

Supplementary data

Isolation and structural characterization of an optically active intermediate in the oxidative addition of methyl iodide on a rhodium(I) centre

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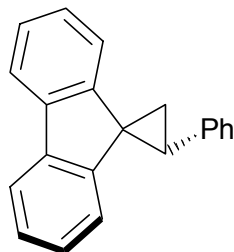
Experimental Section

General Remarks

All reactions, involving air- or moisture-sensitive compounds, and subsequent work-up were carried out under nitrogen using standard Schlenk techniques. The solvents were dried and purified by standard methods. They were deoxygenated and stored under nitrogen. Reagents and solvents were transferred under nitrogen via syringe or cannula. Solutions of crude reactions mixture were filtered through Celite (Fluka 535), neutral alumina (ICN Alumina N, activity super I), deactivated with H₂O. Melting points were measured in a sealed capillary on a Büchi 510 melting point apparatus and are uncorrected. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a Varian Unity 500 (500 MHz, ¹H; 125 MHz, ¹³C; 202 MHz, ³¹P) at ambient temperature. Chemical shifts (δ) are given in ppm relative to SiMe₄ (¹H, ¹³C) and external 85% H₃PO₄ (³¹P). ¹H and ¹³C NMR signal assignments were confirmed by ¹H-¹H COSY, NOE-difference experiments, APT and ¹H-¹³C HETCOR. Mass spectra were obtained with a Finnigan MAT 95 spectrometer by electron impact (EI) or fast atom bombardment (FAB). Elemental analyses were obtained on a Carlo Erba Strumentazione Element Analyzer, Model 1106. Optical rotations were measured on a Perkin Elmer 341 Polarimeter at $\lambda = 589$ nm using CHROMASOLV[®] grade solvents. The complexes [Rh(C₂H₄)₂Cl]₂,¹ [Rh(η^5 -C₅H₄CH₂CH(Ph)PPh₂- κ P)(η^2 -CH₂CH₂)],² [Rh(η^5 -C₅H₄CH₂CH(Ph)PPh₂- κ P)(I)(CH₃)],³ were

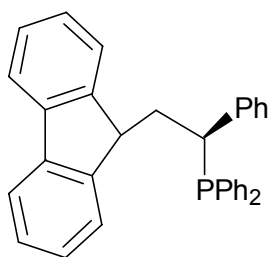
prepared according to published procedures. All other chemicals were purchased and used without further purification.

(S)-Spiro-1-(9-fluorenyl)-2-phenyl-cyclopropane



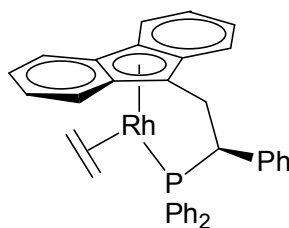
LDA (2.5 eq.) was added dropwise to a solution of fluorene (1.1 eq.) in THF (100 ml), cooled by an ice-water bath. The mixture was stirred for 1/2 h at RT and then cooled again to 0 °C. A solution of (*R*)-Phenyl-1,2- bis(methanesulfonyloxy)ethane (10.0 g) in THF (150 ml) was added dropwise and the mixture was allowed to reach room temperature overnight. A solution of NH₄Cl was then added. The mixture was diluted with Et₂O and the layers separated. The aqueous phase was washed with Et₂O (3x50 ml). The combined organic extracts were washed with brine, dried over MgSO₄, and treated with decolorizing charcoal. The solution was filtered, and the solvent removed under reduced pressure. The oil obtained was purified by chromatography on silica gel with toluene/hexane 1:4 as eluent (R_f= 0.4). Yield: yellow crystals, 7.6 g (83%). Melting point: 93 °C. ¹H NMR (CDCl₃): δ 2.94.12 (m, 2H, CH₂), 3.34 (t, 1H, ³J_{HH} = 8.54 Hz, CHPh), 6.14 (d, 1H, ³J_{HH} = 7.62 Hz, CH, ArH), 6.90 (m, 1H, CH, ArH), 7.12-7.39 (ms, 9H, ArH), 7.67 (d, 1H, ³J_{HH} = 7.63 Hz, CH, ArH), 7.82 (d, 1H, ³J_{HH} = 7.32 Hz, CH, ArH). ¹³C NMR (CDCl₃): δ 22.31 (CH₂), 35.00 (CHPh), 35.60 (C_{spiro}), 118.54 (CH), 119.65 (CH), 119.76 (CH), 121.59 (CH), 125.76 (CH), 125.89 (CH), 126.03 (CH), 126.79 (CH), 126.86 (CH), 128.14 (CH), 130.11 (CH), 137.07 (C), 139.64 (C), 140.39 (C), 144.26 (C), 148.27 (C). [α]_D²⁰ = +154° (chloroform). MS (EI): (*m/z*) 268 (M⁺, 15%), 168 (100%). Elemental Analysis: Calcd. (Found): C, 93.99 (93.80); H, 6.01 (6.11).

