

Easy access to *cis*-1,3-disubstituted cyclopentane 1,4-diphosphines

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Dedicated to Prof. Dr. Roberto A. Rossi on the occasion of his 60th anniversary

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Abstract

cis-1-(Diphenylphosphino)-3-(diphenylphosphinomethyl)cyclopentane (**13a**) and the corresponding dicyclopentylphosphino derivative **13b** have been readily obtained in high yield from 2-cyclopentenone by a five-step sequence which takes advantage of the electrophilic character of positions 1 and 3 of 2-cyclopentenone to introduce the substituents, while their relative *cis*-configuration is established by diastereoselective hydrogenation of the mixture of isomeric alkenes **12a** or **12b**.

Keywords: Addition reactions, carbocycles, diastereoselectivity, hydrogenation, phosphorus

Introduction

As part of our current interest on the synthesis of carbocyclic analogs of *cis*-MCCPM (Figure 1),¹ we have recently described the synthesis of bisphosphinoyl compounds **5a-c** in racemic form (Scheme 1).² Also, compound (**6a**) was prepared by dehydroxylation of **5a** by using the Barton procedure. However, the synthesis of these compounds has serious drawbacks: (a) multi-step reaction sequence; (b) low overall yield; and (c) stereoselectivity problems in the crucial step (nucleophilic opening of epoxide **4** with the lithium derivative of methyl diphenylphosphine oxide, and (d) column chromatography of the acetates derived from the mixture of **5** and **7** was required to isolate the desired minor *cis*-stereoisomers.

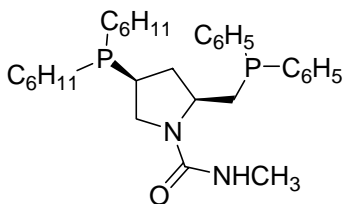
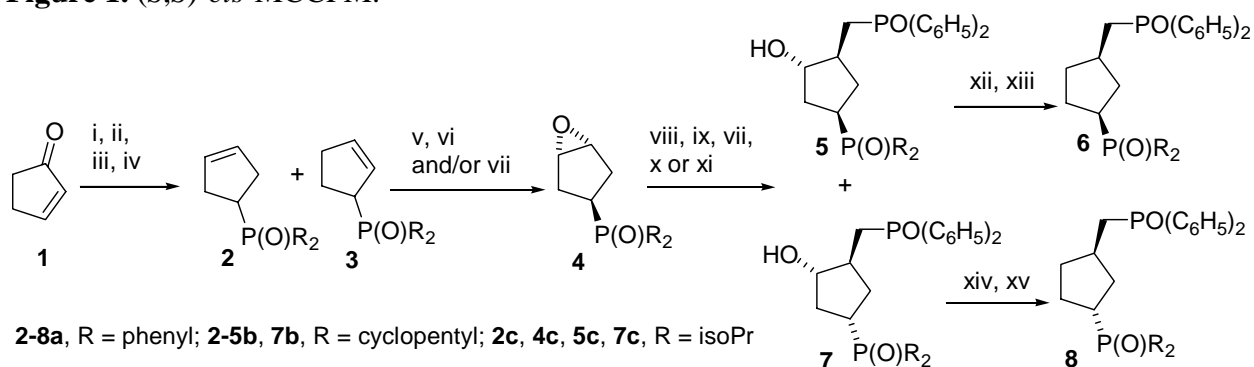


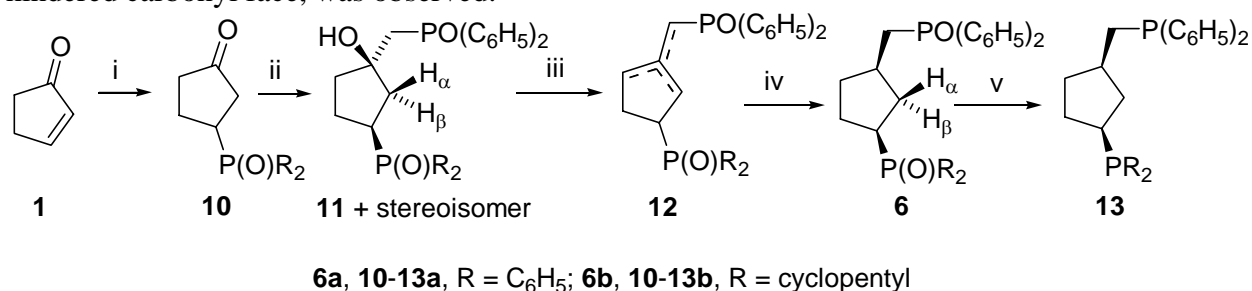
Figure 1. (*S,S*)-*cis*-MCCPM.

