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Synthesis and Structure of *P,N*–Heterodifunctional Ferrocene Ligands and their Transition Metal Complexes for Palladium–Catalyzed Aryl Amination Reaction

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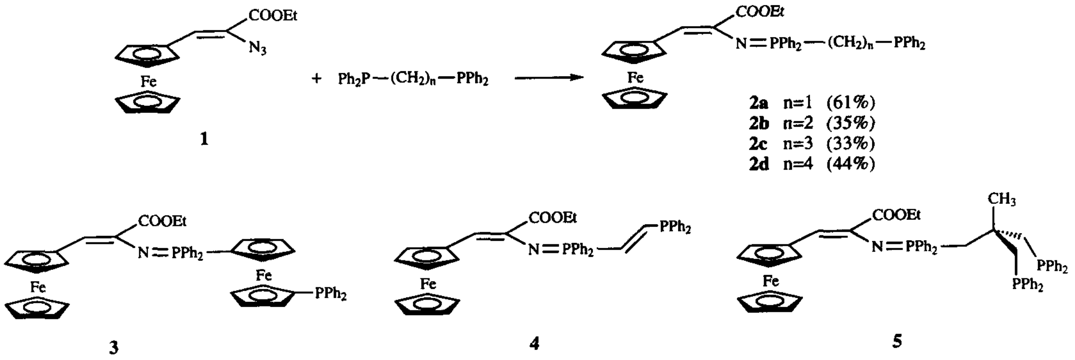
Abstract: *The Staüdinger reaction of the β-ferrocenylvinylazide 1 with di- and triphosphines provided a new range of* P,N*-heterodifunctional ferrocene ligands bearing an iminophosphorane and at least a diphenylphosphino group; reactivity towards Pd (II) and the ability of the resulting complexes for palladium catalyzed aryl amination reaction is described.* © 1997 Elsevier Science Ltd.

Ferrocene derivatives containing the phosphine group have been very successful in coordination chemistry,[1] including their application to asymmetric transition-metal catalyzed reaction.[2] In spite of the large number of ferrocene-derived phosphines, and their complexes, which have the phosphorus atom directly bonded to a cyclopentadienyl ring, ligands where there is a tether connecting the two functionalities are somewhat rare,[3] though chiral versions are attracting interest for their catalytic activity.[4]

Following our work on the preparation of new ferrrocene derivatives through aza Wittig reactions,[5] we

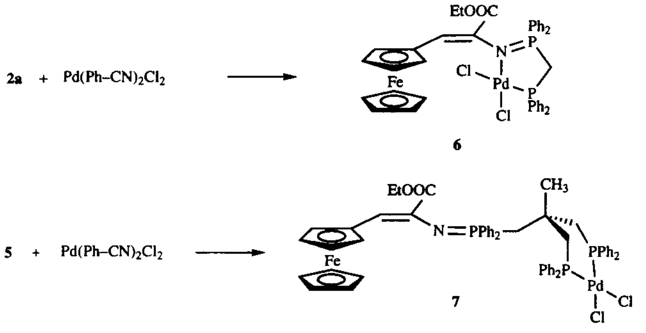


Scheme 1

wish to report now the efficient synthesis of novel *P,N*-heterodifunctional ferrocene-based ligands. Our approach, which is based on the partial oxidation of diphosphines by means of a Staüdinger reaction with β–ferrocenylvinylazide **1**, is applicable to diphosphines of various alkane chain lenghts and even triphosphines.

The new ferrocene chelating ligands **2** have been prepared as shown in Scheme 1. The reaction of the starting β-ferrocenylvinylazide **1**[5] with the appropriate diphosphine (1:1 molar ratio) in dry dichloromethane at room temperature provided the corresponding monoiminophosphorane **2**. The final product could be isolated in yields ranging from 33% to 61% after purification by column chromatography and recrystallization. Similarly, the reaction of **1** with 1,1'-bis(diphenylphosphino)ferrocene, 1,2-bis(diphenylphosphino)ethene and tris(diphenylphosphinomethyl)ethane (triphos) afforded the monoiminophosphorane **3** (36%), **4** (40%) and **5** (21%) respectively. The ^{31}P nmr spectrum for **2a** exhibit two doublets with remarkably large $^{2}J(P,P)$, centered at 3.36 ppm and -24.49 ppm assigned to the pentavalent and trivalent phosphorus atoms, respectively. Similarly, spectrum of compound **5** consists of two singlets at 0.20 ppm (P^{V}) and at -26.86 ppm (P^{III}).

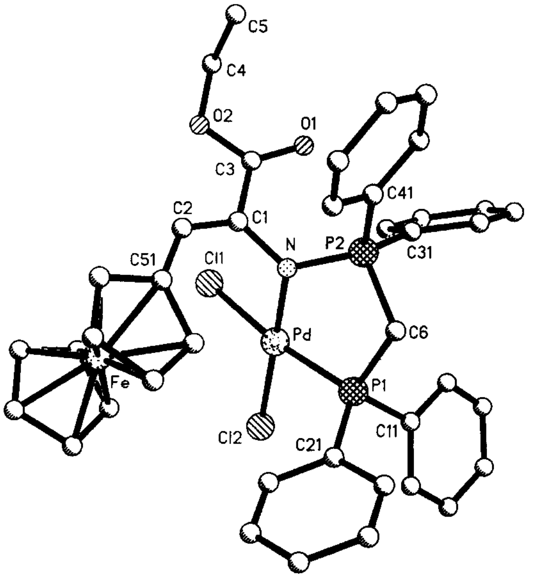
It seemed interesting to us to test the complexation behavior of these heterodifunctional ferrocene derivatives **2** and **5** with palladium (II), as these compounds possess a complex forming diphenylphosphino group and an iminophosphorane function, which also has demonstrated its versatility toward forming M-N σ bonds to metal transition.[6]



