

Preparation and characterization of 1,1'-diphosphaferrocenes with linearly fused six-membered carbocycles

Masamichi Ogasawara ^{*}, Takeshi Sakamoto, Kiyohiko Nakajima, Tamotsu Takahashi ^{*}

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University and SORST, Japan Science and Technology Corporation (JST), Kita-ku, Sapporo 001-0021, Japan
Department of Chemistry, Aichi University of Education, Igaya, Kariya, Aichi 448-8542, Japan

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Abstract

Zirconacyclopentadiene-mediated homologation method was applied to preparation of a couple of 1,1'-diphosphaferrocene derivatives with linearly fused six-membered carbocycles. The solid-state structure of bis(hexapropylidihydro-*iso*-naphthophospholyl)iron(II) complex (**1**) was studied by X-ray single-crystal structure determination.
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1. Introduction

Recently, we developed a novel method of constructing linearly fused six-membered carbocycles (“homologation” method) [1] taking advantage of zirconium-mediated reactions which produced a variety of aromatic compounds [2,3]. Key intermediates of the protocol, zirconacyclopentadienes, have been also known as useful synthetic intermediates to phospholes (Fig. 1) [4,5]. Phospholyl anions (phospholides), which are easily generated from the corresponding phospholes, show a variety of coordination modes and are interesting subjects for coordination chemistry [6]. Among many transition metal-phospholyl complexes, those with divalent iron (phosphaferrocenes) are arguably the most extensively studied class of phosphametalloenes. Here, we would like to report application of the homologation method to synthesis of diphosphaferrocene derivatives in which phospholide ligands fused with six-

membered carbocycles in a linear fashion coordinate to the iron(II) center.

2. Results and discussion

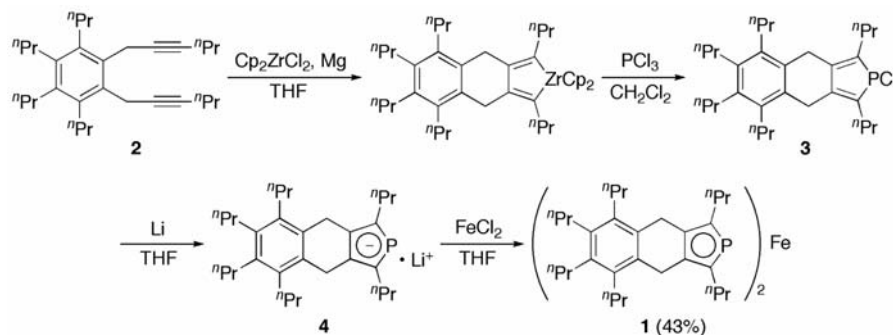
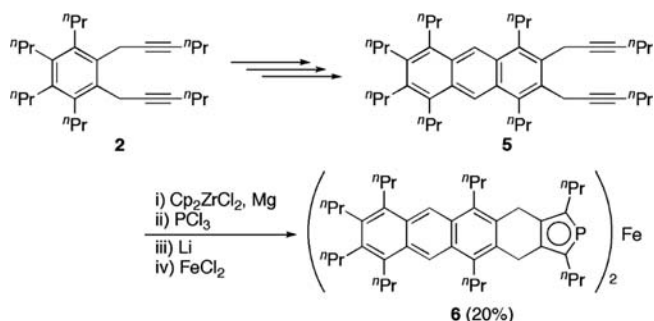
2.1. Preparation of diphosphaferrocenes **1** and **6**

Synthesis of 1,1'-diphosphaferrocene **1**, which is with tricyclic phospholyl ligands, is illustrated in Scheme 1. *P*-Chlorophosphole **3** was prepared from 1,2-di(2-hexynyl)-3,4,5,6-tetrapropylbenzene (**2**) [1] and PCl₃ using zirconacyclopentadiene-mediated reaction as reported by Fagan and Nugent [4]. Treatment of the crude **3** with lithium metal in THF gave the corresponding lithium phospholide **4** as a deep-red solution. Subsequent reaction of **4** with anhydrous FeCl₂ afforded **1** in 43% overall yield as orange-red crystals after purification by column chromatography followed by recrystallization from EtOH.

