New Ferrocene Derivatives for Ligand Grafting

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Five new 1,2-disubstituted ferrocene derivatives have been efficiently synthesized. These compounds contain one protected phosphine function as thiophosphine, another coordination site (nitrogen or oxygen atom) and a function ready for the grafting on various supports. All compounds have been fully characterized by NMR (¹H, ³¹P and ¹³C) and High Resolution Mass Spectroscopy. The molecular structure of three of these ferrocene derivatives have been determined by X ray diffraction analysis on monocrystals.

Introduction

Catalysis is now a major tool to carry out organic transformations. Catalysis is commonly divided in homogeneous catalysis, where catalysts and reagents are in the same phase and heterogeneous catalysis where the catalytic reaction is carried out in multiphasic conditions. Even if homogeneous catalysts are often better defined and more selective, heterogeneous catalysts are much employed in industry because of the easier separation between catalysts and products at the end of the reaction, since the cost of the separation steps from the reaction mixture is estimated to be around 80% of the total cost for most chemical processes [1]. To try to benefit

from the advantages of both homogeneous and heterogeneous catalysis [1], a lot of efforts have been devoted in the last decades to develop supported homogeneous catalysis by grafting homogeneous catalysts on various supports like inorganic supports [2], polymers [3], dendrimers [4].

During the last years, we have been interested in the development of chiral ferrocene ligands for homogeneous catalysis [5] and we used these ligands in various catalytic asymmetric reactions, like asymmetric allylic substitution [6], asymmetric alkoxy-carbonylation [7], asymmetric hydrogenation

[8], asymmetric Suzuki-Miyaura coupling [9], etc.

In this paper, we want to present our work on the modification of P,N and P,O chiral ferrocene ligands with functions ready for the grafting on various supports.

Results and discussion

The synthesis of the different ferrocene ligands ready for grafting is presented in Scheme 1. All syntheses are based on the specific reactivity of the alcohol **1** which can be very efficiently activated by a strong acid like tetrafluoroboric acid, the carbocation-type intermediate being efficiently quenched by various nucleophiles [5]. These one-pot syntheses are realized within 5 minutes, including a chromatographic separation on silicagel. The reactions described in this article have been carried out with racemic **1** but both pure enantiomers of **1** are easily available [6d] and then compounds **2-6** in enantiomerically pure form should be easily available as well. The isolated yields in the desired products were good to excellent (from 61 to 95%). Compound **3** is a BOC-protected form of 2-thiodiphenylphosphino (aminomethyl) ferrocene which could be like compound **2** tether to various supports by reaction with an electrophilic reagents when compounds **4-6** need nucleophilic reagents to be grafted.

Scheme 1. Synthesis of new ferrocene derivatives for ligand grafting.

Monocrystals suitable for X-ray diffraction analysis of compounds **4-6** could be obtained by slow diffusion of hexane into dichloromethane solutions. Molecular view of the three structures are represented in Figures 1, 2 and 3 and comparison of select bond and angles are shown in Table 1. Compounds **5** and **6** differ only by the length of the O-(CH₂)_n-Br chain, 2 CH₂ for **5** and 3 CH₂ for **6**. The bond lengths and angle within the Fc(PS(C₆H₅)₂)CH₂X (X=N, O) framework are similar within experimental errors (Table 2). In compounds **5** and **6**, the Cp rings are roughly eclipsed with twist angle of 2.8(6)° and 2.5(5)° respectively, whereas in **4**, the Cp rings are rather eclipsed with a twist angle of 18.3(8)°. In the 3 compounds, as usual for such substituted ferrocene, the S atom is endo with respect to the Cp ring to which it is attached with distances

from the Cp of 1.23(2), 1.34(1) and 1.256(7) Å respectively for **4**, **5** and **6**. In compound **5** and **6**, the O1 is exo with respect to the C_P ring and the C2-C21-O1 plane is roughly perpendicular to the Cp with a dihedral angle of 88.3(4)° and 79.3(2)° respectively, whereas in compound **4** the N1 atom is endo with respect to the Cp ring and the dihedral angle between the Cp and the C2-C21-N1 plane is -32.9(9)°. In compound **4**, the N1-C22 distance, 1.304(11) Å is shorter than the N1-C21 of 1.444(11) Å indicating a partial double bond character as also underlined by the nearly planar arrangement of the four C21-N1-C22-O1 atoms: the largest deviation from the mean plane being 0.012(7) at C(22).

