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 methyldiphenylphosphine 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.

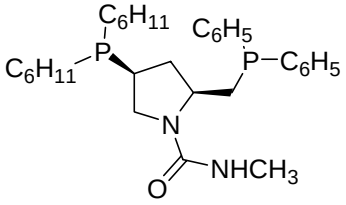
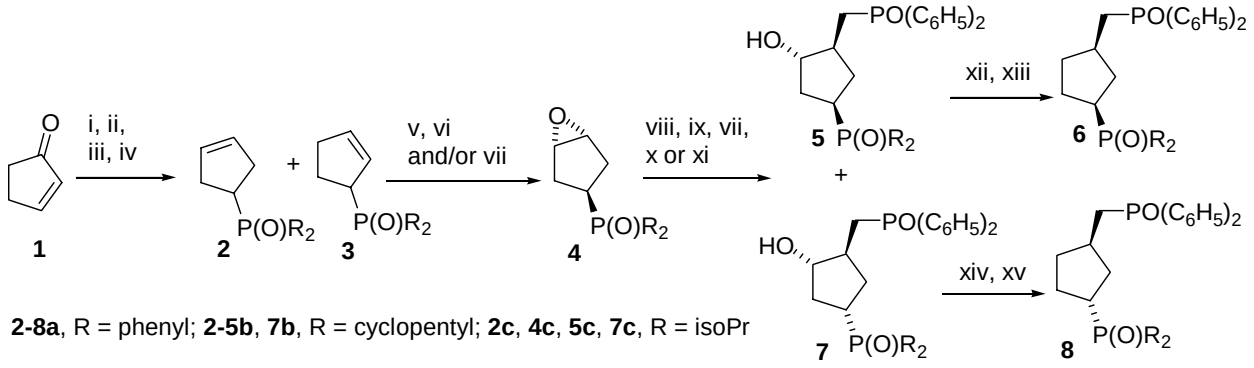


Figure 1. (*S,S*)-*cis*-MCCPM.



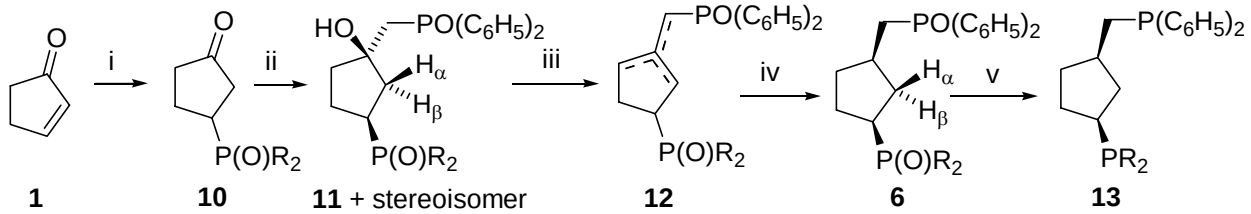
Scheme 1. Reagents and conditions: (i) $ClPR_2$, AcOH, 4 Å molecular sieves, r.t., 2 h; (ii) $NaBH_4$, MeOH; (iii) MsCl, Et_3N, DMAP (10%), CH_2Cl_2; (iv) Pyrolysis; (v) *m*-Chloroperbenzoic acid, CH_2Cl_2; (vi) KOH, EtOH; (vii) Silica gel column chromatography; (viii) Lithium derivative of methyldiphenylphosphine 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 described[2] 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.