Scheme 1. Reagents and conditions: (i) ClPR_2 , AcOH, 4 Å molecular sieves, r.t., 2 h; (ii) NaBH_4 , MeOH; (iii) MsCl, Et_3N , DMAP (10%), CH_2Cl_2 ; (iv) Pyrolysis; (v) *m*-Chloroperbenzoic acid, CH_2Cl_2 ; (vi) KOH, EtOH; (vii) Silica gel column chromatography; (viii) Lithium derivative of methyldiphenylphosphine oxide (**9**) [from **9** and 1.6 M *n*-BuLi (in hexanes)], THF, r.t. (3 h) and reflux (15 h); (ix) Ac_2O , reflux, 2 h; (x) NaMeO, MeOH, reflux, 2 h; (xi) KCN, EtOH, reflux, 12 h; (xii) Thiocarbonyldiimidazole, toluene, reflux, 1 h; (xiii) *n*- Bu_3SnH , AIBN, toluene, reflux, 1 h. (xiv) Thiocarbonyldiimidazole, CH_2Cl_2 , reflux, 4 h; (xv) *n*- Bu_3SnH , AIBN, benzene, reflux, 6 h.

Results and Discussion

Herein we describe a straightforward diastereoselective synthesis of **6a** and the corresponding 3-(dicyclopentylphosphinoyl) derivative (**6b**), starting from 2-cyclopentenone (**1**) (Scheme 2) and their conversion into the corresponding diphosphines, **13a** and **13b**, respectively. Since positions 1 and 3 of 2-cyclopentenone are electrophilic, both substituents of the desired diphosphines (**13**) could be introduced by appropriate nucleophilic addition reactions. It is known that chlorodiphenylphosphine reacts with acyclic α,β -unsaturated ketones in anhydrous acetic acid to give a β -(diphenylphosphinoyl)ketone,³ while we have recently described² the synthesis of **10a** and **10b** by using the same kind of reaction. Also, configurationally stable lithiated P-chiral disubstituted phosphine oxides have been added (Michael reaction) with high diastereoselectivity to 2-cyclopentenone.⁴ Moreover, examples of nucleophilic additions of the lithium derivative of methyldiphenylphosphine oxide (**9**) and related derivatives to ketones are also known.⁵ Initial attempts to carry out the nucleophilic addition of the lithium derivative of **9** to cyclopentanone (**10a**) failed, probably due to the water present in compound (**10a**). When **10a** was made anhydrous by azeotropic distillation of water with toluene and then it was reacted with the lithium derivative of **9**, the corresponding addition product (**11a**) was obtained in high yield.

Only one stereoisomer, probably the one derived from the attack of the nucleophile on the less hindered carbonyl face, was observed.



Scheme 2. Reagents and conditions: (i) see reference 2; (ii) Lithium derivative of methyldiphenylphosphine oxide (**9**) [from **9** and 1.6 M *n*-BuLi (in hexanes)], THF, r.t. (3 h) and reflux (15 h); (iii) Concentrated H₂SO₄, THF, reflux, 3-6 d; (iv) H₂, 5% Pd-C, MeOH, 1 atm, 3-6 d; (v) HSiCl₃, Et₃N, CH₃CN, reflux, 3 h.

