Ethyl α-(Triphenylphosphoranylidene)amino-β-ferrocenylacrylate as a Starting Material for [2+2] Cycloadditions, Including the Aza-Wittig Reaction

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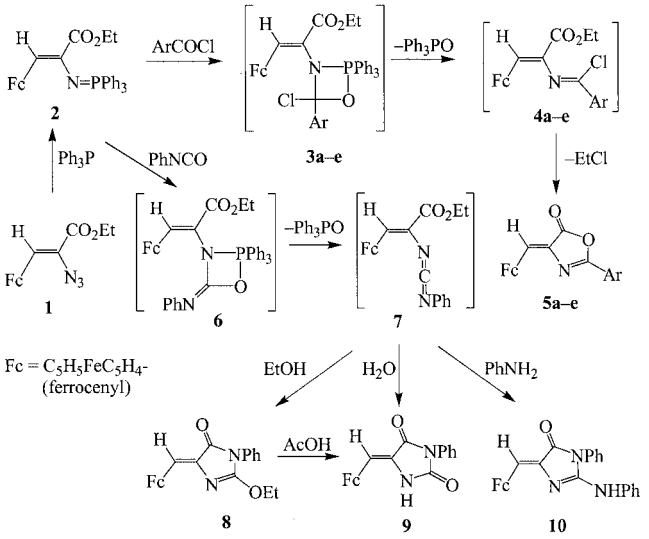
Ethyl α-(triphenylphosphoranylidene)amino-β-ferrocenylacrylate, synthesized from the corresponding azide, was treated with a few selected electrophilic agents potentially capable of undergoing the aza-Wittig reaction. The transformations with aroyl chlorides and phenylisocyanate afforded a series of novel 4-(ferrocenyl)methylidene-2-aryloxazolones. On treatment of the phosphorimino compound with DMAD two competitive reactions took place on the C=C and N=P bonds, giving rise to a novel amino(ferrocenyl)butadiene and a ferrocenyl-substituted aza-pentadienylphosphorylide, respectively. The parent azidoferrocenylacrylate underwent the expected 1,3-dipolar cycloaddition with DMAD, resulting in a triester of a (ferrocenyl)vinyl-substituted *v*-triazoletricarboxylate suitable for a variety of further heterocyclic syntheses. The structures of the new compounds were determined by IR and NMR spectroscopy, mass spectrometry, and X-ray analysis.

Introduction

The easily available ethyl α-azido-β-arylacrylates prepared by Knoevenagel condensation of the corresponding arylaldehydes and ethyl azidoacetate have been applied to the facile synthesis of a variety of condensed pyrrole and pyridine derivatives. These condensation reactions affording pyrroles and/or pyridines proceed through the intramolecular insertion of the thermally generated nitrene intermediate into an aromatic C−H bond.[1] It is, however, noteworthy that no analogous condensation reactions are known for ethyl α-azido-β-ferrocenylacrylate (**1**; Scheme 1), but that its (triphenylphosphoranylidene)amino derivative (**2**; Scheme 1) has been reported to be a good starting material for the preparation of a series of (ferrocenyl)(methylidene)imidazolones[2,3] and imidazo[1,2-*a*]diazepinones.[4] The first step in each reaction sequence was the aza-Wittig reaction with isocyanates to afford carbodiimides,[2−4] and these reactive intermediates were cyclized to give the imidazolone



(3–5)a Ar = 4-tolyl, **(3–5)b** Ar = 4-methoxyphenyl, **(3–5)c** Ar = 4-chlorophenyl, **(3–5)d** Ar = 3-nitrophenyl, **(3–5)e** Ar = 2,6-difluorophenyl.

Scheme 1

ring with the corresponding amino-donor nucleophile in the final step. The importance of iminophosphoranes is also reflected in a series of papers[5−7] providing comprehensive coverage of their versatile application in modern synthetic chemistry. In connection with our program of investigation of synthetic approaches to new ferrocene-containing hetero-

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cycles with potential biological activity we extended the scope of conversions of azide **1** and iminophosphorane **2** as outlined in Schemes 1 and 2.

