Synthesis, Resolution, and Crystallographic Characterization of a C_2-Symmetric Diphosphaferrocene

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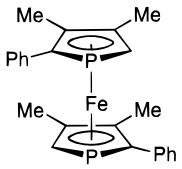
*Summary: Treatment of $FeCl_2$ with potassium 2-phenyl-3,4-dimethylphospholide provides a new C_2-symmetric diphosphaferrocene, (±)-3,3′,4,4′-tetramethyl-2,2′-diphenyl-1,1′-diphosphaferrocene (**1**). Separation by chiral HPLC furnishes both antipodes of complex **1**, the first diphosphaferrocene to be prepared in enantiopure form. The absolute configuration of (−)-**1** has been determined by X-ray crystallography.*

We have initiated a program directed at the development of applications of planar−chiral heterocycles in asymmetric catalysis. Our early work focused on the chemistry of π-bound nitrogen heterocycles, which we established serve as effective chiral nucleophilic catalysts[1] and as useful chiral ligands.[2] More recently, we have begun to explore the corresponding chemistry of π-bound *phosphorus* heterocycles.[3] At the time that we started this investigation, there were no reports of resolutions of this family of planar−chiral complexes. However, very recently Ganter has described the preparation of an enantiopure phosphaferrocene derivative through the use of a chiral auxiliary.[4] In this note, we establish, in the context of obtaining enantiopure diphosphaferrocene complex **1**, that chiral HPLC represents a viable alternate method for the resolution of planar−chiral phosphorus heterocycles. We have determined the absolute configuration of (−)-**1** by X-ray crystallography.



(-)-**1**

In light of Cowley's report that 1,1′-diphosphaferrocenes can serve as bidentate ligands for transition metals,[5] we decided to prepare an enantiopure C_2-symmetric diphosphaferrocene.[6] Complex **1** was an appealing target since phospholide **3** is readily available by a two-step route developed by Mathey.[7] We have found that treatment of **3** with $FeCl_2$ provides the desired diphosphaferrocene **1** and its meso isomer in 73% yield (eq 1). The diastereomers can be separated by HPLC on silica, and the enantiomers of **1** can then be resolved by HPLC on a chiral stationary phase (DAICEL CHIRALCEL OD column; α = 1.70; Figure 1).[8]

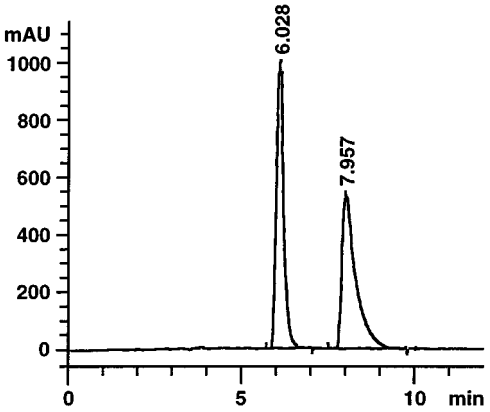
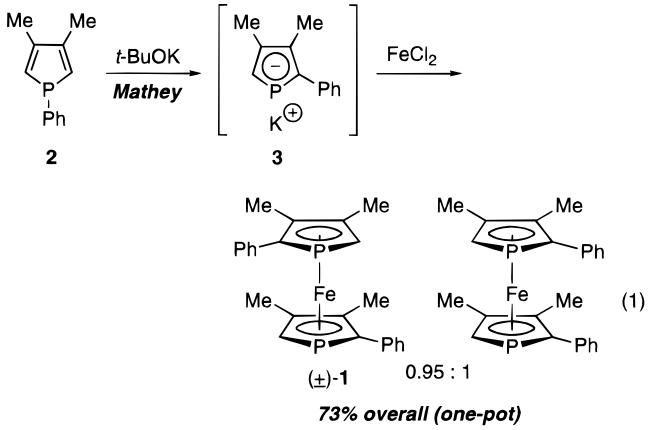


Figure 1. HPLC trace for (±)-**1** on a DAICEL CHIRACEL OD column (α = 1.70).



