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Phosphaferrocenes Containing the Chiral Pinene-Fused Cyclopentadienyl Ligand PCp

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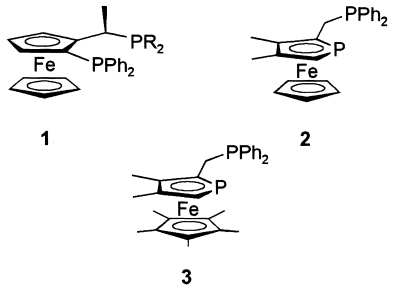
Abstract—The chiral PCp-substituted phosphaferrocene **7** was prepared from the dimeric iron carbonyl complex $[PCpFe(CO)_2]_2$ (**5**) and *t*-butylphosphole (PCp=pinene-fused cyclopentadienyl). In **7**, the PCp ligand is coordinated to the iron atom via its *exo*-side as shown by X-ray crystallography. Formylation of the sandwich complex **7** leads to a mixture of the diastereomeric aldehydes **10a**,**b** in an approximate ratio of 2:1. As a side-product of the synthesis of **7**, the homoleptic ferrocene $(PCp)_2Fe$ (**8**) was obtained by a ring ligand transfer reaction. Complex **8** is formed as a single C_2-symmetrical isomer.

Chiral phosphines relying on the ferrocene skeleton have attracted considerable attention as ligands in asymmetric catalysis and have recently found application in an industrial scale enantioselective hydrogenation.[1] The common feature of these ferrocene ligands is the 1,2-disubstitution of one of the Cp rings with appropriate donor groups resulting in a planar chiral arrangement (e.g. **1**). Recently, we have reported a novel approach to planar chiral π-organometallic ligands based on phosphaferrocenes carrying an additional donor substituent in one of the α-positions of the η^5-coordinated phospholyl ring. A number of different chelate ligands (e.g. **2**) could be prepared which were characterized with respect to their coordination properties towards a variety of transition metal fragments.[2] However, preliminary examination of the performance of the new ligands in asymmetric catalysis resulted in unsatisfactory low *ee* values.[3] In contrast, Fu et al. reported on a slightly different ligand system (**3**) where the cyclopentadienyl (Cp) moiety was replaced by a pentamethylcyclopentadienyl (Cp^*) group.



1 **2** **3**

This sterically more demanding ligand **3** gave *ee* values of up to 96% in the hydrogenation of acetamidocinnamoic acid,[4] while the hydrogenation of the same substrate using Cp derivative **2** resulted in *ee* values <20%, although the reaction conditions are not straightforwardly comparable (rt, 5 mol% Rh, 1 bar of H_2 for **3**; 50°C, 0.1 mol% Rh, 50 bar of H_2 for **2**).

Stimulated by the beneficial effect of the sterically more demanding Cp^* ligand in the catalytic performance, we sought a different approach to a modified ligand structure, whose first results are disclosed in this paper.

Results

Our intention was to pursue two goals simultaneously by the ligand modification. First, we wanted to increase the size of the Cp group and second, we considered how to incorporate additional chirality into the cyclic π-ligand. There are a number of chirally modified Cp ligands known in the literature and an excellent review of the subject has recently been published.[5] From the various possibilities we decided to use the pinene-fused cyclopentadiene (PCpH) ligand **4**, which is accessible from the chiral pool via the inexpensive (−)-nopol in a four-step sequence as developed by Paquette et al.[6] The coordination chemistry of the Pcp ligand has been studied in some detail[7] and it was found that under thermodynamic control, a metal fragment exclusively coordinates to the sterically less hindered *exo*-side as exemplified by the formation of the dimeric iron complex $[PCpFe(CO)_2]_2$ (**5**) from $Fe(CO)_5$ and PCpH in the presence of norbornene.

