Supporting Information

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Palladium-Catalyzed Enantioselective Allylic Phosphination

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Supporting Information

1. General Experimental Methods

All reactions were performed in thermally dried glassware under an argon atmosphere using standard Schlenk techniques or in a MBraun 150B-G glovebox under nitrogen. All solvents were distilled prior to use. All deuterated solvents were distilled, degassed with three freeze-pump-thaw cycles and stored over 3 Å molecular sieves. The phosphines Ph₂PH, Cy₂PH were purchased from STREM Chemicals Inc. and used as received.

Josiphos, bis[(1,2,4,5-η)-1,5-diphenyl-1,4-pentadien-3-one]-palladium, [1] 3-acetoxy-1,3-diphenylprop-1-ene, [2] (E)-1,3-diphenyl-2-propen-1-yl ethylcarbonate, [3] trans-1,3-dicyclohexylpropenyl acetate, [4] and [Palladium(µ-bromo)(η-1,3-diphenylallyl)]_2, [5] were synthesized according to published procedures.

1D- and 2D-NMR spectra were recorded using a Bruker DPX300 or Bruker DPX500 spectrometer. Chemical shifts δ (ppm) are given relative to TMS (1H- and 13C-NMR) and 85% H₃PO₄ (31P-NMR). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). The proton, carbon and phosphorus assignment was performed by 1H-2D-COSY, 1H-13C-HMQC, 1H-13C-HMBC and 1H-31P-HMQC experiments. Enantiomeric excesses were determined by HPLC using a Daicel Chiralcel OJ (OJ00CE-BG068) column and eluting with a hexane/iPrOH solution.

Racemic (E)-(1,3-diphenylpropenyl)diphenylphosphine (4a):

Diphenylphosphine (180 μL, 1.04 mmol) was added to a pale purple solution of bis[(1,2,4,5-η)-1,5-diphenyl-1,4-pentadien-3-one]-palladium (30 mg, 52 μmol) and 1,3-diphenylallyl acetate (160 mg 1.04 mmol) in MeOH (10 mL). The reaction mixture was stirred at 40 °C overnight, giving a white precipitate. After filtration, the product was washed with cold MeOH (5 mL) and dried under vacuum. Yield: 359 mg (92 %) of a white powder.

\[\text{1H-NMR (500.23 MHz, CD}_2\text{Cl}_2): \delta (ppm) = 4.44 (dd, J = 5.6, 8.5 Hz, 1H, P-CH), 6.28 (dd, J = 2.6, 15.8 Hz, 1H, Ph-CH=CH), 6.46 (ddd, J = 6.4, 8.5 Hz, 15.3, 1H, CH=CH-CH), 7.26 (m, 10 H, Ph-CH), 7.38 (m, 8 H, Ph-CH), 7.64 (m, 2 H, Ph-CH).\]

\[\text{13C-NMR (125.8 MHz, CD}_2\text{Cl}_2): \delta (ppm) = 50.5 (1C, P-CH), 126.5 (2C, Ph-CH), 126.7 (1C, Ph-CH), 127.6 (1C, Ph-CH), 128.4 (2C, Ph-CH), 128.6 (2C, Ph-CH), 128.8 (2C, Ph-CH), 128.8 (2C, Ph-CH), 129.1 (2C, Ph-CH), 129.4 (2C, Ph-CH), 129.8 (2C, Ph-CH).\]
130.4 (1C, Ph-CH=CH), 131.4 (1C, CH=CH-CHP), 134.0 (2C, Ph-CH), 134.6 (2C, Ph-CH), 137.2 (1C, PhC-P), 137.3 (1C, PhC-P), 137.7 (1C, PhC-CH=CH), 141.2 (1C, PhC-CHP).

$^{31}$P-NMR (202.5 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 0.6 (Ph$_2$-P-allyl).
EA: C$_{25}$H$_{23}$P (378.45): Calcd. C 85.69, H 6.13; found C 85.18, H 6.25.

**Racemic (E)-(1,3-diphenylpropenyl)diphenylphosphine sulfide (20):**

Rac-4a (101 mg, 0.26 mmol) and $S_e$ (71 mg, 0.28 mmol) were dissolved together in THF and stirred for 20 min. After removal of the solvent the raw product was filtered on silica (5 g, 0 cm, ethyl acetate : $n$-heptane : triethylamine 1 : 1 : 1%). After removal of the solvent the product was dried in vacuo. Yield: 105 mg (98 %) of a white solid.