Results and Discussion

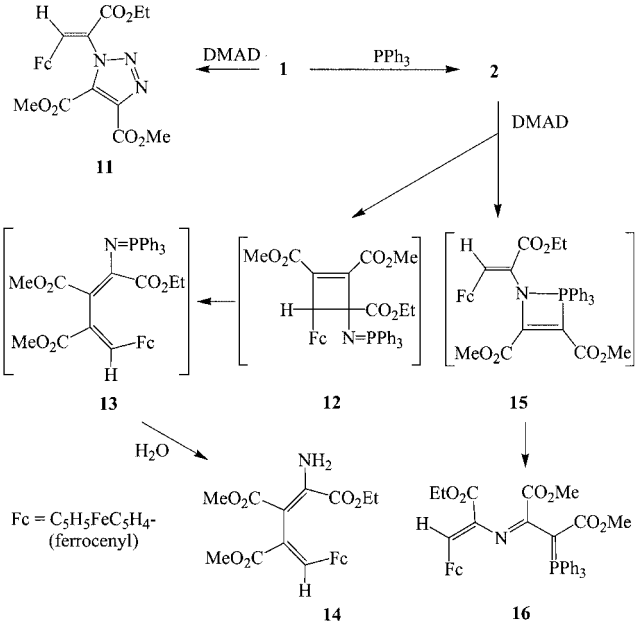
Iminophosphorane **2** was treated with aroyl chlorides in the presence of triethylamine to provide a series of new 4-(ferrocenyl)methylidene-2-aryloxazolones **5a−e**, potential precursors of *N*-acylated derivatives of ferrocenylalanine, in good yields. This procedure has also been used for the preparation of 4-arylidene-2-oxazolones,[8] condensed 1,3-oxazinones[9] and 5-(ferrocenyl)oxazoles.[10] The proposed mechanism for such conversions involves the primary formation of a chloroimidoyl ester (**4a−e**), which then undergoes ring closure through elimination of ethyl chloride[8,9] or hydrogen chloride[10] (Scheme 1).

The reaction between iminophosphorane **2** and phenyl isocyanate has also been studied. The *N*-phenylcarbodiimide **7** formed was treated with ethanol in dry pyridine to give the 2-ethoxyimidazolone **8**, treatment of which with acetic acid at reflux yielded (ferrocenyl)methylidenehydantoin (**9**), a compound with potential biological activity.[11,12]

As well as by conventional hydrolysis, this reaction may also proceed by N(3)-protonation followed by the loss of ethylene.[13] When **7** was treated with water in pyridine, **9** was contaminated by the 2-(phenylamino)imidazol-5-one **10**, the formation of which is obviously due to the action of aniline originating from the partial hydrolysis of the carbodiimide precursor. On the other hand, **7** seems to avoid intramolecular cyclization resulting in a condensed pyridine ring, as has been reported for a variety of analogous aryl-substituted carbodiimides.[14] (Scheme 1).

An interesting difference was detected in the cycloaddition reactions of **1** and **2** with dimethyl acetylenedicarboxylate (DMAD). Azide **1** afforded the *v*-triazole **11**, the product of the well documented 1,3-dipolar cycloaddition involving the azido group,[15] while prolonged treatment of **2** with DMAD under the same conditions simultaneously yielded the 4-(ferrocenyl)dienamine **14** and the phosphorus ylide **16**. The formation of **14** can obviously be interpreted in terms of a [2+2] cycloaddition of DMAD with the C=C double bond[16] of compound **2** to afford the cyclobutene intermediate **12**, which undergoes ring opening to give **13**, the water-sensitive phosphorane derivative of the aminobutadiene **14**. This type of transformation has also been reported for the ring-expansion of the iminophosphoranes of cyclic β-enamino esters and β-enaminonitriles.[17] (Scheme 2).

The alternative reaction affording phosphorus ylide **16** probably takes place through a [2+2] cycloaddition involving the formal P=N double bond followed by the cleavage of the P−N bond in the resulting four-membered ring (**2** → **15** → **16**). This pathway has also been reported previously[18−21] and can be regarded as closely related to aza-Wittig reactions as the carbonyl group is replaced by the highly activated carbon−carbon triple bond in DMAD.



