Pergamon

Tetrahedron 55 (1999) 14701–14718

TETRAHEDRON

Aza-Wittig reactions of iminophosphoranes derived from ferrocenylazido ketones: preparation and electrochemical study of novel ferrocenyl-substituted azaheterocycles

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Dedicated with admiration and respect to Prof. J. Elguero in recognition of his remarkable contributions to so many aspects of Chemistry.

Received 2 August 1999; revised 24 September 1999; accepted 7 October 1999

Abstract

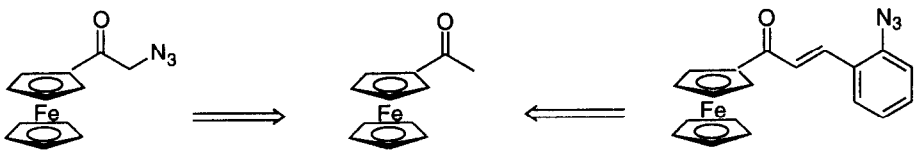
α-Azidoacetylferrocene and 3-(*o*-azidophenyl)-1-ferrocenylpropenone have been prepared from acetylferrocene and they have proven to be useful building blocks for the synthesis of azaheterocycles. Thus, the three-component reaction of α-azidoacetylferrocene, isocyanates or acid chlorides and triphenylphosphine allows the direct formation of ferrocene-substituted oxazoles. Aza-Wittig reaction of the iminophosphorane derived from 3-(*o*-azidophenyl)-1-ferrocenylpropenone with isocyanates provides access to the corresponding carbodiimides which are cyclised either by the action of TBAF or amines to give ferrocenyl-substituted dihydroquinazoline derivatives. The bis(ferrocenyl)oxazole **13** showed in the cyclic voltammogram ($\Delta E_{1/2}$ = 150 mV) moderate electronic coupling between the two ferrocenes through the oxazole ring.

Keywords: Ferrocene,Oxazoles, Quinazolines, Aza-Wittig, Electrochemistry.

The serendipitous discovery of ferrocene has caused organometallic chemistry to progress explosively. Nowadays, ferrocene and its derivatives are also attracting much attention from the viewpoint of catalysis, organic synthesis, new materials such as liquid crystals or polymers [1] and supramolecular chemistry.[2] Ferrocene derivatives containing atoms with good donor abilities have attracted additional interest, since the coordination of a metal to these heteroatoms produces heteropolynuclear organometallic compounds containing ferrocene units, in which the presence of proximal metals in different enviroments may influence the mutual cooperation of these metals in a variety of processes.[3] In this sense, the integration of one or more ferrocene units into a heterocyclic ring system has long been recognised as an attractive way to endow a molecule functionally. This sort of compound is of considerable

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00916-3

interest for the construction of heterobimetallic systems, which can behave either as chemical sensors[4-6] or as redox-active and photoactive molecular devices.[7-9]



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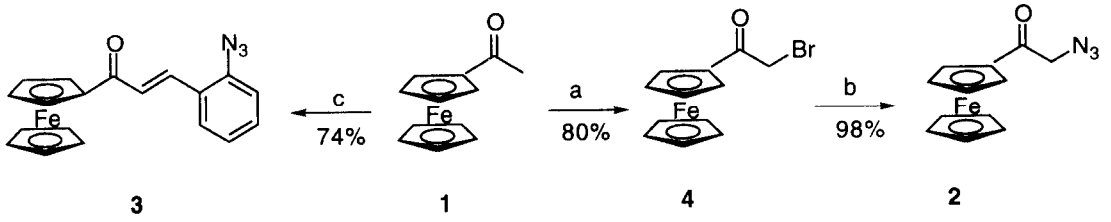
In this context, we have recently reported the preparation and structural characterization of several ferrocene-containing imidazoles bearing one, two or three ferrocene subunits. They were prepared from β-ferrocenylvinyl heterocumulenes or derivatives, which in turn were available by aza-Wittig reactions of the [β-(ferrocenylvinyl)imino]phosphorane with carbon dioxide, carbon disulfide or isocyanates.[10-12]

The present work is undertaken for the synthesis of several ferrocenyl-substituted azaheterocycles such as oxazole and quinazoline derivatives by using the iminophosphorane methodology.[13] We chose the use of the α-azidoacetylferrocene **2** and 3-(*o*-azidophenyl)-1-ferrocenylpropenone **3** as building blocks for the synthesis of the new ferrocene derivatives. An advantage of this approach is that 1-acetylferrocene **1**, starting material for the preparation of **2** and **3**, is now readily available in 88% yield by acylation of ferrocene with the acetic acid/phosphorus trichloride/aluminium trichloride combination.[14]

Results

The α-azidoacetylferrocene **2** has been prepared from α-bromoacetylferrocene **4** by halogen-azido substitution. The only known α -haloacetylferrocene is the α-choro derivative, which has recently been used as starting material for the preparation of chiral ferrocenyl-substituted β-aminocyclopentadienes.[15] However, the only method reported[16] for its preparation, which is based on the Friedel-Crafts acylation of ferrocene with acetyl chloride in the presence of aluminium chloride, affords the desired α-chloroacetylferrocene in 26% yield, together with acetylferrocene. The low yield of the acylated product is due to the fact that the conventional electrophilic substitution is accompained by an electron-transfer from ferrocene to acylium ion to give the oxidised ferrocenium cation, usually in high yield.[17] Therefore, our first goal was to devise a reliable method for the preparation of α-bromoacetylferrocene **4** from acetylferrocene **1**. After several trials with various bromination reagents that included phenyltrimethylammonium tribromide, Br_2/AcOH, $CuBr_2$/MeOH, NBS/AIBN and NBS/HBr, we were unable to accomplish this transformation. This series of frustrating results was finally broken by using the trimethylsilylenolether of **1**. Thus, metallation of **1** with LDA at -78°C followed by sequential treatment with trimethylchlorosilane and an excess of NBS provided the α-bromoacetylferrocene **4** in 80% yield, along with a small amount of the α,α-dibromoacetylferrocene. Conversion of **4** into α-azidoacetylferrocene **2** was achieved in almost quantitative yield (98%) by using polymeric

quaternary ammonium azide.[18] On the other hand, preparation of 3-(*o*-azidophenyl)-1-ferrocenylpropenone **3** was achieved in 74% yield by condensation of **1** with *o*-azidobenzaldehyde under standard condition[19] (Scheme 1).



3 1 4 2

Reagents and conditions: a) LDA, Me_3SiCl, THF -78°C then NBS; **b)** Ⓟ-$\overset{+}{N}R_3$ N_3^-, CH_2Cl_2, rt; **c)** *o*-azidobenzaldehyde, EtOH, NaOH, rt.