Once the diphenylphosphinoyl and diphenylphosphinoylmethyl substituents were introduced, the hydroxyl group of compound **11a** was removed in order to establish the relative *cis*-configuration of the substituents. To this end, compound **11a** was dehydrated, which required quite drastic conditions (2 mol of concentrated H₂SO₄ per mol of **11a**, in THF under reflux for 3 days). The product thus obtained (93% yield) consisted of a mixture of regio- and stereo-isomers (**12a**) which was submitted without separation to hydrogenation under standard conditions. Fortunately, from the hydrogenation, only compound **6a** was obtained in 83% yield. The relative *cis*-configuration of this compound was assigned by comparison of its ¹H and ¹³C NMR data with those of a reference sample of **6a**, prepared by the synthetic sequence of scheme 1, whose relative *cis*-configuration had unequivocally been established by X-ray diffraction analysis.² Moreover, the ¹H and ¹³C NMR data of **6a** differ from those of the corresponding *trans*-stereoisomer (**8a**, scheme 1).²

Similarly, reaction of **10b**² with the lithium derivative of **9** gave in good yield a mixture of **11b** and its stereoisomer in an approximate ratio of 5:1, respectively. The main component was assumed to be **11b**. Dehydration of the mixture of **11b** and its stereoisomer gave a regio- and stereo-isomeric mixture of alkenes **12b**, which on hydrogenation gave **6b**, as a highly hygroscopic solid, whose melting point could not be determined. The relative *cis*-configuration of **6b** was established by comparison of its ¹H and ¹³C NMR spectra with those of **6a**. Compounds **6a** and **6b** were reduced in high yield to the corresponding diphosphines **13a** and **13b** by reaction with trichlorosilane.

The new compounds **11a**, **11b** + stereoisomer, and **6b** have been fully characterized by spectroscopic means (IR, ¹H, ¹³C and ³¹P NMR, MS) and elemental analysis, while diphosphines **13a** and **13b** have been characterized by NMR spectroscopy (¹H, ¹³C and ³¹P). In general, assignment of the NMR spectra has been carried out with the aid of COSY ¹H/¹H, HETCOR ¹H/¹³C and NOESY experiments.

In conclusion, the unexpected stereoselective hydrogenation of the mixture of alkenes **12a** and **12b** to the *cis*-derivatives **6a** and **6b**, opens the way to the synthesis of a new family of *cis*-1,3-disubstituted cyclopentane 1,4-diphosphines, which might be of interest to prepare new chiral catalysts. Work is in progress to prepare and isolate Rh (I) complexes derived from diphosphines **13a** and **13b**, to study their catalytic activity in hydrogenation reactions.

Experimental Section

General Procedures. Melting points were determined with a MFB 595010 M Gallenkamp melting point apparatus. 500 MHz ^1H NMR spectra were recorded on a Varian VXR 500 spectrometer, 75.4 MHz ^{13}C NMR spectra were taken on a Varian Gemini 300 and 121.4 MHz ^{31}P NMR on a Varian Unity 300 Plus, always in CDCl_3 solution. ^1H and ^{13}C NMR chemical shifts (δ) are reported in ppm with respect to internal tetramethylsilane (TMS) and ^{31}P NMR chemical shifts (δ) are reported in ppm relative to 85% H_3PO_4 as external standard. The multiplicity of the signals is: s, singlet; d, doublet; t, triplet; m, multiplet. For the different compounds, the terms H_α or H_β are assigned to hydrogen atoms which are *cis* or *trans* relative to the reference substituent (usually at position 1), respectively. IR spectra were recorded on a FT/IR Perkin–Elmer spectrometer, model 1600; only significant absorption bands are given. Routine MS spectra were taken on a Hewlett–Packard 5988A spectrometer, the sample was introduced directly or through a gas chromatograph, Hewlett–Packard model 5890 Series II, equipped with a 30–meter HP-5 (5% diphenyl–95% dimethyl-polysiloxane) column and the electron impact technique (70 eV). Only significant ions are given: those with higher relative abundance, except for the ions with higher m/z values. NMR and routine MS spectra were performed at the *Serveis Científico-Tècnics* of the University of Barcelona, while elemental analyses were carried out at the Microanalysis Service of the IIQAB (CSIC, Barcelona, Spain).

