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($2S_p$,4*R*,8S_p)-4-Methyl-1-phenyl-diferroceno-5-*Z*-ethylene-1-phosphinoxide

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Abstract: We present a synthesis of the title compound, a homochiral diferroceno cycle intended for use in asymmetric catalysis. We present a hydrovinylation protocol, which allows the production of the title compound in two steps from a known diferrocenyl precursor. We obtained one of two possible diastereomers selectively and propose a plausible regio- and stereoselective reaction mechanism.

Keywords: ferrocene; 8-membered cycle; planar chirality; hydrovinylation; titanium(IV) chloride

1. Introduction

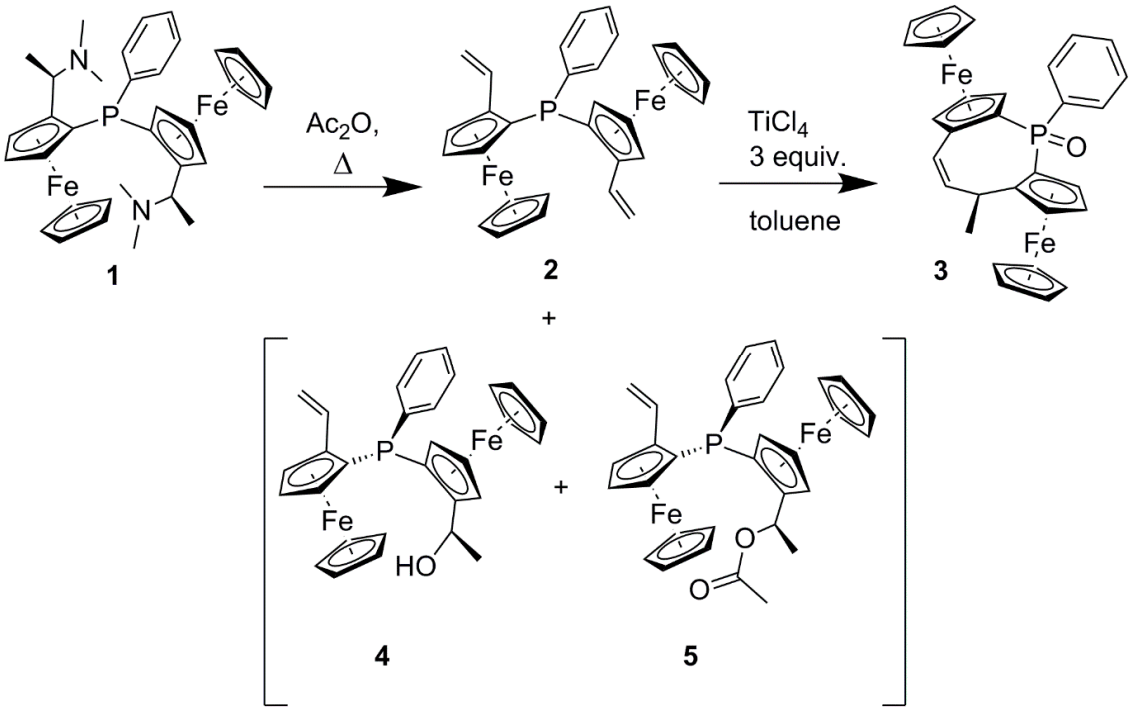
1,2-Disubstituted ferrocenes are planar–chiral if substituents are different [1]. These two substituents can be used to design chelating ligands for transition metal complexes and have attracted considerable academic interest [2]. Beyond foundational research, ferrocene-based asymmetric molecules have been used successfully for industrial-scale asymmetric catalysis, achieving up to 79% e.e. [3].

The asymmetric induction potential of such ligands can often be improved by incorporating a second ferrocene unit. For instance, Barbaro et al. used diferrocenyl phosphorous ligands for Ru(II)-catalyzed hydride transfer to the small molecule acetophenone and observed 72% e.e. at a conversion rate of 99% [4]. The e.e. may be even further increased by constraining the conformational freedom of the two ferrocenyl groups. Xiao et al. fixed the biferrocenyl dihedral angle by forming a diferrocenyl cycle by connecting the side chains. They reported up to 86% e.e. in Pd(II)-catalyzed asymmetric allylic amination [5].