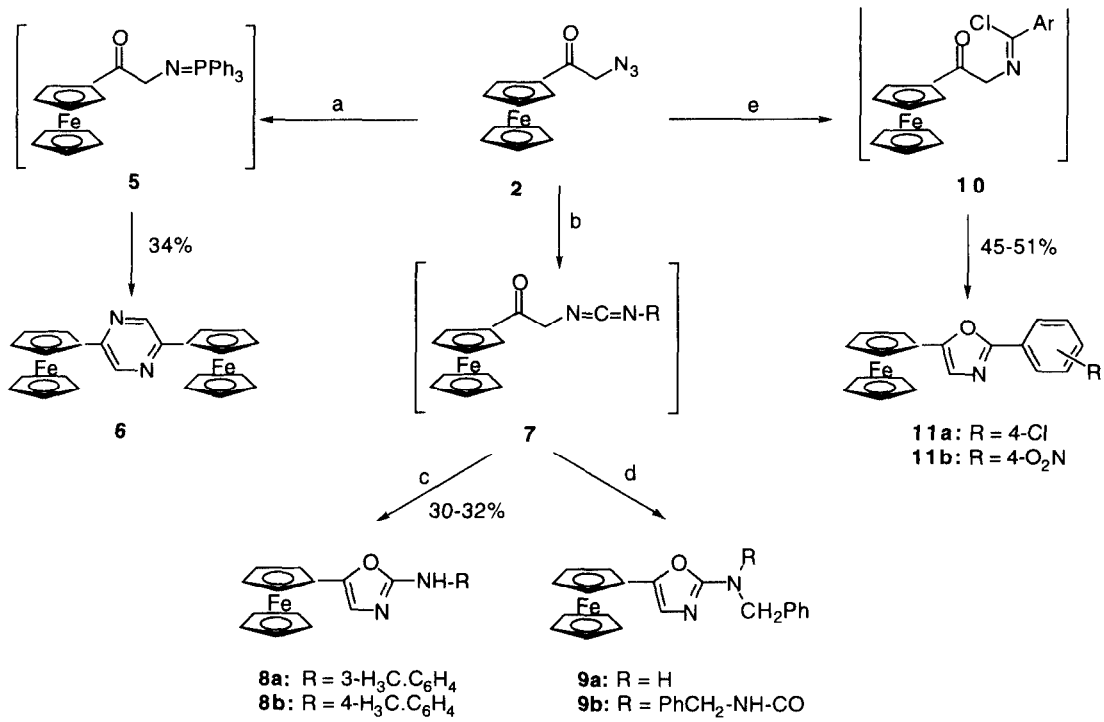
Scheme 1

When the α-azidoacetylferrocene **2** was submitted to react with triphenylphosphine in dry diethylether at 0°C, formation of the expected iminophosphorane was not observed. However, when the Staudinger reaction was carried out at room temperature, an orange solid was obtained, which was found to be the 2,5-bis(ferrocenyl)pyrazine **6**. Formation of compound **6** is explained by initial formation of the iminophosphorane **5** which undergoes cyclocondensation through a double intermolecular aza-Wittig reaction and eventually dehydrogenation of the resulting dihydropyrazine.

Keeping this result in mind and in order to avoid the direct formation of the iminophosphorane **5**, the triazaphosphadiene adduct pathway[20] was used to study the behaviour of the α-azidoacetylferrocene **2** in aza-Wittig reactions towards isocyanates and acyl chlorides. In this way, the reaction is carried out with the isocyanate or acyl chloride present before addition of the triphenylphosphine. The triazaphosphadiene reacts directly with the aza-Wittig reagent: acyl chloride[20] or isocyanate[21] to form a new intermediate, termed the triazaphosphadiene adduct, which decomposes to give the aza-Wittig product and no iminophosphorane is detected under these conditions.

Addition of a solution of triphenylphosphine to a mixture of **2** and an aromatic isocyanate, at room temperature, led to the formation of the corresponding carbodiimide **7** (as evidenced by the appearance of a strong absorption band at 2199 cm^{-1} in the IR spectrum, and its conversion into the urea derivative). Compound **7**, was stable in solution at room temperature, but addition of a base promoted the cyclization to give the corresponding 2-arylamino-5-ferrocenyl oxazole **8**, in moderate yields (30-32%). In a similar way, the reaction with benzyl isocyanate provided two compounds which were separated by column chromatography. The minor product (12%) was found to be the expected 2-benzylamino-5-ferrocenyl oxazole **9a**, whereas the major product **9b** (31%) was derived from the reaction of **9a** with a second equivalent of benzyl isocyanate.

This methodology also allowed the one-flask preparation of 2-aryl-5-ferrocenyl oxazoles **11** (45-51%) from **2**, when substituted benzoyl chlorides were used as aza-Wittig reagents. In this case, cyclization of the intermediate imidoyl chloride **10** took place without the need of a base (Scheme 2).



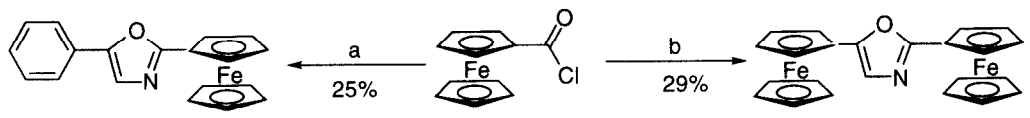
Reagents and conditions: a) PPh_3, Et_2O, 24 h, r.t.; **b)** RNCO, PPh_3, Et_2O, 24 h, rt.; **c)** R-NH_2, 24 h, r.t.; **d)** $PhCH_2NH_2$, 24 h, r.t.; **e)** ArCOCl, PPh_3, Et_2O, 24 h, r.t.

Scheme 2

In spite of the moderate yields for conversions **2** → **8** and **2** → **11** and considering the number of steps: Staudinger reaction, aza-Wittig reaccion accross the triazaphosphadiene to give the intermediates carbodiimides **7** or imidoyl chlorides **10** and finally cyclization, the yields may be considered good.

In order to study the electrochemical behaviour of the 5-ferrocenyloxazoles obtained, preparation of the isomeric 2-ferrocenyloxazole **12** and 2,5-bis(ferrocenyl)oxazole **13** was of interest. Thus, reaction of chlorocarbonylferrocene, prepared from ferrocene carboxylic acid[22] with oxalyl chloride, in the presence of DMAP, with phenacylazide and triphenylphosphine under the conditions described above, gave **12** in 25% yield, and when **2** was used as the azido component the 2,5-bis(ferrocenyl)oxazole **13** was obtained in 29% yield. The ^1H and ^{13}C NMR spectra of compound **13** clearly show two sets of well-separated

signals for the two ferrocene subunits, which were assigned by comparison with those observed in compounds **11** and **12** (Scheme 3).



12 **13**

Reagents and conditions: a) $PhCOCH_2N_3$, PPh_3, Et_2O, 24 h, r.t.; **b)** $FcCOCH_2N_3$, PPh_3, Et_2O, 24 h, r.t.

Scheme 3

In order to probe possible intramolecular electron transfer properties of the compounds described above, cyclic voltammetry was applied. As studies undertaken in dimethylformamide solution appeared to be complicated by solvent interaction, data reported here are from measurements in acetonitrile solution with tetra-*n*-butylammonium perchlorate as the supporting electrolyte. All potentials are referenced to the SCE.

Table 1. Voltammetric Data for 8b, 11a, 11b and 12.[a]

Compound	E_p^a, V	E_p^c, V	ΔE_p, mV	$E_{1/2}$, V
Fc	0.504	0.405	99	0.455
8b	0.506	0.408	98	0.457
11a	0.581	0.488	93	0.535
11b	0.615	0.522	93	0.569
12	0.635	0.531	104	0.583

[a] Acetonitrile solutions of **11a**, **11b** and **12** were 0.1 M in $[n\text{-}Bu_4N][ClO_4]$, 1 x 10^{-3} M in sample, scan rate 200 mV s^{-1}, sweep range 0 to 0.8 V.

Compounds **11a**, **11b** and **12** are all redox active and exhibit reversible processes in their cyclic voltammograms. Table 1 summarises the electrochemical data for these compounds. The oxidation processes correspond to the formation of the appropriate ferrocenium salts and no other process was observed in the available range in acetonitrile. Accordingly, the oxazole ring is not expected to electrochemically interfere with the oxidation of the ferrocenyl fragment.

When the one-electron oxidation waves of these compounds were compared to those of ferrocene, it was observed that they are shifted to more positive potentials. Such an anodic shift must be attributed to π-conjugation of oxazole to a cyclopentadienyl ring of ferrocene that clearly leads to transfer of electron density from the metal centre to the electron deficient heterocyclic system. The effect of substituents is illustrated by the shift of half-wave

potentials. So, the electron-withdrawing abilities of the chloro and nitro groups, in compounds **11a** and **11b**, make the electron removal more difficult: about 84 and 114 mV, respectively. However, in compound **8b**, where the oxazole ring is substituted by an arylamino group, this value is similar to that of ferrocene. On the other hand, in **12** where the ferrocenyl moiety is linked to the 2-position of the oxazole ring, the anodic wave is shifted 128 mV compared to ferrocene.