A diphosphaferrocene with longer fused carbocycles could be prepared by utilizing the zirconium-mediated homologation method twice (Scheme 2). Anthracene derivative **5**, which was derived from **2** in four steps [1], was treated in the similar manner as shown in Scheme 1 and the

^{*} Corresponding authors. Fax: +81 11 706 9150.

E-mail addresses: ogasawar@cat.hokudai.ac.jp (M. Ogasawara), tamotsu@cat.hokudai.ac.jp (T. Takahashi).

Scheme 1. Synthesis of diphosphaferrocene **1** with tricyclic phospholides.Scheme 2. Synthesis of diphosphaferrocene **6** with pentacyclic phospholides.

diphosphaferrocene **6** was obtained in 20% overall yield as an orange solid.

2.2. Spectroscopic characterization of diphosphaferrocenes **1** and **6**

Coordination of the polycyclic phospholyl ligands in an η^5 -fashion at the phosphacyclopentadienyl moiety in **1** was confirmed by ^1H and ^{13}C NMR measurements. Upon η^5 -coordination to the iron(II) center, two faces of the phospholide became inequivalent. And thus, the two CH_2 hydrogens at both 4- and 9-positions were inequivalent each other and were detected as a pair of AB doublets at δ 3.47 and 3.81 with $J = 18.8$ Hz in the ^1H NMR spectrum. The ^{13}C NMR spectrum of **1** showed a C_α signal at δ 97.9 ($J_{\text{PC}} = 57.9$ Hz) and a C_β signal at δ 95.1 ($J_{\text{PC}} = 3.7$ Hz). These chemical shifts and coupling constants are comparable to those reported for phosphaferrrocene derivatives [6]. The diphosphaferrocene **6** shows analogous ^1H and ^{13}C NMR characteristics as well.

The ^{31}P NMR resonances of the diphosphaferrocenes **1** and **6** are detected at -55.3 and -59.6 , respectively. These chemical shifts are comparable to those of known phosphaferrrocenes [6]. It was reported recently that ^{31}P NMR chemical shifts of diphosphaferrocenes were sensitive to relative orientation of two phosphorus nuclei in a single molecule [7]. Diphosphaferrocenes with forced eclipsed geometry of two phosphorus nuclei showed their ^{31}P NMR signals in unusual upper fields at around δ -90 .

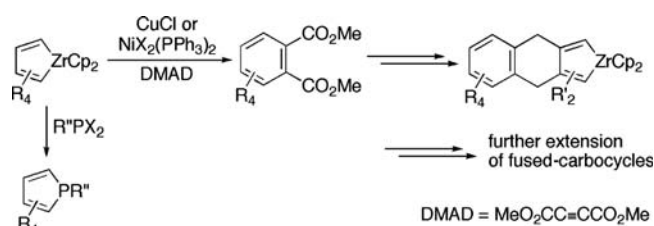
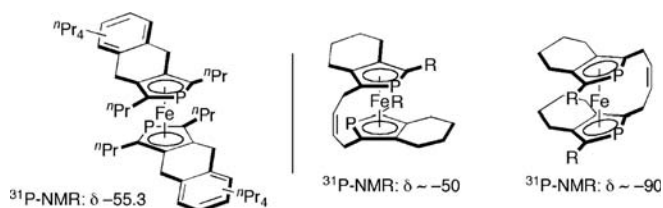


Fig. 1. Zirconacyclopentadiene-mediated synthesis of fused-carbocycles and phospholes.

The observed ^{31}P NMR signals for **1** and **6** indicate that dominant conformations of these diphosphaferrocenes in CDCl_3 are staggered (Fig. 2).