Based on these results, we attempted synthesis of new diferroceno cycles intended to be used as asymmetric ligands. To date, only few diferroceno cycles have been reported. Some of them are bridged biferrocenyls, e.g., Eberhard et al. [6], Metallinos et al. [7], Tews et al. [8], Santi et al. [9] and Jäkle et al. [10]. In other diferroceno cycles, the two ferrocene units are connected through heteroatoms such as silicon [11], sulfur [12], boron [13–16] and phosphorous [16–18]. Both Schlögl [19] and Köhler [20] described two ferrocene moieties connected by carbon chains. In this work, we report on a diferrocenyl cycle inspired by catalysis ligands published by Barreiro et al. [21] and Smith et al. [22].

2. Results and Discussion

The synthesis of the title compound is shown in Scheme 1 and starts with the known [23,24] homochiral diamino precursor (*R*,*R*,S_p,S_p)-**1** according to a protocol published by Togni et al. using *tert*-butyl lithium [21]. The two dimethylamino groups were replaced by acetoxy groups and subsequently eliminated upon heating in acetic anhydride [25] yielding divinyl compound **2**. We also recovered partially eliminated vinyl carbinol **4** and vinyl acetate **5**.



Scheme 1. Synthesis of the title compound. All compounds are of (S_p,S_p)-configuration.

In the beginning, we planned to cyclize divinyl compound **2** via ring-closing metathesis (RCM), yet only recovered starting materials. Since amino groups are known to inhibit olefin metathesis catalysts [26], we suspected the phosphine may inhibit the catalyst. Consequently, we attempted RCM with the phosphine **2** protected as phosphine oxide or phosphine sulfide without success. We assume the two vinyl groups are too far apart to facilitate the metathesis. Hence we looked for an alternative way to couple the vinyl groups.

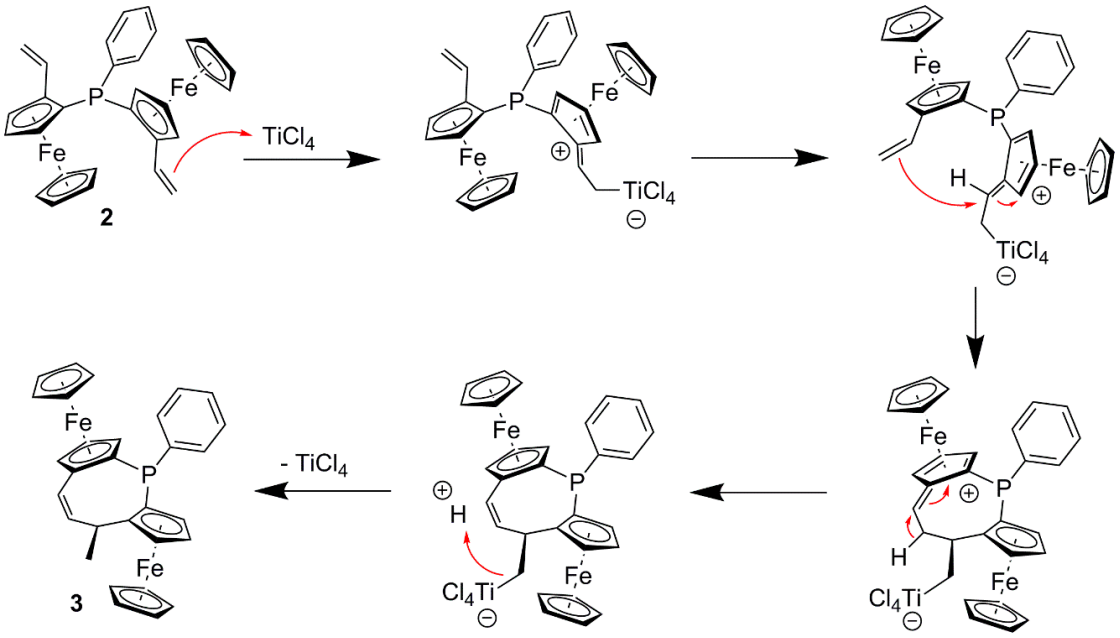
Inspired by radical-driven olefin polymerizations, we attempted vinyl coupling with radical starter AIBN, yet we only recovered oxidized starting material.