As $[CpFe(CO)_2]_2$ is the starting material for the preparation of phosphaferrocenes,[2a,8] we studied the reaction of **5** with

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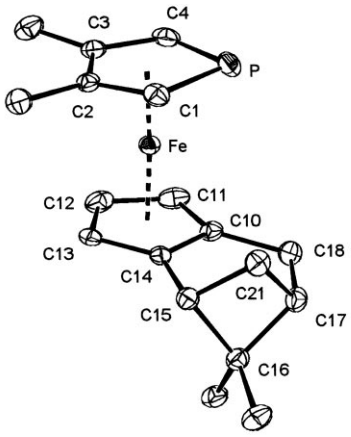


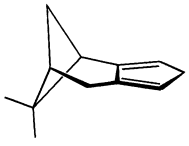
Selected bond lengths and angles:

P-C1 1.770(3), P-C4 1.758(4), C1-C2 1.416(4), C2-C3 1.423(4), C2-C5 1.487(4), C3-C4 1.409(4), C10-C11 1.406(4), C10-C14 1.425(4), C10-C18 1.525(4), C11-C12 1.415(5), C12-C13 1.415(5), C13-C14 1.425(4), C14-C15 1.486(4) Å.

P-C1-C2 113.7(2), C1-C2-C3 112.0(3), C2-C3-C4 110.9(3), P-C4-C3 115.1(3), C11-C10-C14 108.5(3), C14-C10-C18 117.8(3), C1-P-C4 88.3(1), C10-C11-C12 108.0(3), C11-C12-C13 108.3(3), C12-C13-C14 107.9(3), C10-C14-C13 107.3(3), C10-C14-C15 117.8(3)°.

Figure 1. Molecular structure of **7** in the crystal (H-atoms omitted for clarity, ellipsoids at 30% probability level).

t-butylphosphole **6** in xylene under reflux. After workup of the reaction mixture by chromatography on alumina, the desired Pcp modified phosphaferrocene **7** could be isolated as a dark red solid in 65% yield.



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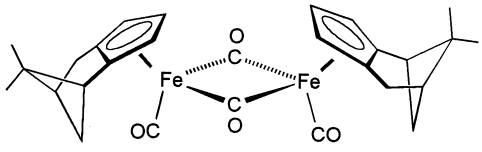
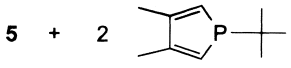
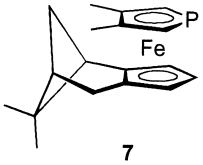


5



6

xylene, rf

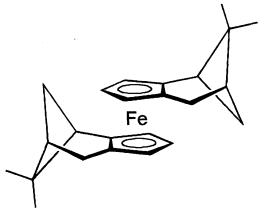


7

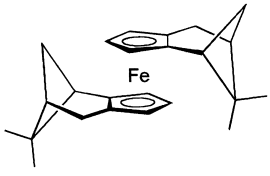
Interestingly, the homoleptic ferrocene derivative $(PCp)_2Fe$ (**8**) was formed as a byproduct in variable amounts depending on the reaction conditions. The amount of **8** was higher (up to 25%) when the reaction temperature did not exceed 130°C, while almost no ferrocene **8** was observed when the reaction mixture was quickly heated to 180°C and kept at this oil bath temperature overnight.

As anticipated, the NMR spectra of the phosphaferrocene **7** displayed a single set of resonances indicating that the PCp ligand was coordinated only from either the *exo*- or the *endo*-side to the phospholyl iron moiety. In analogy with the earlier observations concerning the preferential coordination mode,[7b] we anticipated that the *exo*-isomer of complex **7** was exclusively formed and this assumption was corroborated by the determination of the crystal structure by means of X-ray diffraction. Suitable crystals were obtained from methanol at 4°C. A PLATON[9] plot of the molecular structure of complex **7** is given in Fig. 1 together with selected bond lengths and angles.

The question of the *exo*/*endo* coordination mode of the two PCp ligands is even more interesting in the case of the homoleptic ferrocene **8**. While it is most likely that the iron atom stays attached to the same ligand face during the formation of the phosphaferrocene **7** from the dimeric iron complex **5**, a PCp ligand must be transferred from one iron atom to another in the formation of the ferrocene **8** and in principle this process may well be accompanied by a change of the coordinated side of the transferred cyclic π-ligand. However, the NMR spectra of ferrocene **8** display only a single set of signals which clearly indicates the C_2-symmetry of the molecule in solution. This observation rules out the possibility of an *exo*–*endo* arrangement of



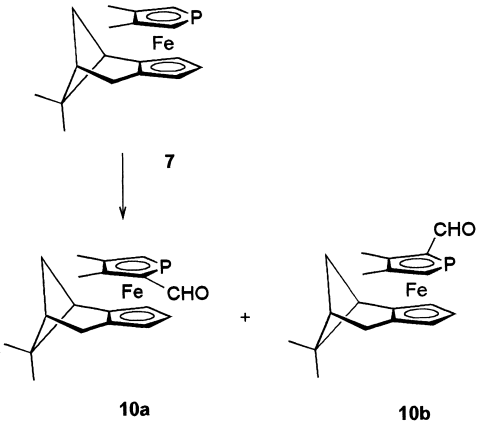
C_2 - **8** (exo-exo)



