Berghof 100 mL stainless steel autoclave. Gas chromatographic analyses were run on a Hewlett-Packard HP 5890A instrument (split/splitless injector, J&W Scientific, HP-5, 25 m column, internal diameter 0.25 mm, film thickness 0.33 mm, carrier gas: 150 kPa He, F.I.D. detector) equipped with a Hewlett-Packard HP3396 series II integrator. Enantiomeric excesses of hydroformylation reaction were measured after oxidation of the aldehydes to the corresponding carboxylic acids on a Hewlett-Packard HP 5890A gas chromatograph (split/splitless injector, J&W Scientific, FS-Cyclodex β-I/P 50 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 100 kPa He, F.I.D. detector). Absolute configuration was determined by comparing retention times with enantiomerically pure (*S*)-(+)-2-phenylpropionic and (*R*)-(−)-2-phenylpropionic acids.

4.1.1. Crystal structure determination

The structure of compound **1** was determined. Data were collected at low temperature (173 K) on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods[15] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[16] CCDC 711400 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Selected data for imide **1**: $C_{27}H_{23}NO_4$, M = 425.46, monoclinic, space group $C2$, a = 30.802(3) Å, b = 9.0155(9) Å, c = 20.6238(19) Å, $\alpha = \gamma = 90°$, β = 131.5430(10)°, V = 4286.5(7) Å^3, Z = 8, crystal size 0.50 × 0.20 × 0.10 mm^3, 9525 reflections collected (4861 independent, R_{int} = 0.0594), 581 parameters, R_1 [$I > 2\sigma(I)$] = 0.0469, wR_2 [all data] = 0.1027, largest difference in peak and hole: 0.216 and −0.184 e Å^{-3}.

4.1.2. Allylic alkylation experiments

The catalytic precursor was generated in situ from [Pd(η^3-C_3H_5)Cl]$_2$ and the appropriate ligand (0.02 mmol of Pd and 0.025 mmol of chiral ligand) dissolved in 2 mL of CH_2Cl_2 for 30 min before adding the substrate. *rac*-3-Acetoxy-1,3-diphenyl-1-propene (252 mg, 1 mmol) dissolved in 2 mL of CH_2Cl_2 was added followed by dimethyl malonate (396 mg, 3 mmol), BSA (610 mg, 3 mmol) and a catalytic amount of KOAc. The mixture was stirred at room temperature and then this solution was diluted with diethylether, filtered over Celite and washed with saturated ammonium chloride solution (4 × 10 mL) and water (4 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered off and the solvent removed under reduced pressure.

4.1.3. Hydroformylation experiments

In a typical experiment, the autoclave was purged three times with CO. The solution was formed from [Rh(acac)(CO)$_2$] (0.013 mmol), diphosphite (0.015 mmol) and styrene (13 mmol) in toluene (15 mL). The autoclave was pressurized to the desired pressure of CO/H$_2$. After the desired reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography. The aldehydes obtained from the hydroformylation were oxidized to carboxylic acids to determine the enantiomeric excess.

4.2. Synthesis of ligands and complexes

4.2.1. Synthesis of compound 1

A solution of *9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride* (1.00 g, 3.6 mmol) and (*1S,3S*)-2-amino-1-phenyl-1,3-propandiol (1.21 g, 7.2 mmol) in toluene (120 mL) was refluxed for 12 h in the presence of molecular sieves 4 Å. The reaction mixture was monitored by TLC (hexane/ethyl acetate = 3/2), then cooled, filtered and the solvent removed under reduced pressure. The residue obtained was dissolved in dichloromethane (20 mL) and washed with ammonium chloride saturated aqueous solution (3 × 20 mL). The combined organic layers were dried on anhydrous Na_2SO_4, filtered and the solvent evaporated under vacuum leading to a white powder recrystallized in ethyl acetate. Yield: 87% (3.15 mmol, 1.34 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37–7.16 (m, 13H, *H*aromatic), 5.03 (d, 1H, *J* = 9 Hz, C*H*-Ph), 4.78 (dd, 2H, *H*C–CO, *J* = 3 Hz, *J* = 5 Hz), 4.19 (m, 1H, C*H*N), 3.16 (m, 2H, *H*C–CH–CO), 3.05 (m, 2H, CH_2).^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 179.4, 176.9 (2C, *C*=O), 141.1–138.9 (*C*aromatic), 129.1–124.3 (*C*Haromatic), 70.8 (*C*H-Ph), 59.8 (*C*H_2), 59.6 (*C*H–N), 46.8 (*C*H–CO), 46.1 (*C*H–CO), 45.5 (*C*H–CH–CO), 45.4 (*C*H–CH–CO). IR (KBr, ν cm^{-1}): 3512 (OH), 3026 (=C–H), 2961 (C–H), 1770 (C=O), 1702 (C=O), 1465–1458 (C=C), 535 (Pd–P). Mass spectrometry (ESI, *m/z*): 448.4 [M+Na], 426.4 [M+H]. Anal. Calcd for $C_{27}H_{23}NO_4$ (*M* = 425.48): C, 76.22; H, 5.45; N, 3.29. Found: C, 76.20; H, 5.24; N, 3.32. Melting point: 200 °C.