Scheme 2

It is noteworthy that the common feature of each conversion of the iminophosphorane **2** with electron-deficient reagents discussed here could be the four-membered ring intermediates, the formation of which is probably promoted by the electron-donating ferrocenyl group (Schemes 1 and 2).

It is also noteworthy that, unlike the butadienyl-substituted iminophosphorane **13**, its vinyl-substituted analogue **2** proved to be completely resistant to hydrolysis under the conditions employed for cycloaddition. This pronounced stability of **2** can be attributed to the electron-releasing ferrocenyl group[22] situated in the crucial β-position relative to the phosphinimine moiety. In **13**, however, the stabilizing ferrocenyl group is separated by two additional carbon atoms, and the β-methoxycarbonyl group obviously produces a considerable decrease in the electron density of the phosphorus atom-containing group, making it more sensitive to the nucleophilic attack of the water present even in traces in the reaction mixture.

Structures

The IR, ^{1}H and ^{13}C NMR spectroscopic data of the compounds investigated are given in Table 1−3. The postulated structures are unambiguously corroborated by these spectroscopic data, and only a few additional remarks are necessary.

The electron affinity of the aryl group only weakly influences the chemical shifts of the hydrogens in the ferrocenyl moiety and the olefinic CH group. The change in the hetero ring from oxazolone (**5a−e**) to imidazolinone or imidazolidinedione (**8**, **9**) causes only moderate downfield shifts of these signals. For **11**, however, the H-2′,5′ is shifted significantly upfield (by about δ = 1.4 ppm), while the olefinic-H

Table 1. ^{1}H NMR spectroscopic data for compounds **5a − e**, **8 −11**, **14** and **16**

Compound[a][b]	CH_3 *s*[c] (3 H)	CH_2 *qa*[c] (2 H)	=CH *s* (1 H)	H-2′,5′ (2 H)	H-3′,4′ (2 H)	H-1"−5" (5 H)[d]	H-2	H-6	H-3	H-5	H-4	
				Substituted cyclopentane ring			Aryl group[e]					
5a	2.44	−	7.23	5.11	4.67	4.21	8.04		7.31		−	
5b	3.90	−	7.19	5.09	4.65	4.21	8.09		7.00		−	
5c	−	−	7.29	5.11	4.71	4.23	8.07		7.48		−	
5d	−	−	7.38	5.13	4.74	4.24	8.97	~8.4[f]	−		7.71	~8.4[f]
5e	−	−	7.32	5.05	4.65	4.17	−		7.00		7.45	
8	1.45	4.62	6.97	4.97	4.47	4.18	7.37		7.46		7.35	
9	−	−	6.50	4.89	4.48	4.22	7.46		7.51		7.42	
10	−	−	6.72	4.95	4.52	4.20	7.44,[g]	7.74[h]	7.53,[g]	7.36[h]	7.48,[g]	7.11[h]
11	1.18	4.15[f]	7.89	3.65	4.37	4.15[f]	−		−		−	
14	1.07	4.04	7.36	4.39	4.34[i]	4.37[i]	4.10	−	−		−	
16	1.10	3.87	6.51	4.19	4.02	3.94	7.75		7.36		7.44	

Further signals, OCH_3, 2 × s (2 × 3 H): δ = 3.84 and 3.96 (**11**), 3.54 and 3.64 (**14**), 3.31 and 3.65 (**16**) ppm; NH, s: δ = 10.5 ppm (1 H, **9**), ≈ 7.8 (2 H) broad (**14**).