***c*-3-(Diphenylphosphinoyl)-1-[(diphenylphosphinoyl)methyl]-*r*-1-cyclopentanol (11a).** To a cold (ice-bath) solution of methyldiphenylphosphine oxide (98%, 580 mg, 2.63 mmol) in anhydrous THF (15 mL) was added dropwise *n*-butyllithium (2.36 mL, 1.6M in hexanes, 3.78 mmol) and the suspension was stirred at 0°C for 45 min. The suspension was cooled to –78°C and a solution of anhydrous ketone **10a** (747 mg, 2.63 mmol, azeotropic distillation of the water content with toluene in a Dean-Stark equipment) in THF (25 mL) was added dropwise. After 3 h at room temperature, the mixture was heated under reflux for 15 h. The mixture was allowed to cool to room temperature, saturated aqueous solution of NH_4Cl (19 mL) was added, and the organic phase was separated and evaporated to dryness *in vacuo*. The residue was taken in H_2O (35 mL) and the solution was extracted with CH_2Cl_2 (3×37 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give **11a** (950 mg, 72% yield) as an orange-brown viscous oil. The analytical sample of **11a** was obtained as a colorless solid by crystallization (ethyl acetate), m.p. 179–180°C. IR (KBr) 3425 (OH st), 1197, 1158, 1119 (P=O

st) cm^{-1} ; ^1H NMR 7.81–7.63 (complex signal, 8H, Ar- H_{ortho}), 7.49–7.36 (complex signal, 12H, Ar- H_{meta} , Ar- H_{para}), 5.80–5.20 (broad signal, 1H, OH), 3.01–2.92 (m, 1H, 3-H), 2.82 (dd, 1H, $J=15.0$ Hz, $J'=12.0$ Hz) and 2.76 (dd, 1H, $J=15.0$ Hz, $J'=11.0$ Hz) ($\text{CH}_2\text{-P}$), 2.52 (ddd, 1H, $J=19.0$ Hz, $J'=14.5$ Hz, $J''=12.0$ Hz, 2- H_β), 2.10–1.95 (complex signal, 2H, 2- H_α , 4- H_α), 1.82–1.70 (complex signal, 3H, 4- H_β , 5- H_α , 5- H_β); ^{13}C NMR 134.4 (C, d, $^1J_{\text{CP}}=98.2$ Hz), 134.0 (C, d, $^1J_{\text{CP}}=98.2$ Hz), 132.1 (C, d, $^1J_{\text{CP}}=98.8$ Hz), 131.6 (C, d, $^1J_{\text{CP}}=98.3$ Hz) (Ar- C_{ipso}), 131.7 (2 CH, d, $^4J_{\text{CP}}=2.2$ Hz), 131.4 (CH, d, $^4J_{\text{CP}}=2.2$ Hz) and 131.3 (CH, d, $^4J_{\text{CP}}=2.5$ Hz) (Ar- CH_{para}), 130.8 (CH, d, $^2J_{\text{CP}}=9.1$ Hz), 130.6 (CH, d, $^2J_{\text{CP}}=9.6$ Hz) and 130.5 (CH, d, $^2J_{\text{CP}}=10.2$ Hz) (Ar- CH_{ortho}), 128.6 (2 CH, d, $^3J_{\text{CP}}=11.1$ Hz), 128.4 (CH, d, $^3J_{\text{CP}}=11.2$ Hz) and 128.3 (CH, d, $^3J_{\text{CP}}=11.7$ Hz) (Ar- CH_{meta}), 78.9 (C, t, $^2J_{\text{CP}}=^3J_{\text{CP}}=2.0$ Hz, C1), 41.6 (CH_2 , t, $^2J_{\text{CP}}=^3J_{\text{CP}}=5.6$ Hz, C5), 39.8 (CH_2 , broad s, C2), 38.6 (CH_2 , d, $^1J_{\text{CP}}=70.3$ Hz, $\text{CH}_2\text{-P}$), 34.3 (CH, d, $^1J_{\text{CP}}=72.5$ Hz, C3), 23.7 (CH_2 , s, C4); ^{31}P NMR 32.3 [$\text{PO}(\text{C}_6\text{H}_5)_2$], 22.0 [$\text{CH}_2\text{PO}(\text{C}_6\text{H}_5)_2$]; MS (EI), m/z (%): 500 (M^+ , 3), 299 [$[\text{M}-\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 76], 281 [$[\text{M}-\text{H}_2\text{O}-\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 20], 215 [$[\text{CH}_2\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 34], 202 (46), 201 [$[\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 100]. Anal. Calcd. for $\text{C}_{30}\text{H}_{30}\text{O}_3\text{P}_2$: C, 71.99; H, 6.05. Found: C, 72.04; H, 6.11.