4.2.2. Synthesis of compound 2

To a solution of freshly distilled THF (10 mL), **1** was added (100 mg; 0.24 mmol) and stirred until total dissolution. The solution was cooled at 0 °C and $LiAlH_4$ (178 mg, 4.80 mmol) was slowly added, giving a white suspension. The mixture was heated at reflux for 24 h, then cooled at 0 °C. Diethylether, 10 mL, and a saturated aqueous solution of Na_2SO_4 were added. The addition of the aqueous solution was slowly performed and was stopped when effervescence was no longer observed in the reaction mixture. The white product was then filtered over Celite and the solution obtained was washed several times with a mixture CH_2Cl_2/MeOH (9:1). The organic phase was washed with water (3 × 20 mL), dried with anhydrous Na_2SO_4, filtered and concentrated at reduced pressure, yielding the corresponding amine as a white powder. Yield: 99% (0.23 mmol, 0.09 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35–7.11 (m, 13H, H_{arom}), 4.31 (d, ^3J = 8 Hz, 1H, C*H–O), 4.22 (m, 2H, C*H*–CH–CH_2), 3.33 (m, 2H, CH_2–OH), 2.99 (m, 2H, CH_2–N), 2.71 (m, 2H, C*H*–CH_2–N), 2.65 (m, 1H, CH_2–N), 2.57 (m, 1H, C*H–N), 2.51 (m, 1H, CH_2–N). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.7–141.7 (*C*aromatic), 128.5–123.6 (*C*Haromatic), 72.2 (1C, *C**H–O), 67.0 (*C**H–N), 59.3 (*C*H_2–OH), 53.8, 51.9 (2C, *C*H_2–N), 48.5 (*C*H–CH–CH_2), 43.5, 43.4 (2C, C*H*–CH_2–N). IR (KBr, ν cm^{-1}): 3409 (OH), 3064–3018 (=C–H), 2935–2788 (C–H), 1477–1456 (C=C), 1093 (C–N), 1060–1020 (C–O). HRMS (ES+): *m/z* (100%) calcd for $C_{27}H_{28}NO_2$ 398.2120, found 398.2113. Melting point: 124 °C.

4.2.3. Synthesis of diphosphite ligands 3 and 4

General procedure. A solution of diols **1** and **2** (0.5 mmol), previously dried azeotropically with toluene (3 × 1 mL), in dry and degassed toluene (5 mL) and cooled to 0 °C, was slowly added to a solution of phosphorochloridite **a** (1.1 mmol), synthesized in situ by standard procedures, in dry and degassed pyridine (0.75 mL). The mixture was allowed to rise to room temperature and stirred overnight. The mixture was then filtered to eliminate the pyridine salts, and the filtrate was concentrated to dryness. The white foam obtained was purified by flash chromatographic techniques over nitrogen.

Synthesis of compound **3**: The synthesis of diphosphite **3** was completed according to the general procedure previously described. The product was isolated as a white solid. Yield: 80% (0.401 mmol, 651 mg) after purification by flash column chromatography (toluene, R_f = 0.77). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51–6.95 (m, 21H, *H*aromatic), 5.33 (m, 1H, C*H–O), 4.77 (d, 1H, *J* = 2.8 Hz, *CH*CO), 4.63 (d, 1H, *J* = 2.4 Hz, *CH*CO), 4.58 (dt, 1H, *J* = 10.4 Hz, 3.6 Hz, C*H–N), 3.30 (m, 1H, CH_2), 3.20 (m, 1H, CH_2), 2.44 (m, 2H, C*H*anthracene), 1.68–1.13 (m, 72H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 176.9, 176.4 (2C, *C*=O), 146.5–122.5 (42C, *C*aromatic), 71.6 (1C, *C**H–O), 59.6 (1C, *C*H_2), 57.6 (1C, *C**H–N), 46.3, 45.9 (2C, *C*HCO), 45.5, 42.3 (2C, *C*Hanthracene), 35.6–29.8 (24C, *C*H_3). ^{31}P{^{1}H} NMR (161.97 MHz, $CDCl_3$) δ: 147.45, 133.78 (2P, *P*O). Anal. Calcd for $C_{83}H_{101}NO_8P_2$: C, 76.53; H, 7.82. Found: C, 76.25; H, 8.01.