Gschwend et al. reported on an unintended Lewis-acid driven reaction of a vinylferrocene leading to a coupling of the vinyl moieties [25]. Similar acid-catalyzed hydrovinylation reactions have been published previously for simple vinyl ferrocenes [27–29]. Thus, we attempted to close the ring via $TiCl_4$-mediated hydrovinylation as well, yielding the carbon-bridged title compound **3** in low yield as confirmed by NMR (see the Supplementary Materials). The compound contains some moisture and impurities which could not be removed after repeated filtration, chromatography and drying. While we did not isolate oligomers of **2**, we conjecture that polymerization of the starting material could explain the observed low yield. Previously, we reported on ring-opening side reactions occurring on 8-membered diferroceno cycles [18]. Hence polymerization may be favored over cyclization.

Only one diastereomer was found in the reaction mixture. The sensitive phosphine was oxidized in the acidic reaction medium despite the inert reaction conditions applied. Attempts to perform the same reaction with a divinyl phosphine sulfide analogue yielded an inseparable mixture of product, hence this compound was not included in this article.

We propose a cationic coupling mechanism depicted in Scheme 2. Initially, the acidic Ti(IV) attacks a vinyl group, inducing a fulvene-like carbenium cation. Since we recovered only one diastereomer, we assume that either the association occurs diastereoselectively, or only one of the two possible intermediates is stable enough to proceed. The resulting electron-poor vinyl group is then nucleophilically attacked by the other vinyl group. This attack occurs regioselectively as to locate the resulting carbenium cation quasi-benzylic, hence forming the 1,3-(3-methyl)propylene bridge. Stereochemically, the methyl group will be oriented away from the ferrocene group it is adjacent to,

since S_N1 reactions on ferrocenyl carbon atoms are known to be stereo-conservatively driven by the voluminous metallocene unit [30]. The Ti-C bond is cleaved upon protonolysis.



Scheme 2. Proposed Lewis acid-hydrovinylation mechanism.

In Reference [25], the authors propose that instead of the Ti-C adduct, the reaction is catalyzed by protons originating from $TiCl_4$ hydrolysis caused by solvent moisture. However, this proposed mechanism cannot explain why the hydrovinylation product was not found when using $AlCl_3$ as a Lewis acid instead [25], which would also readily undergo hydrolysis.

3. Materials and Methods

3.1. General

Melting points were measured on a Reichelt Thermovar Kofler apparatus, uncorrected. HRMS were recorded by a Bruker Maxis ESI oa-RTOF mass spectrometer (maXis ESI-Qq-TOF mass spectrometer, Bruker Daltonics, Bremen, Germany) equipped with a quadrupole analyzer ion guide. Routine NMR spectra were recorded on a 400 MHz Bruker AVIII 400 spectrometer (Bruker Biospin, Billerica, MA, USA) operating at 400.27 MHz (^{1}H), 100.66 MHz (^{13}C) and 162.04 MHz (^{31}P) with autosampler. ^{1}H-NMR spectra and ^{13}C-NMR spectra used for substance characterization were recorded either on a 600 MHz Bruker AVIII 600 spectrometer (Bruker Biospin) operating at 600.25 MHz (^{1}H) and 150.95 MHz (^{13}C) or on a Bruker AVIII 700 spectrometer at 700.40 MHz (^{1}H) and 176.13 MHz (^{13}C). ^{13}C-NMR spectra were recorded in *J*-modulated mode. NMR chemical shifts are referenced to non-deuterated $CHCl_3$ residual shifts: At 7.26 ppm for ^{1}H-NMR, at 77.00 ppm to $CDCl_3$ for ^{13}C-NMR and at 0.00 ppm to 85% H_3PO_4 for ^{31}P-NMR.