Mixture of *c*-3-(dicyclopentylphosphinoyl)-1-[(diphenylphosphinoyl)methyl]-*r*-1- cyclopentanol (11b) and *t*-3-stereoisomer. From methyl diphenyl phosphine oxide (98%, 4.19 g, 19.0 mmol) in anhydrous THF (100 mL), *n*-butyllithium (1.6M in hexanes, 19.0 mL, 30.4 mmol) and a solution of anhydrous ketone **10b** (5.0 g, 18.6 mmol) in THF (100 mL) and following the procedure described for **10a**, a mixture of **11b** and its stereoisomer in the approximate ratio **11b**: stereoisomer of 5:1, was obtained (6.57 g, 73% yield) as a brown foamy solid. The analytical sample of this mixture was obtained as a colorless solid by crystallization (ethyl acetate), m.p. 163–164°C. IR (KBr) 3420 (OH st), 1157, 1119 (P=O st) cm^{-1} . MS (EI), m/z (%): 484 (M^+ , 2), 466 [$[\text{M}-\text{H}_2\text{O}]^+$, 1], 416 [$[\text{M}-\text{C}_5\text{H}_8]^+$, 9], 347 [$[\text{M}-\text{C}_5\text{H}_8-\text{C}_5\text{H}_9]^+$, 16], 299 [$[\text{M}-\text{PO}(\text{C}_5\text{H}_9)_2]^+$, 98], 283 [$[\text{M}-\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 14], 281 [$[\text{M}-\text{PO}(\text{C}_5\text{H}_9)_2-\text{H}_2\text{O}]^+$, 42], 215 [$[\text{CH}_2\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 77], 201 [$[\text{PO}(\text{C}_6\text{H}_5)_2]^+$, 100]. Anal. Calcd. for $\text{C}_{28}\text{H}_{38}\text{O}_3\text{P}_2$: C, 69.40; H, 7.91. Found: C, 69.38; H, 7.95. Data of **11b** from the spectra of the mixture: ^1H NMR 7.78–7.72 (complex signal, 4H, Ar- H_{ortho}), 7.51–7.41 (complex signal, 6H, Ar- H_{meta} , Ar- H_{para}), 5.31 (broad s, 1H, OH), 2.77 (dd, $J=15.0$ Hz, $J'=10.0$ Hz, 1H) and 2.72 (dd, $J=15.0$ Hz, $J'=10.0$ Hz, 1H) ($\text{CH}_2\text{-P}$), 2.30–2.21 (m, 1H, 3-H), 2.20–1.90 (complex signal, 5H, 2 cyclopentyl CH, 2- H_α , 2- H_β , 4- H_α), 1.89–1.50 (complex signal, 19H, cyclopentyl CH_2 , 4- H_β , 5- H_α , 5- H_β); ^{13}C NMR 133.7 (C, d, $^1J_{\text{CP}}=99.2$ Hz, Ar- C_{ipso}), 131.6 (CH, broad s, Ar- CH_{para}), 130.4 (CH, d, $^2J_{\text{CP}}=9.7$ Hz, Ar- CH_{ortho}), 128.52 (CH, d, $^3J_{\text{CP}}=12.2$ Hz) and 128.45 (CH, d, $^3J_{\text{CP}}=11.7$ Hz) (Ar- CH_{meta}), 79.3 (CH, t, $^2J_{\text{CP}}=^3J_{\text{CP}}=4.8$ Hz, C1), 41.6 (CH_2 , t, $^3J_{\text{CP}}=^3J_{\text{CP}}=6.9$ Hz, C5), 40.6 (CH_2 , d, $^3J_{\text{CP}}=5.0$ Hz, C2), 38.7 (CH_2 , d, $^1J_{\text{CP}}=69.9$ Hz, $\text{CH}_2\text{-P}$), 36.4 (CH, d, $^1J_{\text{CP}}=66.3$ Hz) and 36.2 (CH, d, $^1J_{\text{CP}}=66.3$ Hz) (cyclopentyl CH), 34.8 (CH, d, $^1J_{\text{CP}}=64.3$ Hz, C3), 27.1–27.0 (CH_2 , cyclopentyl C2 and C5), 26.1–25.8 (CH_2 , cyclopentyl C3 and C4), 24.6 (CH_2 , d, $^2J_{\text{CP}}=2.0$ Hz, C4); ^{31}P NMR 54.8 [$\text{PO}(\text{C}_5\text{H}_9)_2$], 28.5 [$\text{PO}(\text{C}_6\text{H}_5)_2$]. Data of the stereoisomer of **11b** from the spectrum of the mixture: ^{31}P NMR 52.0 [$\text{PO}(\text{C}_5\text{H}_9)_2$], 31.2 [$\text{PO}(\text{C}_6\text{H}_5)_2$].