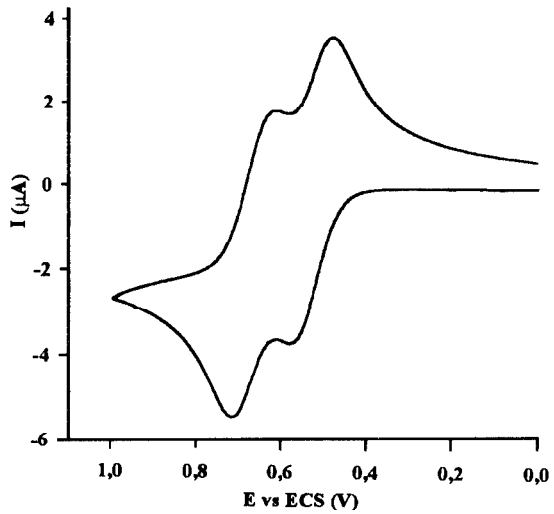


Figure 1: Cyclic voltammograms of **13** in CH_3CN. Experimental conditions : 1 x 10^{-3} M , Pt disk working electrode, SCE reference electrode, 0.1 M $[n\text{-}Bu_4N][ClO_4]$, scan rate: 200 mV s^{-1}.

As shown in Figure 1, the biferrocene **13** undergoes two successive reversible one-electron oxidations to yield the mono and then the dication. The cyclic voltammogram establishes that the oxazole ring acts as a molecular wire connecting the two electron rich organoiron centers. It has been shown that the magnitude ($\Delta E_{1/2}$) gives an indication of the interaction through the bridge between the two Fe sites.[23] In the present work this value has been calculated by the Richarson-Taube method[24] ($E^1_{1/2}$ = 0.542, $E^2_{1/2}$ = 0.692, cf ferrocene +0.455 V vs SCE). From the separation $|E^2_{1/2} - E^1_{1/2}|$ = 0.150 mV a constant Kc = 343 was calculated. This value for the conproportionation constant indicates that the monocation **[13]**$^+$ could be an example of a slightly delocalised mixed-valence species.

$$\text{Fe(II) - Fe(II)} + \text{[Fe(III) - Fe(III)]}^{+2} \underset{}{\overset{K_c}{\rightleftharpoons}} 2\ \text{[Fe(II) - Fe(III)]}^{+}$$

The electron transfer separation $\Delta E_{1/2}$ = 150 mV is moderate. Stronger interactions are known for decamethylbiferrocene ($\Delta E_{1/2}$ = 375 mV),[25] while they are similar for *(E)*-1,2-

bis(ferrocenyl)ethene ($\Delta E_{1/2}$ = 170 mV)[26] and 1,1-bis(1'', 2'', 3'', 4'', 5''-pentamethylferrocen-1'-yl)ethene ($\Delta E_{1/2}$ = 150 mV).[27] It is important to note that this sort of electrochemical behaviour in biferrocenes has only been found when one sp^3-hybridized atom per bridge is introduced as for instance by using $SiMe_2$ groups,[28] or in biferrocenes separated by sp^2-carbon conjugated chains.[26]

The current interest in the use of organometallic materials in optical proccesing, particularly in second harmonic generation (s.h.g) prompted us to determine the suitability of ferrocene derivatives **11b** and **13** as possible non-linear optics (NLO) molecular materials.[29-31] Solvation effects on the solution electronic spectra can be a useful indicator of potential non-linear optics properties.[32] The solution UV-VIS spectra for these compounds were recorded in diethyl ether, acetonitrile and N,N-dimethylformamide, respectively (Table 2). For the ferrocenyl derivatives there are essentially three bands, but an exception to this is seen for compound **11b** which shows two bands in N,N-dimethylformamide. In general, small shifts are observed on change of solvent, with the largest solvatochromic shifts being observed for the low-energy band.

Table 2. UV-Vis Data for Compounds 11b and 13.[a]

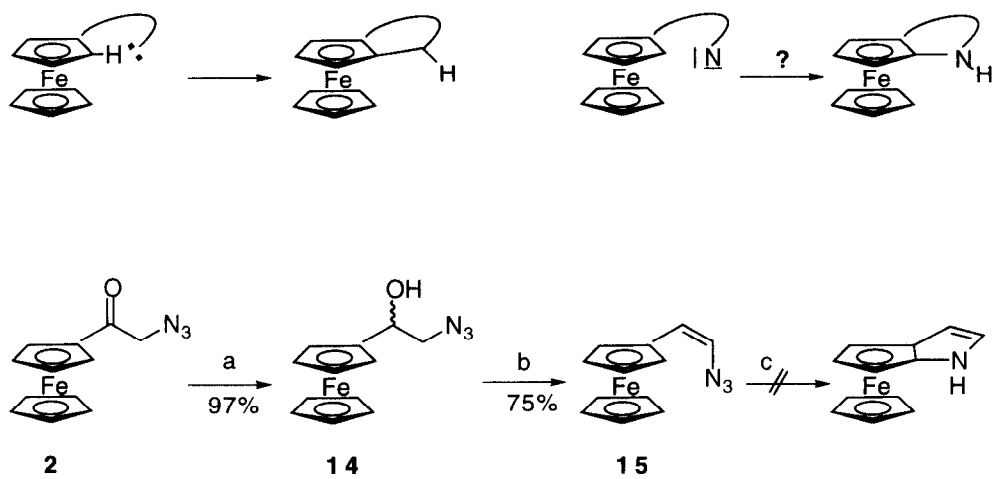
Compound	Et_2O [b]	CH_3CN[b]	DMF[b]	$\Delta\lambda$ (nm)
11b	282 (16.02)	272 (25.68)	283 (13.88)	10
	350 (16.14)	352 (16.06)	356 (12.13)	-
	464 (3.09)	476 (3.69)	-	12
13	276 (13.36)	275 (13.92)	285 (5.80)	10
	314 (15.96)	314 (15.62)	316 (10.52)	-
	450 (1.05)	458 (1.31)	465 (0.75)	15

[a] Solutions of compounds **11b** and **13** were 10^{-5} M in Et_2O, CH_3CN and DMF.
[b] λ_{max}(nm) ($10^{-3}\varepsilon$)(M^{-1} cm^{-1}).

There has recently been reported[33] the first example of intramolecular carbene insertion into a Cp-H bond of ferrocene derivatives. In this sense, we considered whether ferrocenes can also be functionalized by C-H insertion upon reaction with nitrenes. Taking into account the aromatic character of the cyclopentadienyl ring, this sort of reaction is conceptually similar to the formation of indoles and carbazoles based on the thermal elimination of nitrogen from vinyl or arylazides.[34] This transformation is of some interest since the expected reaction products (π-heterocycle)FeCp* have served as nucleophilic catalysts, with varying degrees of effectiveness, for the acylation of alcohols, the cyanosilylation of aldehydes and the addition of alcohols to ketenes.[35]

The synthesis of the azide **14** started with **2**, which was subjected to reduction with sodium borohydride to provide **14** in almost quantitative yield (97%), which in turn was converted

into β-ferrocenylvinylazide **15** in 75% yield by treatment with phenylacetyl chloride and triethylamine at room temperature. Thermolysis of the azide **15** in boiling *o*-xylene or toluene provided a complex mixture from which the desired annelated ferrocene was not detected (Scheme 4).



2 **14** **15**

Reagents and conditions: a) $NaBH_4$, EtOH, AcOH; **b)** $PhCH_2COCl$, Et_3N, THF, 72 h, r.t. **c)** o-xylene, Δ, 30 min. or toluene, Δ, 1 h.