Figure 1: Molecular view of compound **4** with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small circle of arbitrary radii.

Figure 2: Molecular view of compound **5** with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small circle of arbitrary radii.

Figure 3: Molecular view of compound **6** with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small circle of arbitrary radii.

Table 1. Comparison of selected bond lengths [Å] and angles [°] for the 3 structure

	4	5	6
Fe(1)-Ct(1)	1.646(1)	1.637(1)	1.640(1)
Fe(1)-Ct(2)	1.666(1)	1.653(1)	1.658(1)
P(1)-C(1)	1.788(8)	1.798(3)	1.796(5)
P(1)-S(1)	1.962(3)	1.9535(12)	1.9582(17)
P(1)-C(111)	1.825(8)	1.819(4)	1.810(5)
P(1)-C(121)	1.818(8)	1.818(3)	1.808(5)
X(1)-C(21)	1.444(11)	1.426(4)	1.427(7)
X(1)-C(22)	1.304(11)	1.420(4)	1.415(7)
C(2)-C(21)	1.504(13)	1.490(5)	1.497(7)
C(22)-C(23)	1.508(11)	1.498(5)	1.492(9)
C(23)-C(24)		1.505(5)	
Br(1)-C(23)	1.943(8)	1.964(4)	1.935(7)

Ct(1)-Fe(1)-Ct(2)	176.7(2)	177.0(2)	177.2(2)
C(1)-P(1)-C(111)	102.2(2)	105.39(16)	102.8(4)
C(121)-P(1)-C(111)	106.3(2)	106.66(16)	107.1(4)
C(1)-P(1)-C(121)	105.6(2)	101.95(15)	103.3(4)
C(111)-P(1)-S(1)	113.00(17)	111.47(12)	112.9(3)
C(121)-P(1)-S(1)	111.62(18)	113.14(12)	113.3(3)
C(1)-P(1)-S(1)	117.16(17)	117.25(12)	116.3(3)
C(22)-O(1)-C(21)	111.4(4)	111.4(3)	126.2(8)
O(1)-C(21)-C(2)	108.6(4)	107.6(3)	111.1(8)
O(1)-C(22)-C(23)	109.5(5)	108.2(3)	118.2(7)
C(22)-C(23)-C(24)		114.3(3)	
C(22)-C(23)-Br(1)	111.9(4)	111.0(3)	112.6(6)

Conclusions

We successfully synthesized and fully characterized 5 new ferrocene compounds which after grafting and deprotection of the phosphine functions should provide supported P,N and P,P ligands.

Experimental part

General. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were carefully dried by conventional methods and distilled

under argon before use. 2-diphenylthiophosphinoferrocenyl)methanol **1** [10] was synthesized by literature procedures. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded with Bruker Avance 500 FT-NMR spectrometer. The resonances were calibrated relative to the residual solvent peaks and are reported with positive values downfield from TMS. For all characterized compounds, the peak assignments in the ^1H and ^{13}C NMR spectra were based on COSY, HSQC and HMBC 2D experiments. HRMS were obtained from dichloromethane solutions with a Xevo G2 Q TOF spectrometer by the electrospray method.

Synthesis of 2-thiodiphenylphosphino (*n*-hexylaminomethyl) ferrocene **2**

In a Schlenk tube, 2-thiodiphenyl phosphino (hydroxymethyl) ferrocene **1** (0.200 g, 0.46 mmol) was dissolved in 20 mL of dry dichloromethane. A 54% solution of tetrafluoroboric acid in ether (200 μL , 1.45 mmol, 3.15 eq.) was then added. After 1 min stirring, *n*-hexylamine (3.0 mL, 22.7 mol, 50eq) was added. After 1 min of stirring, the crude materials were filtered on silica gel with ether as an eluent. After evaporation of the solvent, 0.23 g of compound **2** as a yellow solid were obtained (yield = 95%).