**HPLC-Conditions:** OJ00CE-BG068 column; temperature: 25°C; injection: 2µL of 4·10$^{-3}$ M solution in Hexane; eluent: Hexane (75%) / PrOH (25%); flow rate: 0.1 ml·min$^{-1}$; detection at 254.8, 230.4, 210.8 nm; 128 min (S)-Enantiomer, 140 min (R)-Enantiomer.

$^1$H-NMR (500.23 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 4.82 (7, $J$ = 10.1 Hz, 1H, P-CH), 6.39 (dd, $J = 4.3$, 15.8 Hz, 1H, Ph-CH=CH), 6.74 (m, 1H, CH=CH=CH), 7.25 (m, 4H, Ph-CH), 7.30 (s, 1H, Ph-CH), 7.31 (m, 4H, Ph-CH), 7.39 (m, 4H, Ph-CH), 7.46 (m, 1H, Ph-CH), 7.57 (m, 2H, Ph-CH), 7.73 (m, 2H, Ph-CH), 8.10 (ddd, $J = 1.4$, 8, 12.1, 2H, Ph-CH).

$^{13}$C-NMR (125.8 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 52.6 (1C, P-CH), 125.5 (1C, PhCH=CH),, 126.7 (1C, Ph-CH), 127.7 (1C, Ph-CH), 128.2 (1C, Ph-CH), 128.4 (2C, Ph-CH), 128.5 (1C, Ph-CH), 128.8 (1C, Ph-CH), 128.9 (1C, Ph-CH), 129.9 (2C, Ph-CH), 131.4 (1C, PhC-P), 131.7 (1C, Ph-CH), 132.0 (1C, Ph-CH), 132.1 (1C, PhC-P), 132.2 (1C, Ph-CH), 134.5 (1C, CH=CH-CHP), 136.2 (1C, PhC-CH=CH), 137.1 (1C, PhC-CHP).

$^{31}$P-NMR (202.5 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 49.8 (1P, Ph$_2$-P-Allyl).
EA: C$_{25}$H$_{23}$PS (410.51): Calcd. C 79.00, H 5.75; found C 78.95, H 5.80.

**[Pd(1,3-diphenylallyl)(JOSIPHOS)][SbF$_6$]** (9):

In a Schlenk flask equipped with a stirring bar, Josiphos (125.0 mg, 0.22 mmol) and [Palladium(µ-bromo)(η-1,3-diphenylallyl)]$_2$ (80.0 mg, 0.11 mmol) were dissolved in MeOH (20 mL). After 20 min stirring, a solution of NaSbF$_6$ (65.4 mg, 0.253 mmol, 1.2 eq) in MeOH (2 ml) was added dropwise, affording a white precipitate immediately. The precipitate was filtrated over celite and washed with MeOH (3 x 5 mL). After removal of the solvent the product was dried in vacuo. Yield: 238 mg (96 %) of an orange solid.

51:49 diastereomeric mixture (A:B).

$^1$H-NMR (500.23 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 0.5 (dd, $J = 10.1$, 22.2, 1 H, Cy-H A/B), 0.71 (s, 1H, Cy-H A/B), 0.83 (dd, $J = 11.8$, 23.5, 1H, Cy-H A/B), 0.97 (dd, $J = 12.1$, 21.8, 2 H, Cy-H A/B), 1.20 (m, 6H, Cy-H A/B), 1.31 (s, 2H, Cy-H A/B), 1.32 (s, 1H, Cy-H A/B), 1.42 (m, 5H, Cy-H A/B), 1.54 (d, $J = 11.3$, 6H, Cy-H A/B), 1.65 8
an orange solid.

