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An Efficient Preparation of Novel Ferrocene Derivatives via Aza Wittig Reaction and X-Ray Structure of Bis(β-Ferrocenylvinyl)carbodiimide

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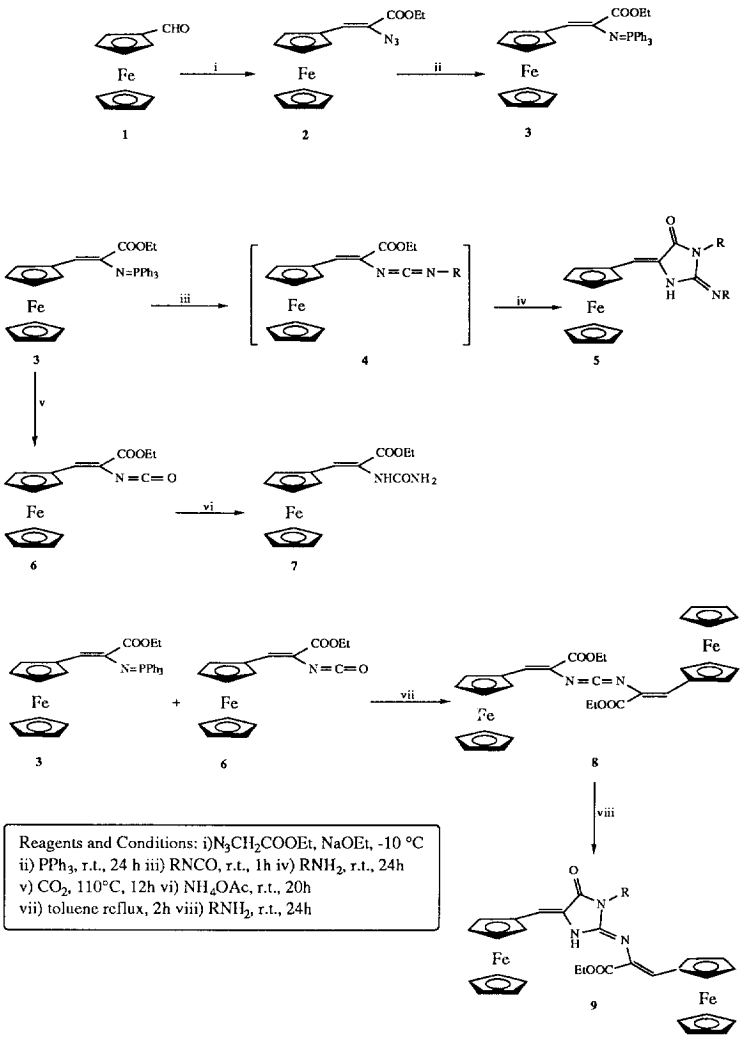
Abstract: *Novel ferrocene derivatives such as β-ferrocenylvinylheterocumulenes and ferrocene-containing imidazole rings have been easily prepared from β-ferrocenylvinyliminophosphorane 3 by Aza Wittig reactions.*

Considerable attention has been paid in the last few years to supramolecular systems containing a ferrocene unit and a fragment able to act as ligand towards transition-metal ions; these systems can behave either as chemical sensors[1] or as redox- and photo-active molecular devices[2]. In addition, since the discovery of a hyperpolarizable ferrocene derivative displaying a large second-order optical nonlinearity[3] a range of suitably functionalized ferrocene derivatives displaying a high degree of nonlinear optical (NLO) behaviour have been reported[4]. On the other hand, supramolecular systems containing more than one metallocene unit have attracted a great deal of attention[5]. In particular, bridging two ferrocene subunits generates redox systems which have been the subject of recent studies due to the great potential for multiple electron transfers and mixed valences of these systems[6].

The present work is undertaken to the synthesis of ferrocene-containing molecules with P- or $sp/sp^2/sp^3$ N-donor groups which are able to act as ligands towards transition-metal ions. To our knowledge, no ferrocenylimidazole derivatives have been described, in spite of the fact that ferrocenyl-substituted pyrazoles[7] and many ferrocenyl-substituted pyridines[8] have been studied specially in the context of the design of redox spectators.

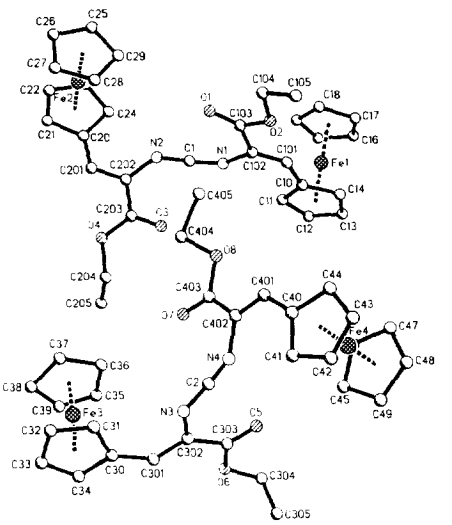
We chose to use the β-ferrocenylvinyliminophosphorane **3** as building block for the synthesis of the new ferrocene derivatives. Ferrocenecarboxaldehyde **1** underwent Knoevenagel condensation with ethylazidoacetate under standard reaction conditions to give the vinylazide **2** (m. p. 84-86°C, 82% yield). Staudinger reaction of compound **2** with triphenylphosphine in dry dichloromethane at room temperature provided the vinyliminophosphorane **3** (m.p. 142-144°C) in almost quantitative yield. Is important to note that the

iminophosphorane moiety posseses a high complex forming capacity with a wide variety of metal compounds[9] and metal carbonyls[10], so compound **3** could be of valuable interest for the preparation for redox-functionalized metal complexes. Vinyliminophosphorane **3** was converted in one-flask reaction into the corresponding highly functionalized ferrocenylimidazoles **5** in yields higher than 70%, by sequential treatment with isocyanates and then primary amines. These new ferrocene derivatives **5** display solvatochromic behaviour[11].