6a, **10**-**13a**, R = C_6H_5; **6b**, **10**-**13b**, R = cyclopentyl

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 H_2SO_4, THF, reflux, 3-6 d; (iv) H_2, 5% Pd-C, MeOH, 1 atm, 3-6 d; (v) $HSiCl_3$, Et_3N, CH_3CN, 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 H_2SO_4 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 ^{1}H and ^{13}C 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 ^{1}H and ^{13}C 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 ^{1}H and ^{13}C 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, ^{1}H, ^{13}C and ^{31}P NMR, MS) and elemental analysis, while diphosphines **13a** and **13b** have been characterized by NMR spectroscopy (^{1}H, ^{13}C and ^{31}P). In general, assignment of the NMR spectra has been carried out with the aid of COSY ^{1}H/^{1}H, HETCOR ^{1}H/^{13}C 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 ^{1}H 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. ^{1}H 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, singulet; 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 0ºC for 45 min. The suspension was cooled to –78ºC 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. 179–180ºC. 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) (CH_2-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, $^1J_{CP}$=98.2 Hz), 134.0 (C, d, $^1J_{CP}$=98.2 Hz), 132.1 (C, d, $^1J_{CP}$=98.8 Hz), 131.6 (C, d, $^1J_{CP}$=98.3 Hz) (Ar-C_{ipso}), 131.7 (2 CH, d, $^4J_{CP}$=2.2 Hz), 131.4 (CH, d, $^4J_{CP}$=2.2 Hz) and 131.3 (CH, d, $^4J_{CP}$=2.5 Hz) (Ar-CH_{para}), 130.8 (CH, d, $^2J_{CP}$=9.1 Hz), 130.6 (CH, d, $^2J_{CP}$=9.6 Hz) and 130.5 (CH, d, $^2J_{CP}$=10.2 Hz) (Ar-CH_{ortho}), 128.6 (2 CH, d, $^3J_{CP}$=11.1 Hz), 128.4 (CH, d, $^3J_{CP}$=11.2 Hz) and 128.3 (CH, d, $^3J_{CP}$=11.7 Hz,) (Ar-CH_{meta}), 78.9 (C, t, $^2J_{CP}$=$^3J_{CP}$=2.0 Hz, C1), 41.6 (CH_2, t, $^2J_{CP}$=$^3J_{CP}$=5.6 Hz, C5), 39.8 (CH_2, broad s, C2), 38.6 (CH_2, d, $^1J_{CP}$=70.3 Hz, CH_2-P), 34.3 (CH, d, $^1J_{CP}$=72.5 Hz, C3), 23.7 (CH_2, s, C4); ^{31}P NMR 32.3 [$PO(C_6H_5)_2$], 22.0 [$CH_2PO(C_6H_5)_2$]; MS (EI), m/z (%): 500 ($M^{\cdot+}$, 3), 299 [[M–$PO(C_6H_5)_2$]$^+$, 76], 281 [[M–H_2O–$PO(C_6H_5)_2$]$^+$, 20], 215 [[$CH_2PO(C_6H_5)_2$]$^+$, 34], 202 (46), 201 [[$PO(C_6H_5)_2$]$^+$, 100]. Anal. Calcd. for $C_{30}H_{30}O_3P_2$: 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 methyldiphenylphosphine 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. 163–164ºC. IR (KBr) 3420 (OH st), 1157, 1119 (P=O st) cm^{-1}. MS (EI), m/z (%): 484 ($M^{\cdot+}$, 2), 466 [$(M–H_2O)^{\cdot+}$, 1], 416 [$(M–C_5H_8)^{\cdot+}$, 9], 347 [$(M–C_5H_8–C_5H_9)^+$, 16], 299 {[M–$PO(C_5H_9)_2$]$^+$, 98}, 283 {[M–$PO(C_6H_5)_2$]$^+$, 14}, 281 {[M–$PO(C_5H_9)_2$–H_2O]$^+$, 42}, 215 {[$CH_2PO(C_6H_5)_2$]$^+$, 77}, 201 [$PO(C_6H_5)_2$, 100]. Anal. Calcd. for $C_{28}H_{38}O_3P_2$: 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) (CH_2-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, $^1J_{CP}$=99.2 Hz, Ar-C_{ipso}), 131.6 (CH, broad s, Ar-CH_{para}), 130.4 (CH, d, $^2J_{CP}$=9.7 Hz, Ar-CH_{ortho}), 128.52 (CH, d, $^3J_{CP}$=12.2 Hz) and 128.45 (CH, d, $^3J_{CP}$=11.7 Hz) (Ar-CH_{meta}), 79.3 (CH, t, $^2J_{CP}$=$^3J_{CP}$=4.8 Hz, C1), 41.6 (CH_2, t, $^3J_{CP}$=$^3J_{CP}$=6.9 Hz, C5), 40.6 (CH_2, d, $^3J_{CP}$=5.0 Hz, C2), 38.7 (CH_2, d, $^1J_{CP}$=69.9 Hz, CH_2-P), 36.4 (CH, d, $^1J_{CP}$=66.3 Hz) and 36.2 (CH, d, $^1J_{CP}$=66.3 Hz) (cyclopentyl CH), 34.8 (CH, d, $^1J_{CP}$=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, $^2J_{CP}$=2.0 Hz, C4); ^{31}P NMR 54.8 [$PO(C_5H_9)_2$], 28.5 [$PO(C_6H_5)_2$]. Data of the stereoisomer of **11b** from the spectrum of the mixture: ^{31}P NMR 52.0 [$PO(C_5H_9)_2$], 31.2 [$PO(C_6H_5)_2$].