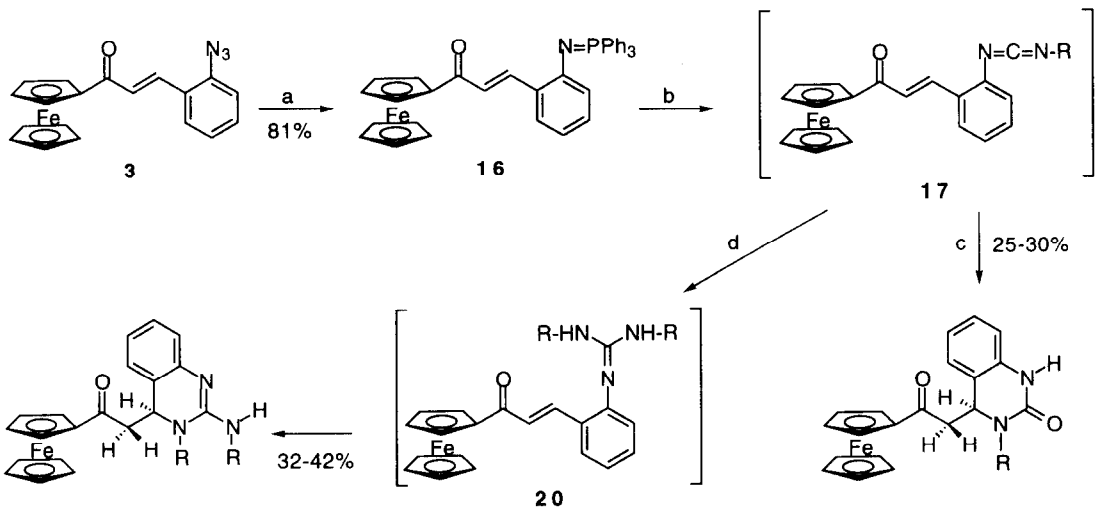
Scheme 4

On the other hand, aza-Wittig reaction of iminophosphorane **16**, readily available in 85% yield from the azide **3** and triphenylphosphine,[19] with aromatic isocyanates in dry tetrahydrofuran at room temperature gave the corresponding carbodiimides **17**, which were used for the next step without further purification. When carbodiimides **17** were treated with a solution of aqueous TBAF in tetrahydrofuran (1:4 molar ratio) in the presence of a mixture of anhydrous $MgSO_4/Na_2SO_4$ at room temperature, the acetylferrocenyl-substituted dihydroquinazoline derivatives **18** were obtained in yields ranging 25 to 31%. When the reaction was carried out in the absence of the dehydrating agent, the corresponding ureas derived from **17** were found to be the major product along with small amount of the cyclised product **18**. Carbodiimides **17** also reacted with aromatic amines at room temperature to give directly the dihydroquinazoline derivatives **19** in 31-40% yields (Scheme 5).

As far as the mechanism of the conversion **17** → **18** is concerned, it must be pointed out that ureas derived from **17** were recovered unchanged after further treatment with TBAF/THF at room temperature. Hence, it is thought that the TBAF strongly increases the nucleophilic character of the nitrogen atom of the carbodiimide[12, 36, 37] promoting in this case an intramolecular N-conjugate addition to the *o*-unsaturated side chain in a Michael-type

fashion, followed by hydrolysis of the resulting cyclised product by the water present in the TBAF/THF solution.

The conversion **17** → **19** could be understood by initial formation of a guanidine as intermediate which under the reaction conditions undergoes cyclization by a N-conjugate addition on the *o*-unsaturated side chain to give the cyclised product **19**. Only in one case, when tosyl isocyanate and phenacylamine were used as reagents, was the intermediate guanidine isolated.



Reagents and conditions: **a)** PPh_3, CH_2Cl_2, rt; **b)** R-N=C=O, CH_2Cl_2, rt; **c)** TBAF, THF/H_2O, r.t.; **d)** R-NH_2, r.t.

Scheme 5

In these transformations one stereogenic center is formed, and the NMR spectral data of compounds **18**, **19** and **20** therefore deserve some comment. The Fc-CO-CH_2 protons were diastereotopic appearing in compound **18** as a two double doublets in the region 3.0-3.18 ppm (J=16.5-16.7 and 2.9-3.8 Hz) and 3.2-3.51 ppm (J=16.6-16-9 and 9.0-10.4 Hz). Similar chemical shifts and patterns were found for these protons in compounds **19**. The methine proton in compounds **18** and **19** appeared as a double doublet in the region 5.0-5.49 (J=8.0-10.4 and 2.9-5,3 Hz).

Conclusion

The results reported here clearly show that azido-functionalised ferrocene derivatives easily prepared from acetylferrocene, are useful building blocks for the preparation of several kinds of ferrocenyl aza-heterocycles. In particular, the reaction of the α-azidoacetyl ferrocene with isocyanates or acid chlorides and triphenylphosphine appears to be a simple but very effective way to prepare ferrocene-substituted oxazoles. The aza-Wittig reaction of the iminophosphorane derived from 3-(*o*-azidophenyl)-1-ferrocenylpropenone with isocyanates provides the corresponding carbodiimide which is converted to ferrocene-substituted dihydroquinazoline derivatives by the action of TBAF or amines.

Cyclic voltammetry experiments reveal that 2,5-bis(ferrocenyl)oxazole **13** exhibits two reversible redox processes, indicating significant electronic interactions between the metal centers through the oxazole ring in this compound. In addition, the UV/Vis spectra of the ferrocenyl oxazoles **11b** and **13** showed moderate solvatochromic behaviour, which augur well for this sort of materials to display NLO properties.

Experimental

General Methods

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 (200 MHz) or a Varian Unity 300 (300 MHz). The EI and FAB mass spectra, using *m*-nitrobenzyl alcohol as matrix, were recorded on a Hewlett-Packard 5993C spectrometer or a Fisons AUTOSPEC 500 VG. Microanalyses were performed on a Perkin-Elmer 240C instrument. UV/Vis spectra were carried out using a Hitachi U-3200 spectrophotometer. The cyclic voltammetric measurements were performed on a QUICELTRON potentiostat/galvanostat controlled by a personal computer.

Electrochemical procedure for cyclic voltammetry

Acetonitrile and tetra-*n*-butylammonium perchlorate supporting electrolyte (polarogrphic grade) were commercial and were used without further purification. Experiments were carried out in a three-electrode cell. The counter electrode was platinum foil and the reference was saturated calomel (SCE). The cyclic voltammetry was performed at a platinum disk working electrode with a variable scan rate. Then, 5 ml of acetonitrile solution containing 0.1M [*n*-Bu_4N][ClO_4] was poured into the cell followed by 5 mmol of the derivative (1mM). Deoxygenation of the solution was achieved by bubbling nitrogen for at least 10 min.

Preparation of α-bromoacetylferrocene, **4.**

To a solution of LDA (72.3 mmol) in anhydrous THF (20 ml) at -78°C and under nitrogen a solution of acetylferrocene (10 g, 43.8 mmol) in the same solvent (20 ml) was added dropwise. The reaction mixture was stirred at -78°C for 2 h and then $ClSiMe_3$ (57 mmol) was

added. After 4 h under these reaction conditions, NBS (9.92 g, 57 mmol) was added and the solution was stirred until the reaction reached room temperature (6-8 h). The reaction mixture was filtered through a silica gel layer and the resulting solution was evaporated to dryness and chromatographed on a silica gel column using dichloromethane/ethyl acetate (20:1) as eluent to give (**4**) (R_f = 0.72) in 80% yield; mp. 68-71°C (red prisms) (Found: C, 46.79; H, 3.55. $C_{12}H_{11}BrFeO$ requires; C, 46.95; H, 3.61 %). ir (Nujol): 1675, 1458, 1387, 1290, 1222, 1114, 1069, 824 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.20 (s, 2H), 4.25 (s, 5H), 4.60 (t, 2H, J=1.7 Hz), 4.84 (t, 2H, J=1.7 Hz); ^{13}C NMR δ ($CDCl_3$): 31.6 (CH_2), 69.8 (2xCH, C_5H_4), 70.1 (5xCH, C_5H_5), 73.1 (2xCH, C_5H_4), 76.6 (ipso-Fc), 195.5 (C=O); m/z (%): 308 (M^++2, 98), 306 (M^+,100), 262 (32), 228 (18), 227 (18), 202 (62), 200 (65), 185 (25), 156 (17), 129 (17), 121 (81), 105 (27), 78 (63).