2.3. X-ray crystal structures of diphosphaferrocene **1**

Recrystallization of the diphosphaferrocene **1** from absolute ethanol gave prismatic crystals and the solid-state structure was clarified by X-ray single-crystal structure determination (Fig. 3). Selected crystallographic data are summarized in Table 1 and selected bond lengths and angles are listed in Table 2. The iron atom in **1** is located at the center of symmetry. The two phospholyl rings are parallel and attain a staggered conformation. This observation is consistent with the solution conformation of **1** deduced from the ^{31}P NMR chemical shift (*vide supra*). The nearly planar phospholyl moieties are slightly distorted and the phosphorus atom lies out of the $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{C}(3)\text{--}\text{C}(4)$ plane by 0.039 Å away from the central metal. The angle between the phospholyl plane and the C_6Pr_4 plane is 20.17° and the $(\text{--CH}_2)_2\text{C}_6\text{Pr}_4$ moiety bends toward the iron atom. The distance between a least-squares

Fig. 2. Relation between diphosphaferrocene conformation and ^{31}P NMR chemical shifts.

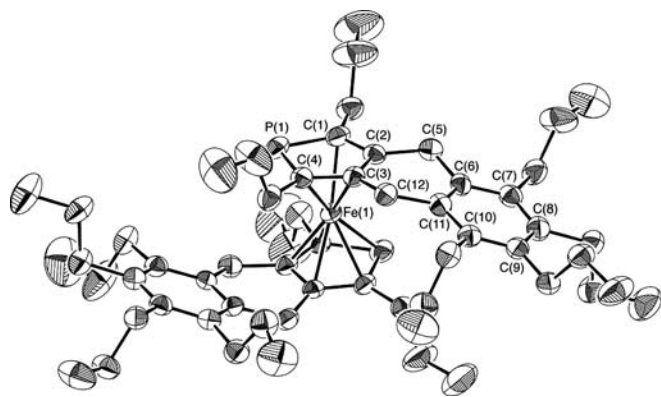


Fig. 3. ORTEP of **1** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data for diphosphaferrocene **1**

Formula	1 C ₆₀ H ₉₂ FeP ₂
fw	931.18
Color, habit	Orange, prismatic
Crystal size (mm)	0.30 × 0.20 × 0.20
Crystal system	Monoclinic
Space group	C2/c (#15)
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	21.472(2)
<i>b</i> (Å)	15.063(1)
<i>c</i> (Å)	18.483(1)
β (°)	104.569(1)
<i>V</i> (Å ³)	5786.0(7)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.069
μ (cm ⁻¹)	0.349
Radiation type	Mo K α
Wavelength (Å)	0.7107
<i>T</i> (K)	298.2
$2\theta_{\max}$ (°)	55
Number of reflections collected	6620
Unique	2194
Parameters	285
Refinements on	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2.0 σ (<i>F</i> ²)]	0.0683
<i>R</i> _w [<i>F</i> ² > 2.0 σ (<i>F</i> ²)]	0.0718
GOF	1.509
Residual ρ (e Å ⁻³)	+0.39 and -0.27

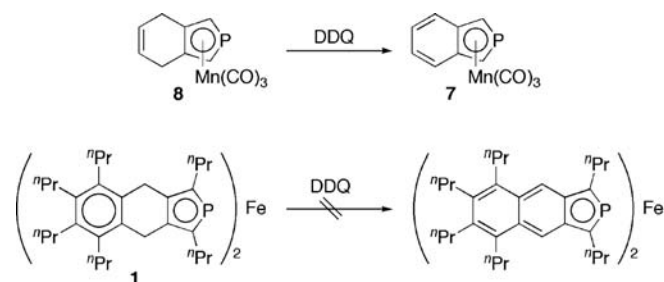
plane of the phospholyl ligand and the iron center is 1.670 Å. This distance is within a range of those in the other structurally characterized diphosphaferrocenes [5d,8]; steric influence of the fused carbocycles on the diphosphaferrocene local structure was hardly detected in **1**.