(S)-[2-(9H-Fluoren-9-yl)-1-phenyl-ethyl]-diphenyl-phosphane



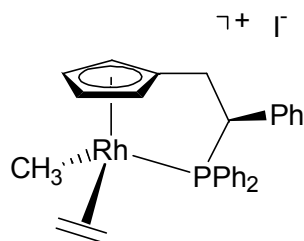
LiPPh₂ was prepared by treating a solution of HPPH₂ (2.5 g) in THF (50 ml) with BuLi (1.1 eq.) at -78 °C. The deep orange solution formed was stirred for 15 minutes at room temperature and then cooled again to -78 °C. The spiro compound (1.1 eq., 4.0 g) dissolved in THF (5 ml) was added to this solution and the reaction mixture was allowed to reach room temperature overnight. The solvent was removed under reduced pressure and the oil left was washed several times with hexane until precipitation of the lithium salt of the ligand. It was dissolved with THF and degassed H₂O was added. After several extractions with CH₂Cl₂, the combined organic phases were dried over MgSO₄ and treated with decolorizing charcoal. The solution was filtered on a short column of alumina (activity I), and the solvent removed under reduced pressure affording the ligand. Yield: yellow oily solid, 5.9 g (96%). ¹H NMR (CDCl₃): δ 1.88 (m, 1H, CH₂), 2.68 (m, 1H, CH₂), 3.61 (m, 1H, CHPh), 3.65 (m, 1H, CH), 6.80-7.50 (ms, 23H, ArH). ¹³C NMR (CDCl₃): δ 37.11 (d, ²J_{CP} = 23.9 Hz, CH₂), 42.93 (d, ¹J_{CP} = 12.44 Hz, CHPh), 45.45 (d, ³J_{CP} = 11.4 Hz, CH), 119.45 (CH), 119.67 (CH), 124.18 (CH), 124.82 (CH), 126.03 (d, J_{CP} = 1.9 Hz, CH), 126.33 (CH), 126.63 (d, J_{CP} = 4.8 Hz, CH), 126.82 (CH), 127.56 (d, J_{CP} = 6.7 Hz, CH), 128.11 (CH), 128.37 (d, J_{CP} = 6.8 Hz, CH), 129.06 (CH), 129.12 (CH), 133.00 (d, J_{CP} = 17.2 Hz, CH), 134.04 (d, J_{CP} = 20.1 Hz, CH), 135.71 (d, J_{CP} = 15.3 Hz, C), 136.62 (d, J_{CP} = 15.3 Hz, C), 140.36 (d, J_{CP} = 8.7 Hz, C), 140.67 (C), 140.74 (C), 146.70 (C), 146.98 (C). ³¹P NMR (CDCl₃): δ 1.88 (s).

(S)-(Ethylene){[η^5 -2-(fluoren-9-yl)-1-phenylethyl]- η^1 -diphenylphosphane}rhodium(I)