Synthesis of compound **4**: The synthesis of diphosphite **4** was completed according to the general procedure previously described. The product was isolated as a white solid. Yield: 86% (0.431 mmol, 737 mg) after purification by flash column chromatography (toluene, R_f = 0.70). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61–6.82 (m, 21H, *H*aromatic), 5.17 (dd, 1H, *J* = 9.2 Hz, 5.2 Hz, C*H–O), 4.12 (m, 2H, *CH*CO), 3.89 (m, 1H, CH_2), 3.48 (m, 1H, CH_2), 3.05 (m, 1H, C*H–N), 2.99, 2.89 (m, 2H, NCH_2), 2.61 (m, 2H, C*H*anthracene), 2.02, 1.93 (m, 2H, NCH_2), 1.83–1.30 (m, 72H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 150.0–122.5 (42C, *C*aromatic), 76.3 (1C, *C**H–O), 66.2 (1C, *C**H–N), 62.2(1C, *C*H_2), 55.1, 52.8 (2C, NCH_2), 47.4, 47.3 (2C, *C*HCH_2N), 44.3, 44.0 (2C, *C*Hanthracene), 35.6–29.8 (24C, *C*H_3). ^{31}P{^{1}H} NMR (161.97 MHz, $CDCl_3$) δ: 141.86, 136.86 (2P, *P*O). Anal. Calcd for $C_{83}H_{105}NO_6P_2$: C, 78.21; H, 8.30. Found: C, 78.00; H, 8.45.

4.2.4. Synthesis of [$PdCl_2$(κ^2-*P,P*-3)]

To a solution of **3** (0.1 g, 0.077 mmol) dissolved in 20 mL of distilled toluene, [$PdCl_2$(COD)] (0.027 g, 0.077 mmol) was added. The solution was heated at 50 °C for 2 h. Then the solvent was removed under reduced pressure and the solid washed three times with diethylether. Yield: 80% (0.062 mmol, 0.09 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57–6.59 (m, 21H, *H*aromatic); 5.65 (dd, 1H, *J* = 10 Hz, *J* = 5 Hz, C*H–O); 5.12 (dd, 1H, *J* = 20 Hz, *J* = 10 Hz, CH_2); 4.57 (d, 1H, *J* = 2 Hz, *CH*CO); 4.49 (d, 1H, *J* = 2 Hz, *CH*CO); 4.27 (m, 1H, C*H–N); 2.62, 2.63 (m, 2H, C*H*anthracene)), 2.46 (dd, 1H, *J* = 10 Hz, *J* = 5 Hz, CH_2); 1.30–1.82 (s, 72H, CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 175.3, 175.1 (2C, *C*=O); 148.2-129.6 (21C, *C*aromatic), 128.2–124.1 (21C, HCaromatic), 77.8 (1C, *C**H–O), 62.0 (1C, *C*H_2); 52.0 (1C, *C**H–N); 46.3, 45.5 (2C, *C*HCO), 45.4, 45.2 (2C, *C*Hanthracene), 32.5-29.6 (24C, *C*H_3). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ: 101.01 (d, 1P, *J* = 67 Hz, Pd–P), 98.97 (d, 1P, *J* = 67 Hz, Pd–P). IR (KBr, ν cm^{-1}): 2962 (–C–H), 1781 (C=O), 1718 (C=O), 1467 (C=C), 1260 (C–O). Anal. Calcd for $C_{83}H_{101}NO_8P_2$ Cl_2Rh: C, 67.3; H, 6.9; N, 0.9. Found: C, 65.7; H, 7.2; N, 0.8. SM (CI, NH_3): *m/z* = 1479 [M]$^+$.

4.2.5. Synthesis of [Rh(μ-Cl)(κ^2-*P,P*-3)]$_2$

To a solution of **3** (0.25 g, 0.192 mmol) dissolved in 10 mL of distilled toluene, [RhCl(COD)]$_2$ (0.09 g, 0.180 mmol) was added. The solution was heated at 50 °C for 4 h. Then the solvent was removed under reduced pressure and the solid washed three times with diethylether. Recrystallization from CH_2Cl_2/Et_2O (4:1). Yield: 80% (0.144 mmol, 0.41 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36–6.43 (m, 21H, *H*aromatic); 5.46 (m, 1H, C*H–O); 4.68 (m, 1H, CH_2); 4.55 (dl, 1H, *J* = 6 Hz, *CH*CO); 4.35 (d, 1H, *J* = 6 Hz, *CH*CO); 3.92 (m, 1H, C*H–N); 2.46, 2.29 (m, 2H, C*H*anthracene)), 1.91 (m, 1H, CH_2); 1.99–0.80 (s, 72H, CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 175.6, 174.9 (2C, *C*=O); 146.3–136.9 (21C, *C*aromatic), 131.6–122.9 (21C, HCaromatic), 75.2 (1C, *C**H–O), 59.4 (1C, *C*H_2); 53.2 (1C, *C**H–N); 45.9 (1C, *C*HCO), 45.3 (1C, *C*HCO), 45.2 (1C, *C*Hanthracene), 44.9 (1C, *C*Hanthracene), 32.9–15.3 (24C, *C*H_3). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ: 134.50 (dt, 1P,

J = 45 Hz, J = 324 Hz, Rh–P), 132.57 (dt, 1P, J = 41 Hz, J = 312 Hz, Rh–P). $^{103}Rh\{^{31}P\}$ NMR (15.7 MHz, $CDCl_3$) δ: −7968. IR (KBr, ν cm^{-1}): 2962 (=C–H), 1785 (C=O), 1719 (C=O), 1464 (C=C), 1262 (C–O), 1093 (P–O). SM (ion spray): m/z = 2878 $[M]^+$.

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