Scheme 2

The ferrocene derivative **2a** reacted cleanly with dichlorobis-(benzonitrile)palladium(II) in toluene at -15°C to afford the new *P,N*-metallacyclic chelate **6** (m.p. 170-172°C, 94%), whose structure has been determined by X-Ray analisis.[7] The ^{31}P nmr spectrum of **6** consisted of two doublets with the iminophosphorane unit resonating at low field (44.23 ppm) compared with the phosphine center (14.16 ppm). The complex **6** represents the first example of a ferrocene derivative containing an iminophosphorane phosphine ligand. The palladium atom has a distorted square planar coordination geometry. The large Pd-Cl1 bond length (2.3719) compared to Pd-Cl2 (2.3133) is consistent with the greater trans influence of P compared to N. The P-N bond distance (1.6282) indicates that this bond is slightly elonganted due to the coordination, since free iminophosphoranes show shorter P-N bond lengths.

The complexation behavior of **5** with Pd(II) under the same reaction conditions was different from that of **2a**, and the *P,P*-chelate **7** was formed (m.p. 247-250°C, 58%) (Scheme 2). The ^{31}P nmr spectrum is very illustrative and only shows two singlets at 0.1 ppm, characteristic of a non-coordinated iminophosphorane function, and at 15.60 ppm assigned to those coordinated diphenylphosphine groups. The difference in the complexation behaviors of **2a** and **5** may be due to their structural features, that is the second diphenylphosphino group of **5** has stronger coordination ability toward Pd(II) that the iminophosphorane group of **2a**.



Crystal structure of **6**

A final word about the conformation of the ligand **5** and its complex **7** is relevant. The chemical shift of the CH_3-C protons in the triphos[8] is 0.95 ppm and in their transition metal complexes[9] lies in the range δ=1.12–2.09 ppm. In the ^{13}C nmr spectrum the CH_3-C carbon atom appears at δ 29.5 ppm and in their complexes at δ 36–40 ppm. In all these cases the triphos fragment adopt a CH_3–*out* conformation. The ^1H nmr of compounds **5** and **7** show the CH_3-C protons at δ 0.85 ppm and δ 0.14 ppm respectively, whereas in the ^{13}C nmr spectra this methyl carbon appears at δ 28.08 ppm and 28.15 ppm respectively. Taking into account that in cyclic compounds with bridgehead 1,1,1–trisubstituted ethane fragment the CH_3–C–*in* group is shifted upfield relative to the CH_3–*out* group,[10] probably the conformation of the triphos fragment in compounds **5** and **7** could be other than the CH_3-*out*.

The palladium-catalyzed cross coupling of amines with aryl halides has recently become an important protocol for the formation of aryl-nitrogen bonds, which provides a fairly general and attractive route to a wide variety of structurally different arylamines.[11] The method is based on the use of Pd(0) complexes with monophosphine P(*o*-tolyl)$_3$ or biphosphine BINAP ligands.[12] However, the arylation of secondary acyclic amines using these ligands remains problematic. A recent report,[13] describes that palladium complex derived from 1-diphenylphosphino-2-(1-methoxyethane)ferrocene is highly effective for the aryl amination reaction of acyclic secondary amines.

Since the complex **6** possesses related structural features compared with the proposed intermediates of the arylamination reaction[13], was carried out this reaction as a preliminary experiment. As we expected, compound **6** showed good efficiency for the palladium–catalyzed arylamination of *p*-iodotoluene with N-methylbenzylamine. The best result was obtained when a mixture of *p*-iodotoluene (1 mmol) N–methylbenzylamine (3 mmol), Na^{t}BuO (1.4 mmol) and 1.5 mmol % of **6** in dioxane was heated in a sealed tube at 160°C until the starting aryl iodide was consumed as determined by GC analysis (24h). The reaction mixture was taken up in diethyl ether, washed with brine, dried and concentrated. Purification by flash chromatography on silica gel afforded the arylamine in 75% yield. When the reaction was carried out without **6** under the same conditions formation of the arylamino compound was detected by GC in poor yield (<2%).

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7. Compound **6**·$2CHCl_3$ crystallized from a chloroform solution as dark red laths. Crystal data: $C_{42}H_{39}Cl_8FeNO_2P_2Pd$, M = 1097.53, 0.60 x 0.20 x 0.06 mm size, space group P2(1)/n with cell parameters a = 12.480(1), b = 25.091(3), c = 14.288(2) Å, β = 93.78(1)°, V = 4465(1) $Å^3$, Z = 4, Siemens P4 diffractometer, MoK_α (λ = 0.71073 Å), ω-scan, 2θmax = 50 °, T = 173 K, 4453 independent reflections collected, Ψ-scans absorption correction (max., min. transmission = 0.792, 0.699), direct primary solution and refinement on F^2 using Siemens-SHELXTL program, 514 refined parameters, rigid methyl hydrogens, other hydrogen atoms riding. Final R1 factor = 0.0248 [I > 2.σ(I)] and wR2 (all data) = 0.0462 [R1 = $\sigma||Fo|-|Fc|| / \sigma|Fo|$, wR2 = $[\sigma[w(Fo^2-Fc^2)^2] / \sigma[w(Fo^2)^2]]^{0.5}$, w = $1/[\sigma^2(F^2) + (aP)^2 + bP]$, P = $(2Fc^2 + Fo^2)/3]$, [1] residual electron density 0.276 (-0.212) $eÅ^{-3}$, maximum shift/esd 0.001. Details of the crystal structure determination may be obtained from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW (UK) on quoting the full journal citation.
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