Preparation of α-azidoacetylferrocene, **2.**

To a suspension of polymeric quaternary ammonium azide [18] (30 g) in dry CH_2Cl_2 (30 ml) α-bromoacetylferrocene (1.5 g, 4.9 mmol) was added. After 24 h of stirring at room temperature, the polymer was filtered and washed with CH_2Cl_2 (30 ml). Evaporation of the combined solvent mixture gave pure α-azidoacetylferrocene (**2**) as a red oil in 98% yield; ir (Nujol): 2109, 1677, 1458, 1381, 1247, 1075, 829 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.24 (s, 7H), 4.59 (t, 2H, J=1.8 Hz), 4.79 (t, 2H, J=1.8 Hz); ^{13}C NMR δ ($CDCl_3$): 54.9 (CH_2), 69.0 (2xCH, C_5H_4), 70.1 (5xCH, C_5H_5), 72.9 (2xCH, C_5H_4), 75.7 (ipso-Fc), 195.5 (C=O); m/z (%): 241 (M^+-N_2, 12), 191 (21), 147 (47), 91 (14), 57 (100).

Preparation of 2,5-bis(ferrocenyl)pyrazine, **6.**

To a solution of α-azidoacetylferrocene (0.21 g, 0.85 mol) in dry diethyl ether (20 ml) a solution of triphenylphosphine (0.25 g, 0.95 mmol) in the same solvent (15 ml) was added dropwise under nitrogen and the mixture was stirred overnight at room temperature. The resulting orange precipitated was filtered and crystallized from ether to give (**6**) in 34% yield; mp. 244-247°C (orange prisms) (Found: C, 64.55; H, 4.28; N, 6.24. $C_{24}H_{20}Fe_2N_2$ requires; C, 64.33; H, 4.50; N, 6.25 %). ir (Nujol): 1623, 1272, 1107, 1039, 814 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.10 (s, 10H), 4.47 (t, 4H, J=1.8 Hz), 4.95 (t, 4H, J=1.8 Hz), 8.57 (s, 2H); ^{13}C NMR δ ($CDCl_3$): 66.9 (4xCH, 2xC_5H_4), 69.7 (10xCH, 2xC_5H_5), 70.3 (4xCH, 2xC_5H_4), 76.0 (2xipso-Fc), 140.7 (2xCH), 151.5 (2xq); m/z (%): 448 (M^+,100), 383 (12), 327 (11), 224 (23), 121 (10).

General procedure for the preparation of 2-arylamino-5-ferrocenyloxazoles **8.**

To a solution of α-azidoacetylferrocene (0.4 g, 1.49 mmol) and the appropriate aryl isocyanate (1.86 mmol) in anhydrous diethyl ether (15 ml) a solution of triphenylphosphine (0.49 g, 1.86 mmol) in the same solvent (10 ml) was added dropwise. The reaction mixture was stirred at room temperature under nitrogen until the corresponding carbodiimide was completely formed. Then the appropriate arylamine (2.98 mmol) was added and the solution was stirred under the same conditions for 20 h. The solvent was evaporated to dryness and the residue chromatographed on a silica gel column, using dichloromethane/ethyl acetate (20:1) as eluent to give **8** which was crystallized from diethyl ether.

8a: (Ar=3-H_3C-C_6H_4) mp. 158-161°C (yellow prisms); 30%; (Found: C, 66.88; H, 5.22; N, 7.69. $C_{20}H_{18}FeN_2O$ requires; C, 67.06; H, 5.06; N, 7.82 %). ir. (Nujol): 1618, 1581, 1135 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.39 (s, 3H), 4.15 (s, 5H), 4.27 (bs, 2H), 4.52 (bs, 2H), 6.78-6.89 (m, 2H), 7.25-7.32 (m, 3H), 7.80 (bs, 1H); ^{13}C NMR δ ($CDCl_3$): 21.7, 65.2 (2xCH, C_5H_4), 68.5 (2xCH, C_5H_4), 69.4 (5xCH, C_5H_5), 73.6 (ipso-Fc), 114.1 (CH), 117.5 (CH), 119. 7(CH) 119.9 (q), 122.9 (CH), 129.1 (CH), 138.8 (q), 139.2 (q), 155.9 (q); m/z (%): 358 (M^+,100), 227 (18), 179 (11), 121 (36), 91 (12), 77 (14), 56 (17).

8b: (Ar=4-H_3C-C_6H_4) mp. 171-174°C (yellow prisms); 32%; (Found: C, 67.20; H, 5.15; N, 7.58. $C_{20}H_{18}FeN_2O$ requires; C, 67.06; H, 5.06; N, 7.82 %). ir. (Nujol): 1611, 1586, 1425, 1133, 896 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.33 (s, 3H), 4.14 (s, 5H), 4.28 (bs, 2H), 4.52 (bs, 2H), 6.77 (s, 1H), 7.16 (d, 2H, J=7.8 Hz), 7.37 (d, 2H, J=7.8 Hz), 8.01 (bs, 1H); ^{13}C NMR δ ($CDCl_3$): 20.7, 66.2 (2xCH, C_5H_4), 68.5 (2xCH, C_5H_4), 69.5 (5xCH, C_5H_5), 73.7 (ipso-Fc), 117.1 (CH), 119.6 (CH), 129.8 (CH), 131.6 (q), 136.4 (q), 144.3 (q), 156.4 (q); m/z (%): 358 (M^+,100), 227 (15), 179 (14), 121 (25), 91 (12), 77 (8), 56 (8).

Preparation of 2-benzylamino-5-ferrocenyloxazole **9a** *and 2-(N,N'-dibenzylureido)-5-ferrocenyloxazole* **9b**.

To a solution of α-azidoacetylferrocene (0.4 g, 1.48 mmol) and benzyl isocyanate (0.39 g, 2.96 mmol) in anhydrous diethyl ether (15 ml) a solution of triphenylphosphine (0.48 g, 1.85 mmol) in the same solvent (10 ml) was added dropwise. The solution was stirred at room temperature and under nitrogen until the corresponding carbodiimide was completely formed. To the solution obtained, benzylamine (0.48 g, 4.46 mmol) was added and then stirred overnight under the above conditions. The solution was filtered and the filtrate evaporated to dryness and chromatographed on a silica gel column to give a mixture of **9a** and **9b.**

9a: (R=H) mp. 179-181°C (R_f = 0.29 using ethyl acetate/n-hexane 9:1 as eluent); 12%; (Found: C, 66.79; H, 5.20; N, 7.58. $C_{20}H_{18}FeN_2O$ requires; C, 67.06; H, 5.06; N, 7.82 %). ir. (Nujol): 3320, 1621, 1594, 725, 700, 668 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.10-4.23 (m, 9H), 5.13 (d, 2H, J=5.7 Hz), 6.40 (s, 1H), 7.14-7.30 (m, 5H), 11.13 (bs, 1H); ^{13}C NMR δ ($CDCl_3$): 44.6 (CH_2), 67.5 (2xCH, C_5H_4), 68.4 (2xCH, C_5H_4), 69.3 (5xCH, C_5H_5), 75.1 (ipso-Fc), 105.7 (CH), 122.1 (q), 126.2 (2xCH), 127.1 (CH), 128.7 (2xCH), 137.7 (q), 155.6 (q); m/z (%): 358 (M^+,100), 267 (76), 211 (25), 121 (28), 91 (28). ^{13}C NMR

9b: (R=$PhCH_2NHCO$) mp. 163-165°C C (R_f = 0.51 using ethyl acetate/n-hexane 1:2 as eluent); 31%; (Found: C, 68.20; H, 4.95; N, 8.71. $C_{28}H_{25}FeN_3O_2$ requires; C, 68.44; H, 5.13; N, 8.55 %). ir. (Nujol): 3295, 1680, 1552, 1411, 1364, 1327, 1222, 922, 822 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.14 (s, 5H), 4.19-4.23 (m, 4H), 4.57 (d, 2H, J=5.7 Hz), 5.02 (s, 2H), 7.08-7.38 (m, 11H), 9.10 (t, 1H, J=5.7 Hz). ^{13}C NMR δ ($CDCl_3$): 43.9 (CH_2), 44.9 (CH_2), 68.1 (2xCH, C_5H_4), 68.9 (2xCH, C_5H_4), 69.5 (5xCH, C_5H_5), 73.3 (ipso-Fc), 104.2 (CH), 123.1 (q), 126.3 (CH), 127.4 (CH), 127.5 (CH), 127.6 (CH), 128.6 (CH), 128.7 (CH), 136.6 (q), 137.8 (q), 150.2 (q), 152.3 (q); m/z (%): 491 (M^+,6), 358 (100), 267 (74), 212 (13), 121 (27), 91 (45).