^1H NMR (δ (ppm), CDCl_3): 7.83 (2H, dd, PPh_2); 7.70 (2H, dd, PPh_2); 7.47 (6H, m: PPh_2); 4.61 (1H, m: subst Cp); 4.32 (5H, s: Cp); 4.30

(1H, d, $J = 13.4$ Hz, AB system, CH₂); 3.76 (1H, m: subst Cp); 3.50 (1H, d, $J = 13.3$ Hz, AB system, CH₂); 2.36 (2H, m, NHCH₂CH₂); 1.80 (1H, bs, NH); 1.15 (8H, m, CH₂, Hex); 0.86 (3H, t: CH₃). **¹³C NMR** (δ (ppm), CDCl₃): 134.9 (d, $J_{PC} = 85.4$ Hz: quat PPh₂); 133.4 (d, $J_{PC} = 86.4$ Hz: quat PPh₂); 132.0 (d, $J_{PC} = 10.5$ Hz: PPh₂); 131.6 (d, $J_{PC} = 10.5$ Hz: PPh₂); 131.4 (d, $J_{PC} = 3.0$ Hz: PPh₂); 131.3 (d, $J_{PC} = 2.9$ Hz: PPh₂); 128.4 (d, $J_{PC} = 12.1$ Hz: PPh₂); 128.1 (d, $J_{PC} = 12.0$ Hz: PPh₂); 90.8 (d, $J_{PC} = 12.4$ Hz: quat Cp); 74.7 (d, $J_{PC} = 9.6$ Hz: substCp); 74.6 (d, $J_{PC} = 95.4$ Hz: quat Cp); 74.6 (d, $J_{PC} = 12.3$ Hz: subst Cp); 70.6 (s: Cp); 49.2 (fc-CH₂-NH); 47.3 (NHCH₂); 31.7 (CH₂, Hex); 29.7 (CH₂, Hex); 26.8 (CH₂, Hex); 22.6 (CH₂, Hex); 14.1 (CH₃). **³¹P NMR** (δ (ppm), CDCl₃): 43.6. **HRMS (ESI+)** m/e : 516.1570 (30%, 516.1577 for C₂₉H₃₅FeNPS (M+H⁺)).

Synthesis of 2-thiodiphenylphosphino (*t*-butyloxycarbonylaminomethyl) ferrocene 3
In a Schlenk tube, 2-thiodiphenyl phosphino(hydroxymethyl)ferrocene **1** (0.120 g, 0.276 mmol) was dissolved in 15 mL of dry dichloromethane. A 54% solution of tetrafluoroboric acid in ether (150 μ L, 1.09 mmol, 3.9 eq.) was then added. After 1 min stirring, *tert*-butylcarbamate (0.421 g, 3.6 mmol, 13 eq.) was added. After 1 min of stirring, the crude materials were filtered on silica gel with ether as an eluent. After evaporation of the solvent, 0.124 g of compound **3** as a yellow solid was obtained (yield = 84%).