cis-1-(Diphenylphosphinoyl)-3-[(diphenylphosphinoyl)methyl]cyclopentane (6a). a) Dehydration of **11a** to the mixture of alkenes **12a**. To a solution of **11a** (1.46 g, 2.92 mmol) in THF (60 mL), concentrated H₂SO₄ (0.32 mL, 5.84 mmol) was added and the mixture was stirred under reflux for 3 days. The mixture was allowed to cool to room temperature and the solvent was evaporated *in vacuo*. The residue was dissolved in CH₂Cl₂ (30 mL), washed with NaHCO₃ (saturated aqueous solution, 3×20 mL), dried (Na₂SO₄), filtered and concentrated to dryness *in vacuo* to give the mixture of alkenes **12a** as a brown foamy solid (1.31 g, 93% yield).

b) Hydrogenation of the mixture of alkenes **12a**. To a solution of the mixture of alkenes **12a** (557 mg, 1.16 mmol) in methanol (25 mL), Pd-C (5% Pd, 54% water content, 223 mg) was added and the mixture was vigorously stirred under hydrogen (1 atm) for 3 days. The suspension was filtered and the filtrate was concentrated to dryness *in vacuo* to give **6a** (464 mg, 83% yield) as a pale yellow foamy solid, whose ¹H and ¹³C NMR spectra coincide with those of a sample of **6a**, previously obtained by a different synthetic procedure.²

cis-1-(Dicyclopentylphosphinoyl)-3-[(diphenylphosphinoyl)methyl]cyclopentane (6b). a) Dehydration of **11b** to the mixture of alkenes **12b**. From a mixture of **11b** and its stereoisomer (6.57 g, 13.6 mmol) and concentrated H₂SO₄ (1.48 mL, 27.2 mmol) in THF (150 mL), following the procedure described for **11a**, but stirring under reflux for 6 days, a mixture of alkenes **12b** was obtained as a brown oil (5.43 g, 86% yield).