2.4. Attempted oxidation of dihydronaphthophospholides in **1**

The phospholyl ligands in the present diphosphaferrocenes possess dihydro-*iso*-phosphindolyl substructure. Whereas η^5 -*iso*-phosphindolyl complexes have been unknown except a very recent report on a phosphacymantine derivative **7** [9], we were interested in dehydrogenation

Table 2
Selected bond distances (Å) and angles (°) for **1**

<i>Bond distances</i> (Å)			
Fe(1)–P(1)	2.287(2)	P(1)–C(1)	1.756(8)
Fe(1)–C(1)	2.086(7)	P(1)–C(4)	1.777(8)
Fe(1)–C(2)	2.050(6)	C(1)–C(2)	1.414(9)
Fe(1)–C(3)	2.092(7)	C(2)–C(3)	1.396(9)
Fe(1)–C(4)	2.108(6)	C(3)–C(4)	1.397(9)
<i>Bond angles</i> (°)			
C(1)–P(1)–C(4)	89.8(4)	C(3)–C(2)–C(5)	120.1(7)
P(1)–C(1)–C(2)	111.9(6)	C(2)–C(3)–C(12)	122.0(6)
C(1)–C(2)–C(3)	113.3(7)	C(2)–C(5)–C(6)	114.5(6)
C(2)–C(3)–C(4)	112.6(7)	C(3)–C(12)–C(11)	115.1(6)
C(3)–C(4)–P(1)	112.3(6)		



Scheme 3. Attempted DDQ-dehydrogenation of **1**.

of **1**. The complex **7** was prepared from the corresponding dihydro-*iso*-phosphindolyl species **8** by DDQ oxidation (Scheme 3). Treatment of **1** under the identical conditions (benzene reflux with 1.2 equiv. of DDQ), however, did not produce the desired dehydrogenated species and the starting compound was cleanly recovered. No reaction was detected even under more harsh conditions (mesitylene reflux with a large excess of DDQ). The robustness of **1** toward dehydrogenation could be ascribed to the fused tetrapropylbenzo-moiety. Dehydrogenation of the central six-membered ring of the phospholide in **1** would result in a thermodynamically unfavorable loss of local aromaticity in the terminal six-membered ring.

3. Experimental section

3.1. General information

All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under pre-purified argon. Tetrahydrofuran (from sodium benzophenone-ketyl) and dichloromethane (from CaH₂) were distilled under nitrogen prior to use. Ethanol was dried over magnesium, distilled, and stored in a flask with a Teflon stopcock. 1,2-Di(2-hexynyl)-3,4,5,6-tetrapropylbenzene (**2**) and 2,3-di(2-hexynyl)-1,4,5,6,7,8-hexapropylanthracene (**5**) were synthesized as reported [1]. All the other chemicals

were obtained from commercial sources and used without further purification. ^1H (400 MHz) and ^{13}C (101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (162 MHz) chemical shifts are externally referenced to 85% H_3PO_4 .