¹H NMR (δ (ppm), CDCl₃): 7.83 (2H, m, PPh₂); 7.49 (8H, m: PPh₂); 5.06 (1H, m, NH); 4.68 (1H, m: subst Cp); 4.54 (1H, dd, CH₂); 4.30 (6H, s: Cp + subst Cp); 4.15 (1H, dd, CH₂); 3.74 (1H, m: subst Cp); 1.34 (9H, s: CH₃). **¹³C NMR** (δ (ppm), CDCl₃): 155.6 (HNCO); 134.9 (d, $J_{PC} = 86.3$ Hz: quat PPh₂); 133.0 (d, $J_{PC} = 84.6$ Hz: quat PPh₂); 132.0 (d, $J_{PC} = 11.1$ Hz: PPh₂); 131.6 (d, $J_{PC} = 10.5$ Hz: PPh₂); 131.4 (d, $J_{PC} = 3.1$ Hz: PPh₂); 131.3 (d, $J_{PC} = 2.9$ Hz: PPh₂); 128.5 (d, $J_{PC} = 12.7$ Hz: PPh₂); 128.1 (d, $J_{PC} = 12.5$ Hz: PPh₂); 90.7 (d, $J_{PC} = 12.2$ Hz: quat Cp); 78.7 (OC(CH₃)₃); 74.9 (d, $J_{PC} = 9.5$ Hz: substCp); 74.5 (d, $J_{PC} = 95.4$ Hz: quat Cp); 74.3 (d, $J_{PC} = 12.3$ Hz: subst Cp); 70.5 (s: Cp); 38.2 (CH₂); 28.3 (CH₃). **³¹P NMR** (δ (ppm), CDCl₃): 41.6. **HRMS (ESI+)** m/e : 554.0982 (100%, 554.0982 for C₂₈H₃₀FeNO₂PSNa (M+Na⁺)).

Synthesis of 2-thiodiphenylphosphino (bromoacetamidomethyl) ferrocene 4

In a Schlenk tube, 2-thiodiphenyl phosphino(hydroxymethyl) ferrocene **1** (0.200 g, 0.46 mmol) was dissolved in 20 mL of dry dichloromethane. A 54% solution of tetrafluoroboric acid in ether (200 μ L, 1.45 mmol, 3.15 eq.) was then added. After 1 min stirring, bromoacetamide (0.320 g, 2.3 mmol, 5 eq.) was added. After 1 min of stirring, the crude materials were filtered on silica gel with ether as an eluent. After evaporation of the solvent, 0.154 g of

compound **4** as a yellow solid was obtained (yield = 61%).

¹H NMR (δ (ppm), CDCl₃): 7.83 (2H, m, PPh₂); 7.52 (8H, m: PPh₂); 7.03 (bs, NH); 4.78 (1H, dd, CH₂); 4.69 (1H, m: subst Cp); 4.36 (1H, dd, CH₂); 4.32 (6H, s: Cp + subst Cp); 3.77 (1H, m: subst Cp); 3.52 (2H, d, AB system, J = 13.4 Hz, CH₂); 3.38 (2H, d, AB system, J = 13.9 Hz, CH₂). **¹³C NMR** (δ (ppm), CDCl₃): 164.8 (HNCO); 134.9 (d, J_{PC} = 86.5 Hz: quat PPh₂); 132.7 (d, J_{PC} = 86.5 Hz: quat PPh₂); 132.0 (d, J_{PC} = 10.9 Hz: PPh₂); 131.8 (d, J_{PC} = 10.5 Hz: PPh₂); 131.6 (d, J_{PC} = 3.0 Hz: PPh₂); 131.3 (d, J_{PC} = 2.9 Hz: PPh₂); 128.6 (d, J_{PC} = 12.7 Hz: PPh₂); 128.2 (d, J_{PC} = 12.5 Hz: PPh₂); 88.7 (d, J_{PC} = 12.5 Hz: quat Cp); 75.2 (d, J_{PC} = 9.4 Hz: substCp); 74.5 (d, Cp); 69.3 (d, J_{PC} = 10.2 Hz: substCp); 38.1 (CH₂); 28.7 (CH₂). **³¹P NMR** (δ (ppm), CDCl₃): 41.4. **HRMS (ESI+)** m/e: 553.9836 (100%, 553.9829 for C₂₅H₂₄BrFeNOPS (M+H))

Synthesis of 2-thiodiphenylphosphino (2-bromoethyloxymethyl) ferrocene **5**

In a Schlenk tube, 2-thiodiphenyl phosphino (hydroxymethyl) ferrocene **1** (0.100 g, 0.23 mmol) was dissolved in 10 mL of dry dichloromethane. A 54% solution of tetrafluoroboric acid in ether (100 μ L, 0.724 mmol, 3.15 eq.) was then added. After 1 min stirring, 2-bromoethanol (0.4 ml, 5.64, 25 eq.) was added. After 1 min of stirring, the crude materials were filtered on silica gel with ether as

an eluent. After evaporation of the solvent, 0.140 g of compound **5** as a yellow solid was obtained (yield = 92%).