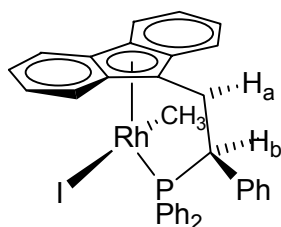
The ligand (2.6 g) was dissolved in THF (50 ml) and treated with BuLi (1.1 eq.) at $-78\text{ }^{\circ}\text{C}$. After stirring for 1/2 h at room temperature, this solution was added to a suspension of the Cramer's complex (0.5 eq., 1.1 g) in THF at $-78\text{ }^{\circ}\text{C}$. The mixture was allowed to slowly warm up to RT overnight. The solvent was removed under reduced pressure and the residue was dissolved in a hexane/toluene mixture (1:1) and filtered through a short pad of alumina (activity IV). The solvent was evaporated and the product dried under high vacuum. Yield: dark red solid, 2.74 g (82%). Mp: 163-167 $^{\circ}\text{C}$. ^1H NMR (CD_2Cl_2): δ 1.42 (m, 2H, C_2H_4), 1.86 (br m, 2H, C_2H_4), 3.17 (ddd, 1H, $^3J_{\text{HP}(\text{Rh})} = 62.56\text{ Hz}$, $J_{\text{HH}} = 6.10, 14.04\text{ Hz}$, CH_2), 3.39 (td, 1H, $^3J_{\text{HP}(\text{Rh})} = J_{\text{HH}} = 14.04\text{ Hz}$, $J_{\text{HH}} = 6.41\text{ Hz}$, CH_2), 5.47 (m, 1H, CHPh), 6.87-7.45 (ms, 19H, ArH), 7.64 (d, 1H, $^3J_{\text{HH}} = 8.24\text{ Hz}$, ArH), 7.69 (d, 1H, $^3J_{\text{HH}} = 8.24\text{ Hz}$, ArH), 7.74 (d, 1H, $^3J_{\text{HH}} = 7.94\text{ Hz}$, ArH), 7.94 (d, 1H, $^3J_{\text{HH}} = 7.94\text{ Hz}$, ArH). ^{13}C NMR (CD_2Cl_2): δ 26.97 (d, $^2J_{\text{CP}} = 8.54\text{ Hz}$, CH_2), 46.88 (d, $^1J_{\text{CRh}} = 13.44\text{ Hz}$, C_2H_4), 65.77 (d, $^1J_{\text{CP}} = 19.22\text{ Hz}$, CHPh), 81.34 (t, $^1J_{\text{CRh}} = ^2J_{\text{CP}} = 4.77\text{ Hz}$, C_{ipso}), 104.40 (d, $^1J_{\text{CRh}} = 6.66\text{ Hz}$, C), 107.90 (d, $^1J_{\text{CRh}} = 6.66\text{ Hz}$, C), 113.02 (d, $^1J_{\text{CRh}} = 2.89\text{ Hz}$, C), 114.02 (d, $^1J_{\text{CRh}} = 2.89\text{ Hz}$, C), 118.48 (d, $J_{\text{CP}} = 3.89\text{ Hz}$, CH), 118.54 (d, $J_{\text{CP}} = 2.89\text{ Hz}$, CH), 118.70 (CH), 119.21 (CH), 121.42 (d, $J_{\text{CP}} = 1.88\text{ Hz}$, CH), 121.84 (d, $J_{\text{CP}} = 2.76\text{ Hz}$, CH), 122.42 (CH), 122.78 (d, $J_{\text{CP}} = 1.88\text{ Hz}$, CH), 127.29 (d, $J_{\text{CP}} = 2.01\text{ Hz}$, CH), 127.48 (CH), 127.56 (CH), 128.25 (CH), 128.31 (CH), 128.34 (CH), 128.43 (CH), 128.50 (CH), 128.90 (d, $J_{\text{CP}} = 36.43\text{ Hz}$, C), 131.09 (d, $J_{\text{CP}} = 1.88\text{ Hz}$, CH), 131.16 (d, $J_{\text{CP}} = 9.67\text{ Hz}$, CH), 133.61 (d, $J_{\text{CP}} = 31.66\text{ Hz}$, C), 137.73 (d, $J_{\text{CP}} = 11.43\text{ Hz}$, CH), 137.86 (d, $J_{\text{CP}} = 9.55\text{ Hz}$, C). ^{31}P NMR (CD_2Cl_2): δ 91.94 (d, $^1J_{\text{PRh}} = 264.3\text{ Hz}$). $[\alpha]_{\text{D}}^{20} = -13^{\circ}$ (toluene). MS (FAB): (m/z) 584 (M^+ , 5%), 556 ($\text{M}^+ - (\text{C}_2\text{H}_4)$, 20%). Elemental Analysis: Calcd. (Found): C, 71.92 (71.62); H, 5.17 (5.44).

**(*S,S*_{Rh})-[$\{\eta^5$ -2-(Cyclopentadienyl)-1-phenyl-ethyl]- η^1 -diphenylphosphane}
(ethylene)(methyl)rhodium(III)] iodide**