(1) (a) Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 1492−1493. (b) Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 7230−7231.

(2) Dosa, P. I.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 444−445.

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(4) Ganter, C.; Brassat, L.; Ganter, B. *Tetrahedron: Asymmetry* **1997**, *8*, 2607−2611.

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(6) (a) For the synthesis of 1, 1′-diphosphaferrocene, see: De Lauzon, G.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1978**, *156*, C33−C36. (b) For the synthesis of a racemic C_2−symmetric 1,1′-diphosphaferrocene derivative, see: de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994−1000.

(7) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98−100. Phosphole **2** can be synthesized in one step from commercially available $PhPCl_2$ and 2,3-dimethyl-1,3-butadiene. See: Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983−985.

(8) For precedent for the use of chromatography to resolve planar-chiral transition metal complexes, see: (a) Falk, H.; Schlögl, K. *Tetrahedron* **1966**, *22*, 3047−3053. (b) Falk, H.; Schlögl, K.; Steyrer, W. *Monatsh. Chem.* **1966**, *97*, 1029−1044.

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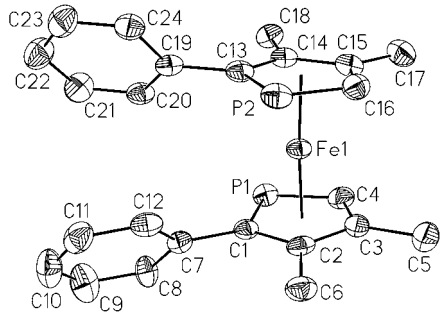

Figure 2. ORTEP illustration, with thermal ellipsoids drawn at the 35% probability level, of **1**.

Table 1. Crystallographic Data for 1

empirical formula	$C_{24}H_{24}FeP_2$
formula weight	430.22
cryst color, habit	red block
cryst dimens ($mm^{3)}$	0.15 × 0.27 × 0.45
cryst syst	monoclinic
space group	*C*2
a (Å)	22.9303(8)
b (Å)	11.3262(4)
c (Å)	16.6256(8)
β (deg)	105.5510(10)
V ($Å^3$)	4159.8(3)
Z	8
ρ_{calc}	1.374 Mg/m^3
radiation, monochromator	Mo Kα (λ = 0.710 69 Å), graphite
temp (K)	183(2)
μ(Mo Kα)	0.885 mm^{-1}
diffractometer	Siemens SMART/CCD (3-circle, χ fixed at 54.78°
scan type; limiting indices	ω; $-19 \le h \le 25$, $-11 \le k \le 12$, $-17 \le l \le 18$
θ range for collection	1.27° to 23.23°
total no. of reflns	8372
no. of unique reflns	5422 (R_{int} = 0.0342)
corrections	Lorentz−polarization; absorption (semiempirical from ψ-scans); max and min trans., 0.6199 and 0.5557
structure solution, refinement	direct methods, full-matrix least-squares on F^2
data/restraints/params	5415/1/488
R_1; wR_2 (data with $I > 2\sigma I$)	0.0396; 0.1020
R_1; wR_2 (all data)	0.0432; 0.1143
goodness of fit	1.057
ext coeff.; largest peak, hole	0.0007(2); 0.348 e $Å^{-3}$, −0.559 e $Å^{-3}$
absolute structure (Flack) param	−0.01(2)
programs used	Siemens software package: SMART, SAINT, XPREP, SHELXTL 5.0

Crystals of (−)-**1** grown from CH_2Cl_2/pentane proved to be suitable for an X-ray diffraction study, which established the absolute configuration of this enantiomer (Figure 2; Table 1). The structure resembles that of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[9] —the two phospholyl rings are nearly parallel (6° deviation from coplanarity) and adopt an eclipsed geometry relative to one another (Figure 3).[10] The Fe−centroid distance is 1.67 Å.