General procedure for the preparation of 2-aryl-5-ferrocenyloxazoles **11**, *2-ferrocenyl-5-phenyloxazole* **12** *and 2,5-bis(ferrocenyl)oxazole* **13**.

To a solution of α-azidoacetylferrocene (0.35 g, 1.3 mmol) and the appropriate acid chloride (1.5 mmol) in anhydrous diethyl ether (15 ml) a solution of triphenylphosphine (0.43 g, 1.63 mmol) in the same solvent (10 ml) was added dropwise, at room temperature and under nitrogen. The reaction mixture was stirred for 24 h and the ethereal solution was concentrated under reduced pressure and chromatographed on a silica gel column with dichloromethane/ethyl acetate as eluent (20:1) to give the corresponding oxazoles which were crystallized from diethyl ether.

11a: (R=4-Cl), mp. 133-136°C; (R_f = 0.66); (45%); (Found: C, 62.66; H, 3.90; N, 3.61. $C_{19}H_{14}ClFeNO$ requires; C, 62.76; H, 3.88; N, 3.85 %). ir. (Nujol): 1616, 1484, 1407, 1098, 1017, 964, 873, 834, 735 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.14 (s, 5H), 4.36 (t, 2H, J=1.7 Hz), 4.66 (t, 2H, J=1.7 Hz), 7.06 (s, 1H), 7.45 (d, 2H, J=8.5 Hz), 8.00 (d, 2H, J=8.5 Hz); ^{13}C NMR δ ($CDCl_3$): 66.0 (2xCH, C_5H_4), 69.2 (2xCH, C_5H_4), 69.7 (5xCH, C_5H_5), 72.3 (ipso-Fc), 122.1 (CH), 126.2 (q), 127.2 (2xCH), 129.1 (2xCH), 135.9 (q), 151.8 (q), 159.3 (q); m/z (%): 365 (M^++2, 58), 363 (M^+, 100), 152 (13), 121 (31), 77 (21), 56 (23).

11b: (R=4-O_2N), mp. 197-199°C; (R_f = 0.83); (51%); (Found: C, 60.78; H, 3.90; N, 7.35. $C_{19}H_{14}FeN_2O_3$ requires; C, 60.99; H, 3.77; N, 7.49 %). ir. (Nujol): 1598, 1544, 1342, 1106, 854, 824, 712 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.15 (s, 5H), 4.41 (t, 2H, J=1.8 Hz), 4.70 (t, 2H, J=1.8 Hz), 7.15 (s, 1H), 8.21 (d, 2H, J=9.1 Hz), 8.34 (d, 2H, J=9.1 Hz); ^{13}C NMR δ ($CDCl_3$): 66.2 (2xCH, C_5H_4), 69.6 (2xCH, C_5H_4), 69.7 (5xCH, C_5H_5), 71.5 (ipso-Fc), 122.9 (CH), 124.2 (2xCH), 126.4 (2xCH), 132.9 (q), 148.1 (q), 153.7 (q), 157.9 (q); m/z (%): 374 (M^+, 100), 344 (24), 328 (55), 222 (11), 121 (37), 77 (22), 56 (30).

12: mp. 115-117°C; (R_f = 0.49); (25%); (Found: C, 69.15; H, 4.48; N, 4.09. $C_{19}H_{15}FeNO$ requires; C, 69.33; H, 4.59; N, 4.25 %). ir. (Nujol): 1586, 1455, 1291, 1135, 1106, 1028, 960, 827, 766, 746, 695 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.16 (s, 5H), 4.42 (bs, 2H), 4.96 (bs, 2H), 7.31-7.69 (m, 6H); ^{13}C NMR δ ($CDCl_3$): 67.5 (2xCH, C_5H_4), 69.6 (5xCH, C_5H_5), 70.1 (2xCH, C_5H_4), 70.9 (ipso-Fc), 123.1 (CH), 123.8 (2xCH), 128.0 (CH), 128.2 (q), 150.2 (q), 163.4 (q); m/z (%): 329 (M^+, 100), 153 (13), 133 (12), 121 (23), 77 (15), 56 (17).

13: mp. 157-160°C; (R_f = 0.49); (29%); (Found: C, 63.25; H, 4.17; N, 3.32. $C_{23}H_{19}Fe_2NO$ requires; C, 63.20; H, 4.38; N, 3.20 %); ir. (Nujol): 1618, 1591, 1442, 1414, 1305, 1280, 1130, 1110, 1023, 1005, 822, 745 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.15 (s, 5H), 4.18 (s, 5H), 4.33 (t, 2H, J=1.8 Hz), 4.40 (t, 2H, J=1.8 Hz), 4.64 (t, 2H, J=1.8 Hz), 4.95 (t, 2H, J=1.8 Hz), 6.92 (s, 1H); ^{13}C NMR δ ($CDCl_3$): 65.7 (2xCH, C_5H_4), 67.3 (2xCH, C_5H_4), 68.9 (2xCH, C_5H_4), 69.5 (5xCH, C_5H_5), 69.6 (5xCH, C_5H_5), 69.9 (2xCH, C_5H_4), 71.4 (ipso-Fc), 73.0 (ipso-Fc), 121.5 (CH), 150.1 (q), 162.2 (q); m/z (%): 437 (M^+, 100), 260 (10), 218 (16), 121 (28), 56 (17).

Preparation of(R)/(S) 2-azido-1-hydroxyethylferrocene **14**

A solution of α-azidoacetylferrocene (0.44g, 1.63 mmol) in anhydrous ethanol (15 ml) was treated with an excess of sodium borohydride (0.091 g, 2.4 mmol) and glacial acetic acid (0.5 ml). After 40 min. the mixture was poured into water (15 ml) and extracted with dichloromethane (3x20 ml). The combined extracts were dried (Na_2SO_4), evaporated under reduced pressure and chromatographed on a silica gel column with dichloromethane/ethyl

acetate (20:1) as eluent to give **14** which was crystallized from diethyl ether; mp. 40-41°C (orange prisms); (97%); (Found: C, 53.39; H, 4.55; N, 15.60. $C_{12}H_{13}FeN_3O$ requires; C, 53.17; H, 4.83; N, 15.50 %); ir. ($CHCl_3$): 3447, 2104, 1449, 1415, 1401, 1315, 1257, 1072, 1033, 823 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.29 (d, 1H, J=3.3 Hz), 3.39 (d, 2H, J=5.4 Hz), 4.20-4.22 (m, 7H), 4.28 (m, 2H), 4.54 (td, 1H); ^{13}C NMR δ ($CDCl_3$): 57.0 (CH_2), 65.5 (CH), 67.1 (CH), 68.2 (CH), 68.3 (CH), 68.4 (5xCH, C_5H_5), 69.3 (CH), 89.6 (ipso-Fc); m/z (%): 271 (M^+, 100), 243 (69), 186 (85), 121 (70).