b) Hydrogenation of the mixture of alkenes **12b**. To a solution of the mixture of alkenes **12b** (1.33 g, 2.85 mmol) in methanol (65 mL) Pd-C (5% Pd, 54% water content, 0.55 g) was added and the mixture was vigorously stirred under a hydrogen atmosphere for 6 days. The suspension was filtered and the filtrate was concentrated to dryness *in vacuo* to give **6b** (1.19 g, 89% yield) as a pale yellow foamy solid. An analytical sample of **6b** was obtained by crystallization (ethyl acetate), as a very hygroscopic white solid, whose m.p. could not be determined. IR (KBr) 1159, 1119 (P=O st) cm⁻¹. ¹H NMR 7.77–7.69 (complex signal, 4H, Ar-H_{ortho}), 7.50–7.41 (complex signal, 6H, Ar-H_{meta}, Ar-H_{para}), 2.48–2.28 [complex signal, 3H, 3-H, CH₂P], 2.14–1.93 (complex signal, 4H, cyclopentyl CH, 1-H, 5-H_α), 1.93–1.45 (complex signal, 19H, 8 cyclopentyl CH₂, 2-H_β, 4-H_β, 5-H_β), 1.45–1.30 (complex signal, 2H, 2-H_α, 4-H_α); ¹³C NMR 133.4 (C, d, ¹J_{CP}=97.7 Hz) and 133.2 (C, d, ¹J_{CP}=97.7 Hz) (Ar-C_{ipso}), 131.5 (CH, d, ⁴J_{CP}=3.0 Hz) and 131.4 (CH, d, ⁴J_{CP}=2.6 Hz) (Ar-CH_{para}), 130.6 (CH, d, ²J_{CP}=9.1 Hz) and 130.4 (CH, d, ²J_{CP}=9.1 Hz) (Ar-CH_{ortho}), 128.5 (CH, d, ³J_{CP}=11.2 Hz, 2 Ar-CH_{meta}), 36.9 (CH, d, ¹J_{CP}=66.3 Hz) and 36.5 (CH, d, ¹J_{CP}=65.3 Hz) (cyclopentyl CH), 35.8 (CH, d, ¹J_{CP}=64.8 Hz, C1), 35.7 (CH₂, d, ³J_{CP}=7.1 Hz, C2), 34.7 (CH, dd, ³J_{CP}=11.3 Hz, ²J_{CP}=3.8 Hz, C3), 34.6 (CH₂, d, ¹J_{CP}=71.3 Hz, CH₂P), 33.6 (CH₂, dd, ³J_{CP}=9.1 Hz, ³J_{CP}=6.6 Hz, C4), 27.1 (2 CH₂, broad s) and 26.9 (CH₂, broad s) (cyclopentyl C2 and C5), 26.8 (CH₂, broad s), 26.1 (2 CH₂, d, ³J_{CP}=6.0 Hz) and 25.9 (2 CH₂, d, ³J_{CP}=6.0 Hz) (cyclopentyl C3 and C4), 24.8 (CH₂, broad s, C5); ³¹P NMR 28.3 [PO(C₆H₅)₂], 55.7 [PO(C₅H₉)₂]. MS (EI), m/e (%): 469 [(M+H)⁺, 2], 468 (M⁺, 1), 400 [(M-C₅H₈)⁺, 13], 331 [(M-C₅H₉-C₅H₈)⁺, 55], 283 {[M-PO(C₅H₉)₂]⁺, 100}, 267 {[M-PO(C₆H₅)₂]⁺, 15}, 253 {[M-CH₂PO(C₆H₅)₂]⁺, 16}, 215 {[CH₂PO(C₆H₅)₂]⁺, 17}, 201 {[PO(C₆H₅)₂]⁺, 63}. Anal. Calcd. for C₂₈H₃₈O₂P₂·1.5H₂O: C, 67.86; H, 8.34. Found: C, 67.74; H, 8.19.