CH

the crude product filtrated on silica (5 g, 0.1 mmol) was added to a solution of di-μ-chlorobis[2-1-(dimethylamino)ethyl]ferrocenyl-kC]-palladium(II) (40.0 mg, 0.05 mmol) in dichloromethane. The mixture was stirred 2 h at r.t., the red solution obtained was evaporated to dryness and the crude product filtrated on silica (5 g, 1.5 cm, CH2Cl2). After removal of the solvent the product was dried in vacuo. Yield: 71 mg (91 %) of an orange solid.

\[\text{C}_5\text{H}_5\text{FePd}_{\text{Me}_2} \text{FePdSb} (410.51): \text{Calcd. C 54.21, H 5.08; found C 54.53, H 5.06.}\]

\[\text{EA: C}_3\text{H}_4\text{F}_6\text{P}_{2}\text{FePdSb} (410.51): \text{Calcd. C 54.21, H 5.08; found C 54.53, H 5.06.}\]

\[\text{Chloro}[2-1-(dimethylamino)ethyl]ferrocenyl-C,N](E)-(1,3-diphenylpropenyl)diphenylphosphine)-palladium(II) (19):\]

4 (38.0 mg, 0.1 mmol) was added to a solution of di-μ-chlorobis[2-1-(dimethylamino-kN)ethyl]ferrocenyl-kC]-palladium(II) (40.0 mg, 0.05 mmol) in dichloromethane. The mixture was stirred 2 h at r.t., the red solution obtained was evaporated to dryness and the crude product filtrated on silica (5 g, 1.5 cm, CH2Cl2). After removal of the solvent the product was dried in vacuo. Yield: 71 mg (91 %) of an orange solid.
Crystals suitable for x-ray diffraction were obtained by slow diffusion of Hexane through a dichloromethane solution.

\(^1\)H-NMR (500.23 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) (ppm) = 1.24 (s, 3 H, NMe\(_2\)-CH-CH\(_2\) A), 1.25 (s, 3 H, NMe\(_2\)-CH-CH\(_2\) B), 2.57 (d, J = 2.3 Hz, 1 H, Cp-H B), 2.70 (d, J = 1.4 Hz, 3 H, N-(CH\(_3\))\(_2\) B), 2.77 (d, J = 1.4 Hz, 3 H, N-(CH\(_3\))\(_2\) A), 2.86 (d, J = 2.3 Hz, 1H, Cp-H A), 3.13 (d, J = 2.9 Hz, 3 H, N-(CH\(_3\))\(_2\) A), 3.19 (d, J = 2.9 Hz, 3 H, N-(CH\(_3\))\(_2\) B), 3.64 (dd, J = 2.4, 4.9 Hz, 1 H, Cp-H A), 3.70 (m, 1 H, Cp-H B), 3.70 (s, 5 H, Cp-H A), 3.97 (d, J = 1.3 Hz, 1 H, Cp-H A), 3.98 (d, J = 1.6 Hz, 1 H, Cp-H A), 4.04 (ddd, J = 1.2, 6.8, 13.5 Hz, 1 H, CH-CH\(_2\) A), 4.04 (ddd, J = 1.2, 6.9, 13.7 Hz, 1 H, C-H-CH\(_3\) B), 5.93 (d, J = 7.3, 13.6 Hz, 1 H, PCH-CH=CHPh B), 6.16 (t, J = 10.7 Hz, 1 H, PCH-CH=CHPh A), 6.46 (dd, J = 5.7, 9.9 Hz, 1 H, PCH-CH=CHPh B), 6.50 (dd, J = 5.6, 9.8 Hz, 1 H, PCH-CH=CHPh A), 6.64, (ddd, J = 3.1 15.80 Hz 1H PhCH=CH A), 6.85 (m, 2 H, Ph-CH A/B), 6.89 (m, 2 H, Ph-CH A/B), 6.90, (dd, J = 3.2 15.98 Hz 1H PhCH=CH B), 7.06 (d, J = 7.96 Hz, 2 H, Ph-CH A/B), 7.17 (m, 2 H, Ph-CH A/B), 7.20 (m, 2 H, Ph-CH A/B), 7.30 (m, 4 H, Ph-CH A/B), 7.40 (m, 10 H, Ph-CH A/B), 7.49 (m, 2 H, Ph-CH A/B), 7.56 (m, 8 H, Ph-CH A/B), 7.64 (m, 2 H, Ph-CH A/B), 7.89 (m, 2 H, Ph-CH A/B), 8.16 (m, 2 H, Ph-CH A/B).