Preparation of (Z)-2-azidovinylferrocene **15**

A solution of 2-azido-1-hydroxyethylferrocene **14** (0.5 g, 1.8 mmol), phenylacetyl chloride (0.26 g, 2 mmol) and triethylamine (0.2 g, 2 mmol) in anhydrous THF (20 ml) was stirred at room temperature until compound **14** was not detected by TLC. Then the solvent was evaporated under reduced pressure and the crude chromatographed on a silica gel column using dichloromethane/ethyl acetate (20:1) as eluent; mp. 50-52°C; (75%); (Found: C, 56.70; H, 4.12; N, 16.81. $C_{12}H_{11}FeN_3$ requires; C, 56.95; H, 4.38; N, 16.60 %); ir. ($CHCl_3$): 2104, 1641, 1469, 1399, 1275, 826 cm^{-1}; ^1H NMR δ ($CDCl_3$): 4.03 (s, 5H), 4.14 (t, 2H, J=1.8 Hz), 4.45 (t, 2H, J=1.8 Hz), 5.37 (d, 1H, J=8.1 Hz), 6.10 (d, 1H, J=8.1 Hz); ^{13}C NMR δ ($CDCl_3$): 68.7 (2xCH, C_5H_4), 69.1 (2xCH, C_5H_4), 69.2 (5xCH, C_5H_5), 78.6 (ipso-Fc), 116.5 (CH), 122.31 (CH); m/z (%): 253 (M^+, 15), 225 (100), 184 (4), 152 (28), 121 (76), 56 (38).

General procedure for the preparation of 3-aryl-4-ferrocenecarbonylmethyl-1,4-dihydroquinazolin-2-one **18**

To a solution of the iminophosphorane **16** (0.5 g, 0.084 mmol) in a mixture of anhydrous dichloromethane (15 ml) and THF (20 ml) an equimolar amount of the appropriate isocyanate was added under nitrogen. The resultant mixture was stirred at room temperature until the corresponding carbodiimide was completely formed. Then, 1M TBAF in THF (3.5 ml) was added and stirring was continued until the carbodiimide band had completely disappeared from the IR spectra. The solvent was removed under reduced pressure and the crude mixture poured into Na_2HPO_4 buffer (pH 7, 20 ml), extracted with ethyl acetate (3x50 ml) and the organic layers were dried over anhydrous $MgSO_4$. After filtration, the solution was concentrated to dryness and the crude product was chromatographed on a silica gel column, using ethyl acetate/n-hexane (1/1) as eluent to give **18** which was crystallized from $CHCl_3$.

18a: (Ar=4-H_3C-C_6H_4) mp. 276-279°C; (30%); (Found: C, 69.70; H, 5.31; N, 5.79. $C_{27}H_{24}FeN_2O_2$ requires; C, 69.84; H, 5.21; N, 6.03 %); ir. (Nujol): 3115, 1679, 1657, 1519, 1599, 1449, 1273, 808, 750 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.35 (s, 3H), 3.47 (dd, 1H, J=16.8Hz, J=10.4 Hz), 3.16 (dd, 1H, J=16.7 Hz, J=3.0 Hz), 3.84 (s, 5H), 4.44 (t, 2H, J=1.9 Hz), 4.60 (bs, 2H), 5.49 (dd, 1H, J=10.4 Hz, J=3.0 Hz), 6.8 (dd, 1H, J=7.2 Hz, J=0.6 Hz), 7.0 (td, 1H, J=7.3 Hz, J=0.6 Hz), 7.23-7.25 (m, 6H), 8.03 (s, 1H); ^{13}C NMR δ ($CDCl_3$): 21.0 (CH_3), 43.7 (CH_2), 58.5 (CH), 68.8 (CH, C_5H_4), 69.3 (CH, C_5H_4), 69.6 (5xCH, C_5H_5), 72.5 (CH, C_5H_4), 72.5 (CH, C_5H_4), 78.9 (ipso-Fc), 114.1 (CH), 122.2 (CH), 127.0 (CH), 128.2 (CH), 126.8 (CH), 129.9 (CH), 122.2 (q), 136.5 (q), 136.6 (q), 138.2 (q), 154.2 (C=O), 200.6 (C=O); FAB-MS, m/z (%): 465 (M^++1, 71).

18b: (Ar=3-H_3C-C_6H_4) mp. 226-227°C; (25%); (Found: C, 69.77; H, 4.98; N, 6.15. $C_{27}H_{24}FeN_2O_2$ requires; C, 69.84; H, 5.21; N, 6.03 %); ir. (Nujol): 3213, 1681, 1660, 1601, 1491, 1459, 1424, 1377, 1108, 756, 777 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.37 (s, 3H), 3.18 (dd, 1H, J=16.9Hz, J=3.8 Hz), 3.51 (dd, 1H, J=16.9 Hz, J=10.4 Hz), 3.85 (s, 5H), 4.45 (t, 2H, J=1.9 Hz), 4.60 (bs, 2H), 5.50 (dd, 1H, J=10.4 Hz, J=3.0 Hz), 6.85 (d, 1H, J=7.8 Hz), 6.96 (t, 1H, J=7.6 Hz), 7.10-7.35 (m, 6H), 8.4 (s, 1H); ^{13}C NMR δ ($CDCl_3$): 21.4 (CH_3), 43.8 (CH_2), 58.4 (CH), 68.8 (CH, C_5H_4), 69.3 (CH, C_5H_4), 69.5 (5xCH, C_5H_5), 72.5 (2xCH, C_5H_4), 78.8 (ipso-Fc), 114.2 (CH), 122.2 (CH), 123.9 (CH), 126.9 (CH), 127.6 (2xCH), 128.8 (CH), 129.0 (CH), 122.5 (q), 136.5 (q), 139.1 (q), 140.8 (q), 154.3 (C=O), 200.6 (C=O); FAB-MS, m/z (%): 465 (M^++1, 84).

18c: (Ar=4-H_3CO-C_6H_4) mp. 270-271°C; (25%); (Found: C, 67.65; H, 4.78; N, 5.79. $C_{27}H_{24}FeN_2O_3$ requires; C, 67.51; H, 5.04; N, 5.83 %); ir. (Nujol): 3235, 1686, 1659, 1516, 1461, 1453, 1298, 1242, 1085, 1029, 756 cm^{-1}; ^1H NMR δ ($CDCl_3$): 3.15 (dd, 1H, J=16.6 Hz, J=2.9 Hz), 3.45 (dd, 1H, J=16.6 Hz, J=10.3 Hz), 3.80 (s, 3H), 3.85 (s, 5H), 4.45 (t, 2H, J=1.9 Hz), 4.60 (bs, 2H), 5.44 (dd, 1H, J=10.3 Hz, J=2.9 Hz), 6.8 (d, 1H, J=7.8 Hz), 6.90-7.00 (m, 3H),7.18-7.25 (m, 2H), 7.40-7.87 (m, 3H); ^{13}C NMR δ ($CDCl_3$): 43.6 (CH_2), 55.5 (CH_3), 58.9 (CH), 68.8 (CH, C_5H_4), 69.3 (CH, C_5H_4), 69.50 (5xCH, C_5H_5), 72.6 (2xCH, C_5H_4), 79.6 (ipso-Fc), 113.8 (CH), 114.6 (CH), 120.3 (q), 122.3 (CH), 127.1 (CH), 128.5 (CH), 128.9 (CH), 133.5 (q), 136.4 (q), 153.0 (q), 154.0 (C=O), 200.5 (C=O); FAB-MS, m/z (%): 481 (M^++1, 52).

18d: (Ar=C_6H_5-CH_2) mp. 214-215°C; (30%); (Found: C, 70.01; H, 5.12; N, 5.79. $C_{27}H_{24}FeN_2O_{32}$ requires; C, 69.84; H, 5.21; N, 6.03 %); ir. (Nujol): 3201, 1680, 1660, 1470, 1455, 1332, 1290, 1629, 778, 756 cm^{-1}; ^1H NMR δ ($CDCl_3$): 3.00 (dd, 1H, J=16.5 Hz, J=3.9 Hz), 3.20 (dd, 1H, J=16.6 Hz, J=9.0 Hz), 3.9 (s, 5H), 4.50 (t, 2H, J=1.9 Hz), 4.60 (bs, 2H), 4.34 (s, 2H), 5.00 (dd, 1H, J= 9.0 Hz, J=2.9 Hz), 6.78 (d, 1H, J=7.9 Hz), 6.9 (t, 1H, J=7.3 Hz), 7.13-7.31 (m, 7H), 7.58 (bs, 1H); ^{13}C NMR δ ($CDCl_3$): 44.8 (CH_2), 49.2 (CH_2), 54.3 (CH), 69.0 (CH, C_5H_4), 69.5 (CH, C_5H_4), 69.7 (5xCH, C_5H_5), 72.6 (CH, C_5H_4), 72.7 (CH, C_5H_4), 113.8 (CH), 121.8 (CH), 122.5 (q), 126.3 (CH), 126.9 (CH), 127.4 (CH), 127.7 (CH), 128.4 (CH), 136.6 (q), 139.2 (q), 155.2 (C=O), 200.9 (C=O); FAB-MS, m/z (%): 481 (M^++1, 81).