Reaction progress was monitored by TLC. Preparative column chromatography was carried out by a Biotage Isolera One automated flash chromatography instrument using self-packed columns containing SiO_2—Macherey–Nagel silica gel 60 M (particle size 40–63 µm). All the other chemicals were analytical grade and used without further purification.

3.2. Synthesis

3.2.1. 1,1-(Phenylphosphinidene)di[(2S_p)-2-vinyl]ferrocene **2**:

Diaminophosphine **1** (760 mg, 1.26 mmol) was suspended in Ac_2O (6.3 mL). The orange solution was degassed three times, then stirred and heated under Ar to about 100 °C (oil bath temperature ~120 °C) for 80 min while the starting material dissolved and the color of the solution changed from orange via red to black. The mixture was cooled to room temperature (r.t.) and Ac_2O was removed under reduced pressure. The black residue was dried and purified by column chromatography (SiO_2; 0%–10% EtOAc in heptane) yielding 74% of divinylphosphine **2** (481 mg) as an orange-to-reddish crystalline solid (eluated at 2% EtOAc in heptane) as well as traces of carbinol **4** (eluated at 9% EtOAc in heptane) and acetate **5** (eluated at 5% EtOAc in heptane).

2: m.p.: 168–169 °C. ^{1}H-NMR (600 MHz) δ = 7.54–7.50 (m, 2H); 7.34–7.30 (m, 3H); 7.23 (ddd, *J* = 17.8, 10.8, 2.7 Hz, 1H); 6.54 (ddd, *J* = 17.5, 10.9, 1.4 Hz, 1H); 5.49 (dt, *J* = 17.6, 1.5 Hz, 1H); 5.22 (dt, *J* = 17.5, 1.3 Hz, 1H); 5.17 (dd, *J* = 10.8, 1.4 Hz, 1H); 4.90 (dd, *J* = 10.8, 1.4 Hz, 1H); 4.79 (m, 1H); 4.56 (m, 1H); 4.38 (pt, *J* = 2.6 Hz, 1H); 4.24 (pt, *J* = 2.5 Hz, 1H); 4.03 (s, 5H); 3.89 (s, 5H); 3.89 (m, 1H); 3.80 (m, 1H) ppm. ^{13}C-NMR δ = 138.48 (d, J_{CP} = 8.1 Hz, C_q); 134.27 (d, J_{CP} = 13.4 Hz, CH); 134.12 (d, J_{CP} = 21.6 Hz, CH); 133.47 (d, J_{CP} = 9.4 Hz, CH); 127.80 (d, J_{CP} = 7.9 Hz,); 111.63 (d, J_{CP} = 1.8 Hz, CH_2); 110.91 (CH_2); 88.72 (d, J_{CP} = 24.7 Hz, C_q); 86.70 (d, J_{CP} = 18.2 Hz, C_q); 80.09 (d, J_{CP} = 6.2 Hz, C_q); 76.32 (d, J_{CP} = 9.6 Hz, C_q); 72.72 (d, J_{CP} = 5.6 Hz, CH); 71.94 (d, J_{CP} = 2.9 Hz, CH); 70.87 (d, J_{CP} = 23.4 Hz, CH); 70.32 (CH); 70.22 (CH); 68.69 (CH); 67.34 (d, J_{CP} = 2.2 Hz, CH); 66.34 (d, J_{CP} = 3.6 Hz, CH) ppm. ^{31}P-NMR δ = −41.89 (s) ppm. HRMS: *m*/*z* calculated for $C_{30}H_{27}Fe_2P$ $[M]^+$: 530.0549, found: 530.0548; $[M + H]^+$: 531.0627, found: 531.0616; $[M + Na]^+$: 553.0447, found: 553.0445.