***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 H_2SO_4 (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 CH_2Cl_2 (30 mL), washed with $NaHCO_3$ (saturated aqueous solution, 3×20 mL), dried (Na_2SO_4), 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 ^{1}H and ^{13}C 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 H_2SO_4 (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}. ^{1}H 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, CH_2P], 2.14–1.93 (complex signal, 4H, cyclopentyl CH, 1-H, 5-H$_\alpha$), 1.93–1.45 (complex signal, 19H, 8 cyclopentyl CH_2, 2-H$_\beta$, 4-H$_\beta$, 5-H$_\beta$), 1.45–1.30 (complex signal, 2H, 2-H$_\alpha$, 4-H$_\alpha$); ^{13}C 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 (CH_2, d, $^3J_{CP}$=7.1 Hz, C2), 34.7 (CH, dd, $^3J_{CP}$=11.3 Hz, $^2J_{CP}$=3.8 Hz, C3), 34.6 (CH_2, d, $^1J_{CP}$=71.3 Hz, CH_2P), 33.6 (CH_2, dd, $^3J_{CP}$=9.1 Hz, $^3J_{CP}$=6.6 Hz, C4), 27.1 (2 CH_2, broad s) and 26.9 (CH_2, broad s) (cyclopentyl C2 and C5), 26.8 (CH_2, broad s), 26.1 (2 CH_2, d, $^3J_{CP}$=6.0 Hz) and 25.9 (2 CH_2, d, $^3J_{CP}$=6.0 Hz) (cyclopentyl C3 and C4), 24.8 (CH_2, broad s, C5); ^{31}P NMR 28.3 [PO(C$_6$H$_5$)$_2$], 55.7 [PO(C$_5$H$_9$)$_2$]. MS (EI), m/e (%): 469 [(M+H)$^+$, 2], 468 (M$^{\cdot+}$, 1), 400 [(M–C$_5$H$_8$)$^{\cdot+}$, 13], 331 [(M–C$_5$H$_9$–C$_5$H$_8$)$^+$, 55], 283 {[M–PO(C$_5$H$_9$)$_2$]$^+$, 100}, 267 {[M–PO(C$_6$H$_5$)$_2$]$^+$, 15}, 253 {[M–CH$_2$PO(C$_6$H$_5$)$_2$]$^+$, 16}, 215 {[CH$_2$PO(C$_6$H$_5$)$_2$]$^+$, 17}, 201 {[PO(C$_6$H$_5$)$_2$]$^+$, 63}. Anal. Calcd. for $C_{28}H_{38}O_2P_2 \cdot 1.5H_2O$: 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 CH_3CN (5 mL), Et_3N (0.117 mL, 0.84 mmol) was added. The mixture was stirred at 0ºC for 5 min, $HSiCl_3$ (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 60ºC for 30 min. The mixture was allowed to cool to room temperature, the organic layer was separated, washed with degassed H_2O (3 mL), degassed saturated aqueous solution of $NaHCO_3$ (3 mL) and degassed brine (3 mL). The organic phase was dried (Na_2SO_4), filtered and concentrated under reduced pressure, to give **13a** as a colorless oil (90 mg, 95% yield), which was kept under argon. ^{1}H 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, CH_2P), 1.93–1.80 (complex signal, 3H, 2-H$_\alpha$, 3-H, 4-H$_\beta$ or 4-H$_\alpha$), 1.78–1.67 (m, 1H) and 1.61–1.48 (m, 1H) (5-H$_\alpha$, 5-H$_\beta$), 1.39–1.31 (m, 1H, 4-H$_\alpha$ or 4-H$_\beta$), 1.22–1.12 (m, 1H, 2-H$_\beta$); ^{13}C 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 (CH_2, 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 (CH_2, d, $^1J_{CP}$=12.7 Hz, CH_2P), 34.1 (CH_2, dd, $^3J_{CP}$=8.6 Hz, $^3J'_{CP}$=6.1 Hz, C4), 29.8 (CH_2, d, $^2J_{CP}$=19.8 Hz, C5); ^{31}P NMR –4.2 [$P(C_6H_5)_2$], –20.6 [$CH_2P(C_6H_5)_2$].

***cis*-1-(Dicyclopentylphosphino)-3-[(diphenylphosphino)methyl]cyclopentane** (**13b**)**.** From **6b** (930 mg, 1.99 mmol), degassed CH_3CN (60 mL), Et_3N (2.5 mL, 17.9 mmol) and $HSiCl_3$ (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). ^{1}H 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, CH_2P), 2.03–1.96 (m, 1H, 2-H$_\alpha$), 1.95–1.30 (complex signal, 24H, 8 cyclopentyl-CH_2, 2 cyclopentyl-CH, 1-H, 3-H, 4-H$_\alpha$, 4-H$_\beta$, 5-H$_\alpha$, 5-H$_\beta$), 1.18–1.09 (m, 1H, 2-H$_\beta$). ^{13}C 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 (CH_2, 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 (CH_2, d, $^1J_{CP}$=12.1 Hz, CH_2P), 33.8 (CH_2, dd, $^3J_{CP}$=9.0 Hz, $^3J'_{CP}$=6.7 Hz, C4), 31.1–30.7 (CH_2, complex signal, cyclopentyl C2 and C5), 29.7 (CH_2, d, $^2J_{CP}$=15.2 Hz, C5), 26.2–25.8 (CH_2, complex signal, cyclopentyl C3 and C4); ^{31}P NMR 4.1 [$PO(C_5H_9)_2$], –20.5 [$CH_2PO(C_6H_5)_2$].

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