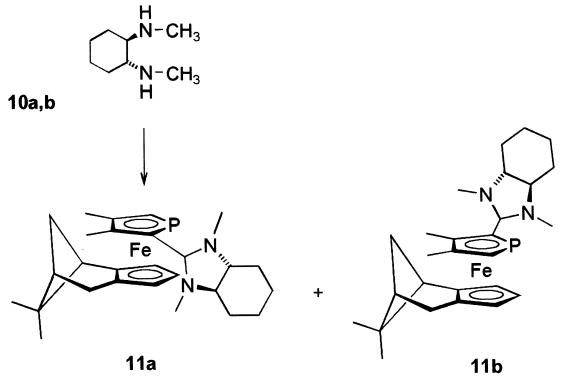
C_1 - **9** (exo-endo)

the two PCp ligands since the resulting C_1-symmetrical molecule **9** would give rise to two sets of NMR signals. The fact that both the carbonyl dimer **5** and the phosphaferrocene **7** contain the PCp ligands coordinated with the *exo*-side strongly suggests that the same is true for the ferrocene which we therefore believe to have the *exo–exo* structure as depicted in formula **8**. We are currently trying to obtain crystals suitable for X-ray diffraction.

For the preparation of chiral chelate ligands starting from the PCp-phosphaferrocene **7** it is necessary to introduce a substituent into the 2-position of the phospholyl ring. In our previous work on the Cp-phosphaferrocenes, we made use of the synthetically valuable formyl group which could be transformed to a number of different donor functions as for example in the P,P-ligand **2**.[2b] Treatment of the PCp-phosphaferrocene **7** in a Vilsmeyer-reaction leads in 70% yield to the diastereomeric aldehydes **10a**,**b** in a ratio of ca. 2:1. Attempts to separate the diastereomers by chromatography or recrystallization were unsuccessful.



However, following a strategy previously used for the separation of enantiomeric 2-formyl-3,4-dimethylphosphaferrocene,[10] the aldehydes **10a**,**b** were transformed to the corresponding aminals **11a** and **b** by treatment with enantiopure (*R*),(*R*)-1,2-di(*N*-methylamino)cyclohexane in ether at room temperature. The aminals could then successfully be separated by column chromatography on silica. Based on the diastereomerically pure aldehydes **10a** and **10b**, which can be obtained by acidic hydrolysis of the respective aminals, we are currently preparing different chelate ligands which will be tested in enantioselective catalytic reactions.



Experimental

All manipulations were carried out under dry N_2 in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N_2. NMR spectra were recorded on a Varian Unity 500 spectrometer (500 MHz, ^{1}H, int. TMS; 126 MHz, ^{13}C{^{1}H}, APT, int. TMS; 202 MHz, ^{31}P{^{1}H}, ext. 85% H_3PO_4). Mass spectra were recorded on a Finnigan MAT 95. Commercially available (−)-Nopole with $[\alpha]_D^{25}=-37$ (neat) was used to prepare PCpH according to the literature.[6] The obtained PCpH was found to have $[\alpha]_D^{25}=-21.1$ (c: 1.8, MeOH) similar to the value reported in the literature.[6]