General procedure for the preparation of 2-arylamino-4-ferrocenecarbonylmethyl-3,4-dihydroquinazolines **19** *and 1-ferrocenyl-3-[o-(2-phenacyl-3-tosyl)guanidinophenyl]propenone* **20**.

To a solution of the iminophosphorane **16** (0.5 g, 0.84 mmol) in a mixture of anhydrous dichloromethane (15 ml) and THF (20 ml) an equimolar amount of the appropriate isocyanate was added under nitrogen. The resultant mixture was stirred at room temperature until the corresponding carbodiimide was completely formed.Then, a solution of an equimolar amount of the appropriate amine (0.84 mmol) in the same solvent (5 ml) was added and the reaction mixture was stirred under nitrogen for 48 h. The solvent was removed under reduced pressure and the residual product was chromatographed on a silica gel column with ethyl acetate/n-hexane (1:1) as eluent to give **19** or **20**, which were crystallized from dichloromethane/n-hexane (1:2).

19a: (Ar=4-$CH_3.C_6H_5$) mp. 144-145°C; (32%); (Found: C, 73.69; H, 5.47; N, 7.39. $C_{34}H_{31}FeN_3O$ requires; C, 73.78; H, 5.65; N, 7.59 %); ir. (CH_2Cl_2): 3440, 3325, 1663, 1616, 1594, 1513, 1465, 1452, 1377, 1073, 1029, 826, 762 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.30 (s, 3H), 2.63 (s, 3H), 3.28 (dd, 1H, J=16.5 Hz, J=4.6 Hz), 3.55 (dd, 1H, J=16.5 Hz, J=9 Hz), 3.92 (s, 5H), 4.54 (bs, 2H), 4.72 (bs, 1H), 4.79 (bs, 1H), 5.47 (dd, 1H, J=9Hz, J=4.6 Hz), 6.90-7.33 (m, 12 H), 7.72 (s, 1H); ^{13}C NMR δ ($CDCl_3$): 20.7 (CH_3), 20.8 (CH_3), 44.7 (CH_2), 58.6 (CH), 68.9 (CH, C_5H_4), 69.6 (5xCH, C_5H_5), 69.8 (CH, C_5H_4), 72.6 (CH, C_5H_4), 72.7 (CH, C_5H_4), 79.2 (ipso-Fc), 119.9 (CH), 122.9 (CH), 123.7 (q), 123.8 (CH), 125.6 (CH), 128.5 (CH), 129.4 (CH), 129.9 (CH), 132.2 (q), 135.2 (q), 140.7 (q), 151.2 (q), 201.3 (C=O); FAB-MS, m/z (%): 554 (M^++ 1, 100).

19b: (Ar=4-$CH_3O.C_6H_5$) mp. 134-135°C; (40%); (Found: C, 69.90; H, 5.15; N, 7.33. $C_{34}H_{31}FeN_3O_3$ requires; C, 69.75; H, 5.34; N, 7.18 %); ir. (CH_2Cl_2): 3312, 1662, 1583, 1561, 1534, 1508, 1477, 1245, 1106, 1029, 830 cm^{-1}; ^1H NMR δ ($CDCl_3$): 3.28-3.50 (m, 2H), 3.73 (s, 6H), 3.94 (s, 5H), 4.50 (bs, 2H), 4.70 (bs, 1H), 4.74 (bs, 1H), 5.34 (t, 1H, J=7.7 Hz), 6.72 (d, 1H, J=7.9 Hz), 6.97-7.51 (m, 12H); ^{13}C NMR δ ($CDCl_3$): 44.7 (CH_2), 55.5 (CH_3), 55.6 (CH_3), 59.1 (CH), 68.9 (CH, C_5H_4), 69.7 (5xCH, C_5H_5), 69.8 (CH, C_5H_4), 72.6 (CH, C_5H_4), 72.7 (CH, C_5H_4), 79.0 (ipso-Fc), 114.2 (CH), 114.7 (CH), 118.7 (CH), 122.9 (q), 125.3 (CH), 128.3 (CH), 128.6 (CH), 132.5 (CH), 132.7 (CH), 135.7 (q), 140.7 (q), 156.0 (q), 157.8 (2xq), 201.5 (C=O); FAB-MS, m/z (%): 586 (M^++ 1, 100).

19c: (Ar=$C_6H_5.CH_2$) mp. 161-162°C; (43%); (Found: C, 73.58; H, 5.80; N, 7.70. $C_{34}H_{31}FeN_3O$ requires; C, 73.78; H, 5.65; N, 7.59 %); ir. (CH_2Cl_2): 3320, 1660, 1541, 1465, 1457, 1379, 1285, 1126, 1073, 995, 831 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.94 (dd, 1H, J=16.8 Hz, J=6.6 Hz), 3.10 (dd, 1H, J=16.8 Hz, J=6.6 Hz), 4.00 (s, 5H), 4.40-4.80 (m, 8H), 5.0 (t, 1H, J=6.6 Hz), 7.15-7.25 (m, 10H), 7.51-7.70 (m, 5H); ^{13}C NMR δ ($CDCl_3$): 44.8 (CH_2), 46.1 (CH_2), 53.7 (CH_2),, 57.2 (CH), 68.9 (CH, C_5H_4), 69.6 (5xCH, C_5H_5), 69.7 (CH, C_5H_4), 72.5 (CH, C_5H_4), 72.6 (CH, C_5H_4), 79.2 (ipso-Fc), 124.77 (CH), 125.7 (q), 126.8 (CH), 127.1 (CH), 127.6 (CH), 127.7 (q), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 131.9 (CH), 132.1 (CH), 136.8 (q), 138.8 (q), 152.3 (q), 202.0 (C=O); FAB-MS, m/z (%): 554 (M^++ 1, 100).

20: mp.91-94°C; (45%); ir. (CH_2Cl_2): 3290, 1654, 1589, 1490, 1380, 1290, 1074, 825 cm^{-1}; ^1H NMR δ ($CDCl_3$): 2.42 (s, 3H), 4.23 (s, 5H), 4.58 (t, 2H, J=1.9 Hz), 4.75 (d, 2H, J=4.0 Hz), 4.93 (t, 2H, J=1.9 Hz), 6.0 (bs, 1H), 7.20 (d, 1H, J=16.0 Hz), 7.32 (d, 2H, J=8.0 Hz), 7.37-7.40 (m, 1H), 7.43-7.6 (m, 6H), 7.80-7.87 (m, 3H), 8.00 (d, 2H, J=16 Hz), 9.33 (bs, 1H)); ^{13}C NMR δ ($CDCl_3$): 29.7 (CH_3), 48.2 (CH_2), 69.9 (2xCH, C_5H_4), 70.1 (5xCH, C_5H_5), 73.0 (2xCH, C_5H_4), 80.3 (ipso-Fc), 123.2 (q), 126.1 (2xCH), 126.8 (CH), 127.9 (2xCH), 128.8 (CH), 129.1 (CH), 129.5 (CH), 129.6 (2xCH), 129.8 (CH), 131.2 (CH), 133.7 (q), 133.9 (q), 134.3 (CH), 134.9 (CH), 140.6 (q), 142.4 (q), 153.6 (q), 192.5 (C=O), 193.4 (C=O); FAB-MS, m/z (%): 646 (M^++ 1, 100).

Acknowledgements. We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (project number PB95-1019). We also thank Fundación Séneca (CARM) for a studentship (JLL).

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