4: ^{1}H-NMR (600 MHz) δ = 7.65–7.60 (m, 2H); 7.40–7.35 (m, 3H); 7.21 (ddd, J = 17.5, 10.8, 2.4 Hz, 1H); 5.49 (d, J = 17.5 Hz, 1H); 5.17 (pd, J = 10.9 Hz, 1H); 4.87 (m, 1H); 4.80 (m, 1H); 4.41 (m, 1H); 4.34 (m, 1H); 4.19 (pt, J = 2.3 Hz, 1H); 4.07 (s, 5H); 4.03 (s, 1H); 3.86 (s, 5H); 3.83 (m, 1H); 1.38 (d, J = 6.5 Hz, 3H); 1.10 (s, 1H) ppm. ^{13}C-NMR δ = 139.36 (d, J_{CP} = 8.2 Hz, C_q); 134.27 (d, J_{CP} = 22.1 Hz, CH); 134.11 (d, J_{CP} = 13.7 Hz, CH); 129.52 (CH); 128.41 (d, J_{CP} = 8.0 Hz, CH); 111.13 (CH_2); 94.96 (d, J_{CP} = 18.9 Hz, C_q); 88.96 (d, J_{CP} = 26.0 Hz, C_q); 79.83 (d, J_{CP} = 6.1 Hz, C_q); 75.04 (d, J_{CP} = 10.1 Hz, C_q); 72.58 (d, J_{CP} = 5.7 Hz, CH); 71.30 (d, J_{CP} = 3.2 Hz, CH); 70.67 (CH); 70.18 (CH); 69.56 (CH); 68.45 (d, J_{CP} = 3.3 Hz, CH); 68.12 (CH); 66.54 (d, J_{CP} = 4.0 Hz, CH); 65.48 (d, J_{CP} = 6.9 Hz, CH); 21.74 (CH_3) ppm. ^{31}P-NMR δ = −42.86 (s) ppm. HRMS: *m*/*z* calculated for $C_{30}H_{29}Fe_2OP$ $[M + H]^+$: 549.0733, found: 549.0711; $[M + Na]^+$: 571.0553, found: 571.0539.

5: ^{1}H-NMR (600 MHz) δ = 7.52 (pt, J = 7.2 Hz, 2H); 7.35–7.28 (m, 3H); 7.23 (dd, J = 17.0, 10.6 Hz, 1H); 6.10 (m, 1H); 5.45 (d, J = 17.7 Hz, 1H); 5.13 (d, J = 10.8 Hz, 1H); 4.77 (m, 1H); 4.43 (m, 1H); 4.39 (m, 1H); 4.27 (m, 1H); 4.04 (s, 5H); 3.96 (m, 1H); 3.95 (m, 1H); 3.81 (s, 5H); 1.56 (d, J = 6.3 Hz, 3H); 1.17 (s, 3H) ppm. ^{13}C-NMR δ = 169.85 (C_q); 138.95 (d, J_{CP} = 8.3 Hz, C_q); 134.43 (d, J_{CP} = 13.7 Hz, CH); 134.14 (d, J_{CP} = 22.0 Hz, CH); 128.59 (CH); 127.71 (d, J_{CP} = 7.9 Hz, CH); 110.72 (CH_2); 90.08 (d, J_{CP} = 22.2 Hz, C_q); 88.67 (d, J_{CP} = 26.2 Hz, C_q); 80.91 (d, J_{CP} = 8.3 Hz, C_q); 76.25 (d, J_{CP} = 10.8 Hz, C_q); 72.90 (d, J_{CP} = 7 Hz, CH); 72.08 (d, J_{CP} = 4.0 Hz, CH); 70.51 (CH); 70.24 (CH); 69.67 (CH); 68.80 (d, J_{CP} = 3.2 Hz, CH); 68.54 (CH); 68.28 (d, J_{CP} = 8.9 Hz, CH); 66.19 (d, J_{CP} = 3.9 Hz, CH); 20.26 (CH_3); 18.74 (CH_3) ppm. ^{31}P-NMR δ = −45.17 (s) ppm. HRMS: *m*/*z* calculated for $C_{32}H_{31}Fe_2O_2P$; $[M + O + Na]^+$: 629.0607, found 629.0590.