The intermediate species of the oxidative addition reaction could be isolated in a crystalline form by performing the reaction in CH₃NO₂/Et₂O 5:2. Typically, **1** was dissolved in the mixture of solvents (1.5 ml/0.1 g). Excess amount of CH₃I was added (10 eq.) and the solution was placed without stirring in a fridge at 5 °C. After few days dark-red crystals of **3** were formed. The red solution was discarded and the crystals collected. The crystals are stable at -30 °C and only for a short time at room temperature. Yield: dark-red crystals (~40%). Mp: 80-90 °C (dec.). ¹H NMR (200 MHz, CD₂Cl₂): δ 0.10 (dd, 3H, ²J_{HRh}= 6.59 Hz, ³J_{HP}= 2.20 Hz, CH₃), 2.50-3.05 (m, 2H, CH₂), 3.08 (m, 2H, C₂H₄), 3.56 (m, 2H, C₂H₄), 5.94 (m, 1H, Cp), 5.99 (m, 1H, Cp), 6.08 (m, 1H, CHPh), 6.15 (m, 2H, Cp), 6.7-7.9 (m, 15H, Ph). ³¹P NMR (81 MHz, CD₂Cl₂): δ 90.69 (d, ¹J_{PRh}= 135.9 Hz). MS (FAB): (*m/z*) 583 (M⁺-(Me, C₂H₄)+I, 45%), 497 (M⁺-2, 50%), 456 (M⁺-(Me, C₂H₄), 100%), 127 (I⁻, 100%).

(*S,S*_{Rh})-[$\{\eta^5$ -2-(Fluoren-9-yl)-1-phenyl-ethyl]- η^1 -diphenylphosphane}(iodo)(methyl)rhodium(III)



The rhodium complex **5** (0.20 g) was dissolved in CH₂Cl₂ (5 ml) and excess amount of CH₃I (10 eq.) was added. The progress of the reaction was monitored by ³¹P NMR. After completion, the solvent was removed under reduced pressure, and the compound was

recovered as a crude product. It was dissolved in CH_2Cl_2 and filtered through alumina (activity IV). Evaporation of the solvent afforded the pure compound. Only one diastereomer could be detected by ^{31}P NMR analysis of the crude reaction mixture. The configuration around the metal was unambiguously determined to be *S* by means of ^1H NMR NOE difference experiment: irradiation of the coordinated methyl group at $\delta = 0.94$ enhanced the signal ($\delta = 4.38$) of the benzylic H_b proton of the linker. Analogously, irradiation of H_b revealed contacts with the coordinated methyl group and with the H_a proton ($\delta = 1.62$). Yield: dark-red solid, 0.21 g (88%). Mp: 195-200 °C. ^1H NMR (CD_2Cl_2): δ 0.94 (t, 3H, $J_{\text{HRh(P)}} = 2.75$ Hz, CH_3), 1.62 (m, 1H, CH_2), 2.42 (m, 1H, CH_2), 4.38 (m, 1H, CHPh), 6.83 (d, 2H, $J_{\text{HH}} = 8.55$ Hz, ArH), 6.92 (td, 1H, $J_{\text{HH}} = 0.6, 7.32$ Hz, ArH), 7.00-7.58 (ms, 19H, ArH), 8.09 (d, 1H, $J_{\text{HH}} = 7.32$ Hz, ArH). ^{13}C NMR (CD_2Cl_2): δ 7.32 (dd, $^1J_{\text{CRh}} = 33.5$ Hz, $^2J_{\text{CP}} = 9.1$ Hz, CH_3), 41.90 (d, $^2J_{\text{CP}} = 15.83$ Hz, CH_2), 51.36 (d, $^1J_{\text{CP}} = 23.62$ Hz, CHPh), 120.34 (CH), 121.11 (CH), 121.84 (CH), 122.95 (CH), 124.45 (CH), 125.12 (CH), 126.18 (CH), 127.12 (CH), 127.58 (d, $J_{\text{CP}} = 9.30$ Hz, CH), 127.80 (d, $J_{\text{CP}} = 9.30$ Hz, CH), 128.68 (CH), (CH), 128.90 (CH), 129.24 (C), 130.07 (CH), 131.34 (CH), 132.53 (C), 132.90 (C), 133.90 (d, $J_{\text{CP}} = 7.16$ Hz, CH), 136.13 (C), 137.55 (C), 137.90 (C), 138.10 (d, $J_{\text{CP}} = 10.43$ Hz, CH), 148.73 (d, $J_{\text{CP}} = 2.76$ Hz, C), 155.16 (C). ^{31}P NMR (CD_2Cl_2): δ 77.51 (d, $^1J_{\text{PRh}} = 158.38$ Hz). $[\alpha]_{\text{D}}^{20} = -4^\circ$ (CH_2Cl_2). MS (FAB): (m/z) 571 ($\text{M}^+ - \text{I}$, 45%), 556 ($\text{M}^+ - \text{MeI}$, 100%). Elemental Analysis: Calcd. (Found): C, 58.47 (58.71); H, 4.18 (4.37)

References

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