Preparation of 7

A mixture of 1-*t*-butyl-3,4-dimethylphosphole (**6**)[11] (772 mg, 4.6 mmol) and $[PCpFe(CO)_2]_2$ (**5**)[6] (1.0 g, 1.8 mmol) in xylene (20 mL) is heated at 180°C bath temperature with stirring overnight. After removal of the solvent under vacuum the residue is chromatographed on alumina with hexane to give a deep orange oil, yield 769.2 mg (65%). Crystals suitable for X-ray diffraction were obtained from methanol at 4°C. ^{1}H NMR ($CDCl_3$): δ=0.43 (s, 3H, PCp–CH_3), 1.32 (s, 3H, PCp–CH_3), 2.10 (m, 1H, PCp), 2.17 (s, 3H, phospholyl–CH_3), 2.19 (s, 3H, phospholyl–CH_3), 2.29 (d, 2H, PCp–CH_2), 2.33 (m, 1H, PCp), 2.37 (m, 2H, PCp) 3.66 (dd, ^2J(HP)=36 Hz, ^4J(HH)=1.8 Hz, phospholyl–α-CH), 3.71 (dd, ^2J(HP)=36 Hz, ^4J(HH)=1.8 Hz, phospholyl–α-CH), 3.67 (m, 1H, PCp–CH), 3.89 (m, 1H, PCp–CH), 3.97 (m, 1H, PCp–CH); ^{13}C NMR ($CDCl_3$): δ=15.8 (phospholyl–CH_3), 16.2 (phospholyl–CH_3), 21.2 (PCp–CH_3), 26.7 (PCp–CH_3), 26.8 (PCp–CH_2), 35.9 (PCp–CH_2), 40.6 (PCp–CH), 41.4 (PCp–Cq), 41.7 (PCp–CH), 68.2 (PCp–CH), 69.0 (PCp–CH), 69.2 (PCp–CH), 79.8 (d, ^1J(CP)=58.7 Hz, phospholyl–α-CH), 80.3 (d, ^1J(CP)=59.3 Hz, phospholyl–α-CH), 84.5 (PCp–Cq), 100.6 (PCp–Cq), 93.8 (d, ^2J(CP)=7.1 Hz, phospholyl–Cq), 94.1 (d, ^2J(CP)=7.2 Hz, phospholyl–Cq); ^{31}P NMR ($CDCl_3$): δ=−79.5; $[\alpha]_D^{25}$ (CH_2Cl_2): −385 (c 0.130); $C_{18}H_{23}FeP$, calcd.: 326.08868, found: 326.08895 (HRMS).

As a side-product of the synthesis of **7**, the ferrocene $(PCp)_2Fe$ (**8**) was obtained as a first fraction in the chromatography. **8**: ^{1}H NMR ($CDCl_3$): δ=0.44 (s, 6H, CH_3), 1.31 (s, 6H, CH_3), 2.10 (m, 2H, CH), 2.26 (d, 4H, CH_2), 2.33 (m, 6H, CH, CH_2), 2.69 (m, 4H, CH_2), 3.75 (d, 2H, CH), 3.92 (m, 2H, CH); ^{13}C NMR ($CDCl_3$): δ=21.3 (CH_3), 26.9 (CH_3), 26.6 (CH_2), 35.6 (CH_2), 41.0 (CH), 41.9 (CH), 41.6 (Cq), 64.6 (CH–Cp), 64.8 (CH–Cp), 66.7 (CH–Cp), 81.2 (Cq–Cp), 98.2 (Cq–Cp); $[\alpha]_D^{25}$ (CH_2Cl_2): −652 (c 0.29); $C_{24}H_{30}Fe$, calcd.: 374.16969, found: 374.16973 (HRMS).

X-Ray crystal structure determination of 7

ENRAF-Nonius CAD4-diffractometer, $Mo_{K\alpha}$-radiation, graphite monochromator; data collection with $\omega/2\theta$-scan at 203 K, crystal size 0.4×0.4×0.4 mm; orthorhombic, space group $P2_12_12_1$ (no. 19); a=6.599(2), b=12.648(4), c=18.818(3) Å, V=1570.6(7) Å^3, Z=4, $\rho_{calcd.}$=1.379 g cm^{-3}, μ=10.47 cm^{-1}, F(000)=688; 5017 reflections with $2<\theta<26°$, 2595 independent reflections with $I>\sigma(I)$ in

solution and refinement[12] for 181 parameters; R=0.036, R_w=0.043, $w^{-1}=\sigma^2(F_0)$, GOF=1.352. Hydrogen atoms were calculated into idealized positions (C–H=0.98 Å, $B_H=1.3B_C$) and allowed to ride on their C-atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as 'supplementary publication no. CCDC 119654'. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: int. +1223-336-033; e-mail: teched@chemcrys.cam.ac.uk).