Vinyliminophosphorane **3** also reacted with solid carbon dioxide at 110°C in a sealed tube to afford the β-ferrocenylvinyl isocyanate **6** (m. p. 103-105 °C, 86 % yield), which was converted into the corresponding urea **7** (m. p. 174-176°C, 98% yield) by treatment with ammonium acetate in dry acetonitrile at room temperature. Intermolecular aza Wittig-type reaction between the vinyliminophosphorane **3** and the vinylisocyanate **6** in toluene at reflux temperature gave the bis(β-ferrocenylvinyl)carbodiimide **8** (m.p. 195-197°C, 99%), whose structure has been determined by X-Ray analysis[12]. The ^1H- and ^{13}C-nmr spectra of compound **8** revealed that

the two ferrocene subunits are equivalent. Compound **8** represents a novel example of bis(ferrocene)compounds, in which the bridging unit is an unsaturated carbodiimide.



Crystal Structure of **8**

The present approach to ferrocenylimidazoles enables the design of novel complex ferrocene-containing heterocycles such as **9**. These type of compounds were prepared in yields ranging from 83 to 95 % by treatment with the corresponding primary amine at room temperature. The ^{1}H- and ^{13}C-nmr spectra of compounds **9** showed that the two ferrocene fragments are nonequivalents[13]. Thus, the aza Wittig reaction which has not been used before in the ferrocene chemistry appears to be a very efficient way to prepare a wide variety of ferrocene derivatives bearing one or two ferrocene subunits.

The physical properties of compounds **5** and **9** will be published elsewhere[14].

In conclusion, the work described here affords a simple but effective new route to novel ferrocene derivatives, in which the ferrocene is conjugated either to a heterocumulene fragment or to a highly functionalized imidazole ring. The method also works for the preparation of bis(ferrocene) derivatives. These relatively complex and unreported structures are prepared under mild reaction conditions, in high yields and from the readily available starting material β-ferrocenylvinyliminophosphorane **3**.

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11. The uv-vis spectra of compounds **5** recorded in toluene, dichloromethane and dimethylformamide gave different spectra in each solvent. For R=$C_6H_5CH_2$ toluene λ=490, 424, 366, 300, 285 nm; dichloromethane λ=496, 428, 364, 301, 230 nm; dimethylformamide λ=489, 426, 369, 303, 266 nm.
12. Compound **8** crystallized from dichloromethane/diisopropyl ether as dark reed needles. Space group $P_{21/n}$ with cell parameters a=13.597(4), b=11.840(2), c=35.181 (9)Å, β=101.09(2)°, and z=8 (two molecules at the asymmetric unit). Final R1 factor=0.0691 [I>2σ (I)] and wR2=0.11902 for 9781 reflections. Details of the crystal structure determination may be obtained from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge (UK) on quoting the full journal citation.
13. **General Procedure:** To a solution of carbodiimide **8** (0.25 g, 0.41 mmol) in dry dichloromethane (15 ml) the corresponding amine (0.41 mmol) was added. The resultant reaction mixture was stirred at room temperature for 24 h. The solution was concentrated to dryness and the residual material was chromatographed on a silica gel columm using ethyl acetate/*n*-hexane (1:3) as eluent to give **9** which were recrystallized from the appropriate solvent. Compound **9a** (R=$C_6H_5CH_2$) (83%), m.p. 173-176°C (red prisms from dichlorometane/Et_2O); ^{1}H-n.m.r. (300 MHz, $CDCl_3$) δ 1.36 (t, 3H, *J*=7.1 Hz, $COOCH_2CH_3$), 4.06 (s, 5H, unsubstituted ferrocene), 4.08 (s, 5H, unsubstituted ferrocene), 4.16 (t, 2H, *J*=1.8 Hz, H-3 and H-4 ferrocene), 4.25-4.33 (m, 8H), 5.05 (s, 2H), 6.38 (s, 1H, -CH=), 7.01 (s, 1H, NH), 7.09 (s, 1H, -CH=), 7.32-7.41 (m, 3H, aromatics). 7.53-7.55 (m, 2H, aromatics); ^{13}C-n.m.r. (75 MHz, $CDCl_3$) δ 14.4 (CH_3), 42.7 (CH_2), 61.4 (CH_2,) 68.7, 69.4, 69.5, 70.3, 70.4, 70.5, 77.2 (q), 77.8 (q), 109.2 (-CH=), 125.7 (q), 127.5, 127.7, 128.3, 128.6, 130.3 (q), 136.7 (q), 144.5 (q), 163.7 (C=O), 165.9 (C=O); IR (Nujol) 3309, 1682, 1657 cm^{-1}; EI mass spectrum m/z (%) 667 (M^+, 6), 219 (35), 121 (41), 91 (100).
14. Satisfactory ^{1}H-, ^{13}C-n.m.r., mass spectra and elemental analyses were obtained for all new compounds.

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