¹H NMR (δ (ppm), CDCl₃): 7.83 (2H, dd, PPh₂); 7.67 (2H, dd, PPh₂); 7.46 (6H, m: PPh₂); 4.96 (1H, d, J = 11.3 Hz, AB system, CH₂); 4.65 (1H, m: subst Cp); 4.47 (1H, d, J = 10.9 Hz, AB system, CH₂); 4.35 (6H, s: Cp, CH₂, subst Cp); 3.81 (1H, m: subst Cp); 3.54 (2H, m, CH₂); 3.01 (2H, m, CH₂). **¹³C NMR** (δ (ppm), CDCl₃): 134.8 (d, J_{PC} = 87.9 Hz: quat PPh₂); 133.4 (d, J_{PC} = 86.5 Hz: quat PPh₂); 132.1 (d, J_{PC} = 10.9 Hz: PPh₂); 132.0 (d, J_{PC} = 10.7 Hz: PPh₂); 131.3 (d, J_{PC} = 3.0 Hz: PPh₂); 131.2 (d, J_{PC} = 2.9 Hz: PPh₂); 128.1 (d, J_{PC} = 4.1 Hz: PPh₂); 128.0 (d, J_{PC} = 4.7 Hz: PPh₂); 87.7 (d, J_{PC} = 11.8 Hz: quat Cp); 75.3 (d, J_{PC} = 12.3 Hz: subst. Cp); 74.6 (d, J_{PC} = 94.3 Hz: quat Cp); 74.3 (d, J_{PC} = 9.2 Hz: subst Cp); 70.7 (s: Cp); 70.1 (CH₂); 69.4 (d, J_{PC} = 10.5 Hz: quat Cp); 67.3 (CH₂); 30.0 (CH₂). **³¹P NMR** (δ (ppm), CDCl₃): 41.7. **HRMS (ESI+)** m/e: 562.9695 (34%, 562.9695 for C₂₅H₂₄BrFeOPSNa (M+Na⁺)).

Synthesis of 2-thiodiphenylphosphino (3-bromo- *n*-propyloxymethyl) ferrocene **6**

In a Schlenk tube, 2-thiodiphenyl phosphino (hydroxymethyl) ferrocene **1** (0.100 g, 0.23 mmol) was dissolved in 10 mL of dry dichloromethane. A 54% solution of tetrafluoroboric acid in ether (100 μ L, 0.724 mmol, 3.15 eq.) was then added. After 1 min stirring 3-bromopropanol (0.4 ml, 4.4 mmol, 19

eq.) was added. After 1 min of stirring, the crude materials were filtered on silica gel with ether as an eluent. After evaporation of the solvent, 0.104 g of compound **6** as a yellow solid was obtained (yield = 82%).

¹H NMR (δ (ppm), CDCl₃): 7.82 (2H, dd, PPh₂); 7.67 (2H, dd, PPh₂); 7.46 (6H, m: PPh₂); 4.94 (1H, d, J = 10.8 Hz, AB system, CH₂); 4.63 (1H, m: subst Cp); 4.34 (7H, s: Cp, CH₂, subst Cp); 3.81 (1H, m: subst Cp); 3.39 (2H, m, CH₂); 3.07 (2H, m, CH₂); 1.76 (2H, m, CH₂). **¹³C NMR** (δ (ppm), CDCl₃): 134.9 (d, J_{PC} = 87.9 Hz: quat PPh₂); 133.6 (d, J_{PC} = 85.9 Hz: quat PPh₂); 132.3 (d, J_{PC} = 9.6 Hz: PPh₂); 132.0 (d, J_{PC} = 9.8 Hz: PPh₂); 131.2 (d, J_{PC} = 3.0 Hz: PPh₂); 131.2 (d, J_{PC} = 2.9 Hz: PPh₂); 128.1 (d, J_{PC} = 7.2 Hz: PPh₂); 128.0 (d, J_{PC} = 7.0 Hz: PPh₂); 88.0 (d, J_{PC} = 12.0 Hz: quat Cp); 75.3 (d, J_{PC} = 12.2 Hz: subst. Cp); 74.6 (d, J_{PC} = 94.9 Hz: quat Cp); 74.4 (d, J_{PC} = 9.8 Hz: subst Cp); 70.6 (s: Cp); 69.4 (d, J_{PC} = 9.7 Hz: quat Cp); 68.0 (CH₂); 67.3 (CH₂); 32.9 (CH₂); 30.8 (CH₂). **³¹P NMR** (δ (ppm), CDCl₃): 41.7. **HRMS (ESI+)** m/e : 576.9863 (38%, 576.9852 for C₂₆H₂₆BrFeOPSNa (M+Na⁺)).