Preparation of aldehydes 10a,b

A mixture of **7** (2.26 g, 6.92 mmol), $POCl_3$ (0.64 mL) and *N*-methylformanilide (936 mg, 6.92 mmol) in dichloromethane (50 mL) is heated at 70°C overnight. The mixture is hydrolysed by the addition of $NaHCO_3$ solution and extracted with CH_2Cl_2. After neutralization with 2N HCl, the CH_2Cl_2 layer is washed with water and brine, dried over sodium sulphate and evaporated. The residue is chromatographed with hexane–ether (4:1) to give a mixture of the diastereomeric aldehydes in an approximate ratio of 2:1, yield 1.70 g (70%). The diastereomers were separated via formation of the aminals **11a**,**b** as described below—**10**: major diastereomer: ^{1}H NMR ($CDCl_3$): δ=0.42 (s, 3H, PCP–CH_3), 1.30 (s, 3H, PCp–CH_3), 2.11 (m, 1H, PCp), 2.22 (s, 3H, phospholyl–CH_3), 2.29 (m, 3H, PCP), 2.45 (s, 3H, phospholyl–CH_3), 2.76 (m, 2H, PCp), 3.81 (m, 1H, PCp), 3.83 (m, 1H, PCp), 4.13 (m, 1H, PCp), 4.25 (d, ^2J(HP)=36.3 Hz, 1H, phospholyl–α-CH), 10.0 (br. s; 1H, CHO); ^{13}C NMR ($CDCl_3$): δ=15.3 (phospholyl–CH_3), 16.3 (phospholyl–CH_3), 21.2 (PCp–CH_3), 26.5 (PCp–CH_3), 26.6 (PCp–CH_2), 29.7 (PCp–CH_2), 40.2 (PCp–CH), 41.6 (PCp–CH), 41.3 (PCp–Cq), 69.3 (PCp–CH), 71.1 (PCp–CH), 71.7 (PCp–CH), 85.5 (d, ^1J(CP)=58.7 Hz, phospholyl–α-CH), 87.1 (PCp–Cq), 103.3 (PCp–Cq), 197.9 (d, ^2J(CP)=71 Hz, CHO); ^{31}P NMR ($CDCl_3$): δ=−54.1; $[\alpha]_D^{25}$ (CH_2Cl_2): −274 (c: 0.073); $C_{19}H_{23}FeP$, calcd.: 354.08359, found: 354.08348 (HRMS)—minor diastereomer: ^{1}HNMR ($CDCl_3$): δ=0.41 (s, 3H, PCP–CH_3), 1.29 (s, 3H, PCp–CH_3), 2.15 (m, 1H, PCp), 2.22 (s, 3H, phospholyl–CH_3), 2.29 (m, 3H, PCP), 2.42 (s, 3H, phospholyl–CH_3), 2.59 (m, 2H, PCp), 3.83 (m, 1H, PCp), 3.84 (m, 1H, PCp), 4.04 (m, 1H, PCp), 4.21 (d, ^2J(HP)=36.3 Hz, 1H, phospholyl–α-CH), 9.86 (br. s; 1H, CHO); ^{31}P NMR ($CDCl_3$): δ=−55.9; $C_{19}H_{23}FeP$, calcd.: 354.08359, found: 354.08350 (HRMS).

Preparation of aminals 11a,b

The procedure is similar to that previously described in the literature.[9] An equimolar mixture of **10a**,**b** and (*R*),(*R*)-1,2-di(*N*-methylamino)cyclohexane is stirred in ether at room temperature in the presence of molecular sieves (3 Å) for 10 days. The mixture is filtered and evaporated to dryness. Absence of the signal for the formyl proton in the ^{1}H-NMR spectrum indicated complete conversion to the aminals **11a**,**b**. Major isomer: ^{1}H NMR ($CDCl_3$): δ=0.39, 1.29, 1.98, 2.16, 2.21, 2.32 (6×s, 3H, CH_3); ^{31}P NMR ($CDCl_3$): δ=−73.0; minor isomer: ^{1}H NMR ($CDCl_3$): δ=0.39, 1.28, 2.19, 2.24, 2.31, 2.32 (6×s, 3H, CH_3); ^{31}P NMR ($CDCl_3$): δ=−74.6. The isomers **11a** and **11b** were separated by chromatography on basic silica. The minor isomer is eluted first with hexane/ether (4:1), the major isomer is obtained with methanol as the eluent. To liberate the diastereomerically pure aldehydes, CH_2Cl_2 solutions of the aminals were stirred in the presence of 2N HCl for 5 days. The organic phases were then separated, dried with Na_2SO_4 and evaporated to dryness in vacuum. The crude products were purified by filtration through a 1 cm plug of alumina with hexane/ether (2:1) and removal of the solvent.

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