Thus, we have developed a straightforward method for the synthesis and resolution of a new C_2-symmetric diphosphaferrocene (**1**), the first diphosphaferrocene to be prepared in enantiopure form. HPLC on a chiral stationary phase provided an effective means for separating the enantiomers of **1**. We anticipate that complex **1** will find application in asymmetric catalysis.

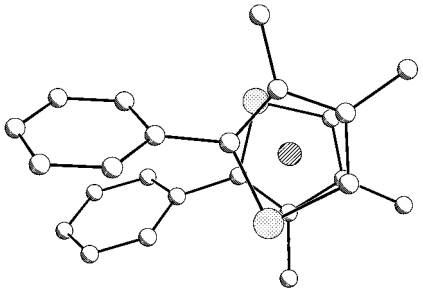

Figure 3. View of **1** from above.

Experimental Section

Synthesis of 3,3′,4,4′-Tetramethyl-2,2′-diphenyl-1,1′-diphosphaferrocene (1). In a closed Schlenk tube, a mixture of 3,4-dimethyl-1-phenylphosphole (1.88 g, 10.0 mmol) and *t*-BuOK (1.35 g, 12.0 mmol) in THF (10 mL) was heated (140 °C) with stirring under N_2 for 12 h.[7] The resulting yellow solution was transferred by cannula to a stirred slurry of $FeCl_2$ (Strem; 0.89 g, 7.0 mmol) in THF (20 mL) at room temperature, immediately forming a dark red mixture. The reaction was stirred at room temperature for 12 h, and then the solvent was removed in vacuo. The resulting dark brown residue was purified by column chromatography (20% benzene/hexane), which afforded 1.58 g (73%) of complex **1** and its meso isomer (0.95:1) as a red solid. The diastereomers were separated by HPLC (Alltech Econosphere 10 μ silica; 250 mm × 22 mm; CH_2Cl_2:hexane 8:92; 20 mL/min; the racemate eluted from 11.5 to 12.6 min).

(±)-**1**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.30 (m, 4H), 7.14 (m, 6H), 3.44 (m, 2H), 2.15 (s, 6H), 2.09 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 139.6 (apparent t, J_{C-P} = 8.6 Hz), 131.0 (apparent t, J_{C-P} = 4.8 Hz), 128.1, 126.5, 100.8, 94.5, 83.4 (d, J_{C-P} = 6.1 Hz), 82.6 (d, J_{C-P} = 6.2 Hz), 15.5, 13.9; ^{31}P NMR (CD_2Cl_2, 122 MHz): − 63.7; IR (KBr) 3448, 3025, 2922, 1595, 1492, 1441, 1374, 1028, 839, 749; HRMS calcd for $C_{24}H_{24}P_2Fe$ 430.0703, found 430.0704. Anal. Calcd for $C_{24}H_{24}P_2Fe$: C, 67.00; H, 5.62. Found: C, 67.30; H: 5.89.

The enantiomers of complex **1** were separated by chiral HPLC (14 mg per injection; DAICEL CHIRALCEL OD; 25 cm × 1 cm; chloroform:hexane 14:86; 2.5 mL/min). Enantiomer (+)-**1** ($[\alpha]^{20}_D$ = +441°, *c* = 0.10, THF) was collected from 5.8 to 6.8 min, and (−)-**1** was collected from 7.6 to 10.0 min.

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Supporting Information Available: Text giving the experimental details of the X-ray crystal structure determination and tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates (13 pages). Ordering information is given on any current masthead page.

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(10) For the structural characterization of 2,2′,5,5′-tetraphenyl-1,1′-diphosphaferrocene, see: Hitchcock, P. B.; Lawless, G. A.; Marziano, I. *J. Organomet. Chem.* **1997**, *527*, 305−308.