cis-1-(Diphenylphosphino)-3-[(diphenylphosphino)methyl]cyclopentane (13a). To a solution of **6a** (100 mg, 0.21 mmol) in degassed CH₃CN (5 mL), Et₃N (0.117 mL, 0.84 mmol) was added. The mixture was stirred at 0°C for 5 min, HSiCl₃ (0.07 mL, 0.69 mmol) was added and the mixture was heated under reflux for 3 h. The mixture was allowed to cool to room temperature, degassed benzene (5 mL) and degassed aqueous solution of NaOH (30%, 2.2 mL) were added and the mixture was stirred at 60°C for 30 min. The mixture was allowed to cool to room temperature, the organic layer was separated, washed with degassed H₂O (3 mL), degassed saturated aqueous solution of NaHCO₃ (3 mL) and degassed brine (3 mL). The organic phase was dried (Na₂SO₄), filtered and concentrated under reduced pressure, to give **13a** as a colorless oil (90 mg, 95% yield), which was kept under argon. ¹H NMR 7.37–7.29 (complex signal, 8H, Ar-H_{ortho}) 7.25–7.20 (complex signal, 12H, Ar-H_{meta}, Ar-H_{para}), 2.55–2.46 (m, 1H, 1-H), 2.10–2.01 (complex signal, 2H, CH₂P), 1.93–1.80 (complex signal, 3H, 2-H_α, 3-H, 4-H_β or 4-H_α), 1.78–1.67 (m, 1H) and 1.61–1.48 (m, 1H) (5-H_α, 5-H_β), 1.39–1.31 (m, 1H, 4-H_α or 4-H_β), 1.22–1.12 (m, 1H, 2-H_β); ¹³C NMR 139.0 (C, d, ¹J_{CP}=11.7 Hz), 138.8 (C, d, ¹J_{CP}=11.7 Hz) and 138.6 (2 C, d, ¹J_{CP}=13.2 Hz) (Ar-C_{ipso}), 133.2 (CH, d, ²J_{CP}=18.2 Hz), 133.0 (CH, d, ²J_{CP}=18.2 Hz), 132.7 (CH, d, ²J_{CP}=18.7 Hz) and 132.5 (CH, d, ²J_{CP}=18.2 Hz) (Ar-CH_{ortho}), 128.4–128.1 (CH, complex signal, Ar-CH_{meta}, Ar-CH_{para}), 39.7 (CH₂, dd, ³J_{CP}=19.2 Hz, ²J_{CP}=8.6 Hz, C2), 38.4 (CH, dd, ³J_{CP}=13.2 Hz, ²J_{CP}=8.1 Hz, C3), 35.5 (CH, d, ¹J_{CP}=8.6 Hz, C1), 34.7 (CH₂, d, ¹J_{CP}=12.7 Hz, CH₂P), 34.1 (CH₂, dd, ³J_{CP}=8.6 Hz, ³J_{CP}=6.1 Hz, C4), 29.8 (CH₂, d, ²J_{CP}=19.8 Hz, C5); ³¹P NMR –4.2 [P(C₆H₅)₂], –20.6 [CH₂P(C₆H₅)₂].

cis-1-(Dicyclopentylphosphino)-3-[(diphenylphosphino)methyl]cyclopentane (13b). From **6b** (930 mg, 1.99 mmol), degassed CH₃CN (60 mL), Et₃N (2.5 mL, 17.9 mmol) and HSiCl₃ (1.62 mL, 16.1 mmol) and following the procedure described for **13a**, pure **13b** was obtained as a yellow oil (920 mg, quantitative yield). ¹H NMR 7.43–7.37 (complex signal, 4H, Ar-H_{ortho}), 7.32–7.27 (complex signal, 6H, Ar-H_{meta}, Ar-H_{para}), 2.17–2.04 (m, 2H, CH₂P), 2.03–1.96 (m, 1H, 2-H_α), 1.95–1.30 (complex signal, 24H, 8 cyclopentyl-CH₂, 2 cyclopentyl-CH, 1-H, 3-H, 4-H_α, 4-H_β, 5-H_α, 5-H_β), 1.18–1.09 (m, 1H, 2-H_β). ¹³C NMR 139.1 (C, d, ¹J_{CP}=12.1 Hz) and 138.9 (C, d, ¹J_{CP}=12.7 Hz) (Ar-C_{ipso}), 132.8 (CH, d, ²J_{CP}=20.3 Hz) and 132.5 (CH, d, ²J_{CP}=20.3 Hz) (Ar-CH_{ortho}), 128.4–128.2 (CH, complex signal, Ar-CH_{meta}, Ar-CH_{para}), 40.1 (CH₂, dd, ²J_{CP}=11.8 Hz, ³J_{CP}=7.6 Hz, C2), 38.1 (CH, dd, ²J_{CP}=13.0 Hz, ³J_{CP}=7.4 Hz, C3), 35.4–35.0 (CH, complex signal, cyclopentyl CH, C1), 34.9 (CH₂, d, ¹J_{CP}=12.1 Hz, CH₂P), 33.8 (CH₂, dd, ³J_{CP}=9.0 Hz, ³J_{CP}=6.7 Hz, C4), 31.1–30.7 (CH₂, complex signal, cyclopentyl C2 and C5), 29.7 (CH₂, d, ²J_{CP}=15.2 Hz, C5), 26.2–25.8 (CH₂, complex signal, cyclopentyl C3 and C4); ³¹P NMR 4.1 [PO(C₅H₉)₂], –20.5 [CH₂PO(C₆H₅)₂].

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