\(^13\)C-NMR (125.8 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) (ppm) = 15.3 (1 C, CH-CH\(_3\) B), 15.8 (1 C, CH-CH\(_3\) A), 43.7 (1 C, N-CH\(_3\) B), 44.1 (1 C, N-CH\(_3\) A), 49.9 (1 C, N-CH\(_3\) A), 50.0 (1 C, N-CH\(_3\) B), 50.1 (1 C, PCH-CH=CHPh B), 50.7 (1 C, PCH-CH=CHPh A), 62.5 (1 C, Cp-CH A), 62.8 (1 C, Cp-CH B), 64.6 (1 C, Cp-CH B), 64.7 (1 C, Cp-CH A), 67.5 (1 C, CH-CH\(_3\) A), 67.6 (1 C, CH-CH\(_3\) B), 69.2 (10 C, Cp-CH A/B), 126.6 (Ph-C-H A/B), 126.7 (1 C, PhCh=CH A), 127.0 (Ph-C-H A/B), 127.4 (Ph-C-H A/B), 127.6 (Ph-C-H A/B), 127.7 (Ph-C-H A/B), 127.8 (Ph-C-H A/B), 128.0 (Ph-C-H A/B), 128.1 (Ph-C-H A/B), 128.4 (Ph-C-H A/B), 128.9 (Ph-C-H A/B), 129.0 (Ph-C-H A/B), 130.2 (Ph-C-H A/B), 130.5 (Ph-C-H A/B), 130.8 (Ph-C-H A/B), 131.1 (Ph-C-H A/B), 131.3 (Ph-C-H A/B), 131.4 (Ph-C-H A/B), 131.8 (1 C, Ph-C A/B), 133.5 (1C Ph-CH=CH A), 133.7 (Ph-C-H A/B), 134.1 (Ph-C-H A/B), 134.5 (1C Ph-CH=CH B), 135.4 (Ph-C-H A/B), 136.1 (Ph-C-H A/B), 139.9 (Ph-C-H A/B), 137.1 (Ph-C-H A/B), 137.6 (1 C, Ph-C), 137.9 (1 C, Ph-C A/B), 138.1 (1 C, Ph-C A/B), 138.2 (1 C, Ph-C A/B), 138.3 (1 C, Ph-C A/B), 138.7 (1 C, Ph-C A/B).

\(^31\)P-NMR (202.5 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) (ppm) = 49.3 (P\(_2\)-Allyl B, minor), 49.1(Ph\(_2\)-P- Ally1 A, major).

2. Crystal Data

CCDC 654095, 668371, contain the supplementary crystallographic data for 19 and 20. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; tel.: +44-1223 336031; fax: (+44) 1223-336-03-033; or e-mail: deposit@ccdc.cam.ac.uk

Table 2. Crystal data and structure refinement for 19 (CCDC 654095).

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Table 2. Crystal data and structure refinement for 20 (CCDC 668371).

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<tr>
<td>Crystal system, space group</td>
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</table>
| Unit cell dimensions                           | a = 6.4860(4) Å, \(\alpha = 90\) deg.  
|                                                | b = 17.7474(11) Å, \(\beta = 90\) deg.  
|                                                | c = 19.2571(11) Å, \(\gamma = 90\) deg.  |
| Volume                                         | 2216.7(2) Å³           |
| Z, Calculated density                          | 4, 1.230 Mg/m³         |
| Absorption coefficient                         | 0.229 mm⁻¹             |
| F(000)                                         | 864                    |
Crystal size: 0.54 x 0.15 x 0.14 mm

Data collection:
- Siemens SMART PLATFORM
- with CCD Detector
- Graphite monochromator

Detector distance: 50 mm

Method; exposure time/frame: omega-scans; t = 5 sec

Solution by: direct methods

Refinement method: full matrix least-squares on F^2, SHELXTL

Theta range for data collection: 2.12 to 36.38 deg.

Limiting indices: -10<=h<=10, -29<=k<=29, -32<=l<=32

Reflections collected / unique: 94205 / 10755 [R(int) = 0.0554]

Completeness to theta: 36.38 = 99.8 %

Absorption correction: Empirical (Sadabs V. 2.03)

Max. and min. transmission: 0.9687 and 0.8869

Refinement method: Full-matrix least-squares on F^2

Data / restraints / parameters: 10755 / 0 / 262

Goodness-of-fit on F^2: 1.060

Final R indices [I>2sigma(I)]: R1 = 0.0433, wR2 = 0.1001

R indices (all data): R1 = 0.0515, wR2 = 0.1046

Absolute structure parameter: 0.01(5)

Largest diff. peak and hole: 0.407 and -0.175•10^-3

3. Literature