3.2. Bis(1,2,3,10,13- η^5 -1,3,5,6,7,8-hexapropyl-4,9-dihydro-2H-2-phosphacyclopenta[b]naphthalen-2-yl)iron(II) (**1**)

The 1,1'-diphosphaferrocene **1** was prepared according to the method reported by Mathey and co-workers for preparation of octaethyl-1,1'-diphosphaferrocene with slight modifications [5d]. To a suspension of activated magnesium (170 mg, 7.0 mmol) in THF (5 mL) was added a solution of Cp_2ZrCl_2 (2.00 g, 6.84 mmol) and 1,2-di(2-hexynyl)-3,4,5,6-tetrapropylbenzene (**2**, 2.77 g, 6.81 mmol) in THF (20 mL), and the mixture was stirred at room temperature over night. During this period, most of Mg were consumed. The resulting mixture was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 (20 mL), which was then filtered through a pad of Celite. To the filtrate was added PCl_3 (1.0 g, 7.3 mmol) at 0 °C and the mixture was stirred at room temperature for 2 h. The solution was evaporated to dryness under reduced pressure and the residue was extracted with hexane. After filtration, the hexane solution was concentrated to give a crude *P*-chlorophosphole. The *P*-chlorophosphole was dissolved in THF (15 mL) and to this was added lithium (ca. 240 mg; ca. 35 mmol) which was cut in small pieces, then the mixture was stirred at room temperature for 1 h. The dark-red mixture was transferred onto a slurry of FeCl_2 (420 mg, 3.3 mmol) in THF (5 mL) using cannula and the mixture was stirred at 60 °C for 2 h. The mixture was evaporated to dryness under reduced pressure and the residue was extracted with hexane. The crude product was chromatographed on silica gel (hexane/benzene = 10/1) under nitrogen and following recrystallization from EtOH gave three crops of **1** in analytically pure form. Yield: 1.33 g (43%). ^1H NMR (CDCl_3): δ 0.79 (t, $J = 7.3$ Hz, 12H), 1.05–1.10 (m, 24H), 1.15–1.38 (m, 8H), 1.46–1.74 (m, 20H), 1.93–2.08 (m, 4H), 2.50–2.60 (m, 16H), 3.47 (d, $J = 18.8$ Hz, 4H), 3.81 (d, $J = 18.8$ Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 14.31, 15.17, 15.19, 23.66, 25.18, 25.85 (d, $J_{\text{PC}} = 6.2$ Hz), 27.33, 30.63 (d, $J_{\text{PC}} = 18.1$ Hz), 31.90, 32.13, 95.11 (d, $J_{\text{PC}} = 3.7$ Hz), 97.88 (d, $J_{\text{PC}} = 57.9$ Hz), 130.21, 136.43, 136.88. ^{31}P NMR (CDCl_3) δ –55.3. Anal. Calc. for $\text{C}_{60}\text{H}_{92}\text{P}_2\text{Fe}$: C, 77.39; H, 9.96. Found: C, 77.23; H, 10.01%.

3.3. Bis(1,2,3,14,21- η^5 -1,3,5,7,8,9,10,12-octapropyl-4,13-dihydro-2H-2-phosphacyclopenta[b]naphthalen-2-yl)iron(II) (**6**)

The diphosphaferrocene **6** was prepared in a similar manner as for the preparation of **1** starting with 2,3-di(2-hexynyl)-1,4,5,6,7,8-hexapropylanthracene (**5**, 1.06 g, 1.79 mmol). The crude product was chromatographed on

silica gel (hexane/ $\text{Et}_2\text{O} = 10/1$) under nitrogen and following recrystallization from CHCl_3 /hexane gave **6** as orange powder. Yield: 230 mg (20%). ^1H NMR (CDCl_3): δ 0.88 (t, $J = 7.3$ Hz, 12H), 1.12 (t, $J = 7.3$ Hz, 12H), 1.13 (t, $J = 7.3$ Hz, 12H), 1.16 (t, $J = 7.3$ Hz, 12H), 1.25–1.47 (m, 8H), 1.63–1.80 (m, 24H), 1.84–1.92 (m, 4H), 2.06–2.16 (m, 4H), 2.78–2.95 (m, 16H), 3.00–3.16 (m, 8H), 3.64 (d, $J = 19.3$ Hz, 4H), 4.03 (d, $J = 19.3$ Hz, 4H), 8.54 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 14.34, 15.02, 15.04, 15.13, 23.28, 24.49, 25.07, 25.76, 27.78, 30.45 (d, $J_{\text{PC}} = 19.6$ Hz), 31.00, 31.85, 32.88, 95.20 (d, $J_{\text{PC}} = 1.9$ Hz), 96.80 (d, $J_{\text{PC}} = 58.9$ Hz), 119.23, 128.76, 128.81, 129.10, 133.35, 133.51, 135.90. ^{31}P NMR (CDCl_3) δ –59.6. Anal. Calc. for $\text{C}_{88}\text{H}_{124}\text{P}_2\text{Fe}$: C, 81.32; H, 9.62. Found: C, 81.09; H, 9.73%.

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