3.2.2. (2S_p,4*R*,8S_p)-4-Methyl-1-phenyl-diferroceno-5-*Z*-ethylene-1-phosphinoxide **3**:

Divinylphosphine **2** (52 mg, 0.10 mmol) was dissolved in toluene (3 mL) set under Ar. The orange solution was degassed three times and cooled in an ice bath. TiCl4 (33 μL, 0.30 mmol, 3.0 equiv.) was added to the solution. The resulting dark green suspension was stirred at 0 °C for 30 min, warmed to r.t., stirred for 1 h, heated to reflux and stirred for 1 h. The green suspension was cooled to r.t. Sat. aq. $NaHCO_3$ (3 mL) was added, upon which the color of the suspension turned back to orange.

The reaction mixture was filtered over SiO_2 and washed after with EtOAc. The resulting solution was washed with 3 mL of water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, 40–100% EtOAc in heptane) yielding 13% of phosphineoxide diferrocenyl cycle **3** (7 mg) as a glassy yellow solid.

^{1}H-NMR (700 MHz) δ = 7.98–7.94 (m, 2H); 7.45–7.40 (m, 3H); 6.30 (d, J = 10.3 Hz, 1H); 5.67 (dd, J = 10.2, 9.3 Hz, 1H); 4.99 (m, 1H); 4.46 (m, 1H); 4.37 (m, 1H); 4.35 (m, 1H); 4.31 (m, 1H); 4.24 (m, 1H); 4.23 (m, 1H); 4.22 (s, 5H); 3.78 (s, 5 H); 1.33 (d, J = 6.8 Hz, 3H) ppm. ^{13}C-NMR δ = 141.33 (CH); 131.37 (d, J_{CP} = 10.2 Hz, CH); 130.76 (d, J_{CP} = 2.3 Hz, CH); 127.51 (d, J_{CP} = 12.2 Hz, CH); 125.52 (CH); 95.71 (C_q); 84.63 (C_q); 74.56 (d, J_{CP} = 11.7 Hz, CH); 72.25 (d, J_{CP} = 13.0 Hz, CH); 72.23 (d, J_{CP} = 10.0 Hz, CH); 70.38 (CH); 70.30 (CH); 69.93 (d, J_{CP} = 9.9 Hz, CH); 69.40 (d, J_{CP} = 11.2 Hz, CH); 68.76 (d, J_{CP} = 10.2 Hz, CH); 32.32 (CH); 21.35 (CH_3) ppm; 4 C_q not observed. ^{31}P-NMR δ = 29.84 (s) ppm. HRMS: *m*/*z* calculated for $C_{30}H_{27}Fe_2OP$ $[M + H]^+$: 547.0577, found: 547.0564.

Supplementary Materials: The following are available online: Figure S1: ^{1}H-NMR spectrum of compound **2**, Figure S2: ^{13}C-NMR spectrum of compound **2**. Figure S3: ^{31}P-NMR spectrum of compound **2**, Figure S4: HRMS spectrum of compound **2**, Figure S5: ^{1}H-NMR spectrum of compound **3**. Figure S6: ^{13}C-NMR spectrum of compound **3**. Figure S7: ^{31}P-NMR spectrum of compound **3**. Figure S8: HRMS spectrum of compound **3**. Figure S9: ^{1}H-NMR spectrum of compound **4**. Figure S10: ^{13}C-NMR spectrum of compound **4**. Figure S11: ^{31}P-NMR spectrum of compound **4**. Figure S12: HRMS spectrum of compound **4**. Figure S13: HRMS spectrum of compound **4** (detailed). Figure S14: ^{1}H-NMR spectrum of compound **5**. Figure S15: ^{13}C-NMR spectrum of compound **5**. Figure S16: ^{31}P-NMR spectrum of compound **5**. Figure S17: HRMS spectrum of compound **5**.

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