diffractometer for **6** or a Bruker APEXII for **5** and **4**.

The structures were solved by direct methods (SHELXT-2013 [11]) and refined by least-squares procedures on F^2 using SHELXL-2014 [11]. All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. In compound **6**, there is a twin by inversion as indicated by the Flack's parameter [12] (Table 1). In compound **4**, the unsubstituted Cp displayed large ellipsoids but no reasonable disordered model could be defined, so some strong restraints (EADP) were applied on three of the carbon atoms. The drawing of the molecules was realised with the help of ORTEP32 [13] or PLATON. Crystal data and refinement parameters are shown in Table 2.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1433061-1433061. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336 033; e mail: deposit@ccdc.cam.ac.uk].

X-ray structural analyses.

Single crystal of each compound was mounted under inert perfluoropolyether at the tip of glass fiber and cooled in the cryostream of either an Agilent Technologies GEMINI EOS

Table 2. Crystal Data

Identification code	4	5	6
Empirical formula	C ₂₅ H ₂₃ BrFeNO PS	C ₂₅ H ₂₄ BrFeOPS	C ₂₆ H ₂₆ BrFeOPS
Formula weight	552.23	539.23	553.26
Temperature, K	173(2)	173(2)	180(2)
Wavelength, Å	0.71073	0.71073	0.71073 Å
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	P1	Pna2 ₁	P2 ₁ 2 ₁ 2 ₁
a, Å	7.696(4)	8.7426(5)	8.7877(2)
b, Å	8.300(5)	23.5904(15)	11.2614(3)
c, Å	9.322(6)	10.9934(7)	23.8534(9)
α, °	70.995(18)	90	90
β, °	89.31(2)	90	90
γ, °	85.092(19)	90	90
Volume, Å ³	560.8(6)	2267.3(2)	2360.58(12)
Z	1	4	4
Density (calc), Mg/m ³	1.635	1.580	1.557
Abs. coefficient, mm ⁻¹	2.636	2.605	2.504
F(000)	280	1096	1128
Crystal size, mm ³	0.5 x 0.37 x 0.05	0.350 x 0.200 x 0.070	0.28 x 0.19 x 0.12
Theta range, °	2.311 to 26.368	2.484 to 27.115°	3.062 to 26.372
Reflections collected	16265	20019	13755
Indpt reflections (R _{int})	4557 (0.0695)	4839 (0.0543)	4805 (0.0272)
Completeness, %	99.8	99.9	99.2
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. / min. transmission	0.7457 / 0.5687	0.7455 / 0.5019	1.0 / 0.7994
Refinement method	F ²	F ²	F ²
Data / restraints / parameters	4557 / 3 / 268	4839 / 1 / 271	4805 / 0 / 281
Goodness-of-fit on F ²	1.010	1.026	1.009
R1, wR2 [I > 2σ(I)]	0.0507, 0.1272	0.0398, 0.0755	0.0279, 0.0521
R1, wR2 (all data)	0.0639, 0.1361	0.0627, 0.0820	0.0333, 0.0537
Flack's parameter	0.057(8)	0.025(8)	0.324(9)
Residual density, e.Å ⁻³	1.035 / -0.947	0.832 / -0.730	0.578 / -0.474

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