[a] In $CDCl_3$ solution ([D_6]DMSO for **9**) at 500 MHz. Chemical shifts in ppm (δ_{TMS} = 0 ppm), coupling constants in Hz. [b] Assignments were supported by HMQC measurements for **5a,c,e, 8−10, 14, 16** and HMBC (for **9**, **11**, **14, 16**), COSY (for **11**) and DIFFNOE (for **9**), respectively. [c] Ethyl group, t, J = 6.7 (**8**), 7.3 (**11**), 7.1 Hz (**14, 16**). [d] Unsubstituted cyclopentadiene ring. [e] Multiplicity (intensity, for both phenyl rings in **10**): "d" (2 × 1 H) for H-2,6 (**5a−c** and **8−10**), H-3,5 (**5a−c**) and H-4,6 (**5d**), "t" for H-5 (1 H, **5d**), H-3,5 (2 H, **5e, 8−10, 16**) and H-4 (1 H, **8−10** and **16**), J = 8.5 ± 0.4 Hz), "s" (1 H) for H-2 (**5d**), dd (2 H) for H-2,6 (**16**) and "quint", J ≈ 6 Hz (1 H, **5e**). The triplet/quintet split of H-3,5 and H-4 signals for **5e** are due to $^{3/4}J_{F,H}$ couplings, double split of doublet for H-2,6 in **16** is due to $^3J_{P,H}$ coupling, respectively. [f] Overlapping signals. [g]/[h] Phenyl bonded to amide N/amine NH. [i] Intensity: 1 H.

Table 2. ^{13}C NMR chemical shifts of compounds **5a − e, 8−11, 14** and **16**

Compound[a][b][c]	=CH	C-2/α	C-4/β	C-5/γ	C-1′	C-2′,5′	C-3′,4′	C-1"-5"	C-1	C-2	C-6	C-3	C-5	C-4
		Oxazolone ring[d]			Substituted Cp ring				Aryl group					
5a	135.8	161.1	130.7	167.8	76.9	72.7	73.4	70.6	124.0	128.2		130.1		143.7
5b	134.8	160.9	131.0	167.8	77.1	72.5	73.1	70.6	119.2	130.2		114.9		163.6
5c	137.3	159.9	130.2	167.3	76.9	72.8	73.8	70.8	125.3	129.4		129.8		139.1
5d	139.2	158.5	129.5	166.6	76.5	73.1	74.3	70.9	128.8	122.9	133.3	149.2	130.6	126.8
5e	139.2	153.9 [e]	129.0	166.9	76.4	73.1	74.2	70.9	106.5[e]	161.8[e]		113.1[e]		133.9[e]
8	125.7	159.3	135.6	167.6	78.1	71.5	71.7	70.1	132.9	126.3		129.4		128.0
9	112.8	154.5	124.4	163.3	77.2	70.6	71.4	70.3	132.9	127.7		129.6		128.7
10	120.8	152.9		166.5	78.6	71.4	71.6	70.4	132.6	129.1		130.3		129.8
11	143.8	119.7	139.3	132.1	72.5	70.9	72.9	70.3	−	−		−		−
14	140.7	149.0	92.5	122.9	78.0	69.9[f]	70.5[f]	68.9	−	−		−		−
16	123.6	161.3 [g]	134.6 [g]	126.4 [f]	79.8	70.7	69.8	69.6	125.7[f]	134.4[g]		128.7[g]		132.2

[a] In $CDCl_3$ (for **9** and **10** [D_6]DMSO) solution at 125 MHz. Chemical shifts in ppm (δ_{TMS} = 0 ppm), coupling constants in Hz. [b] Assignments were supported by DEPT (except for **5a** and **5d**), by HMQC for **5a**, **5c** and **5e**, **8−10**, **14** and **16** and by HMBC measurements for **5a−e, 11** and **16**. [c] Further signals: CH_3: δ = 22.3 (**5a**), 13.3 (**11**, **14**) and 14.7 ppm (**8**, **16**), OCH_3: δ = 55.9 (**5b**), 52.8, 53.3 (**11**), 50.4, 51.8 (**14**) and 50.4, 51.9 ppm (**16**), OCH_2: δ = 66.2 (**8**), 61.9 (**11**), 61.3 (**14**) and 60.8 (**16**) ppm; C=O (ester): δ = 157.9 (position 5), 160.2 (position 4) and 162.3 ppm (side chain) for **11**, in **14** and **16** COOMe (β to Fc/P): δ = 167.7 and 165.7 ppm, (d, $^3J_{P,C}$ = 14.0 Hz), COOMe (β to N): δ = 168.8 and 169.3 ppm, (d, $^2J_{P,C}$ = 14.4 Hz), COOEt: δ = 163.6 and 164.9 ppm. [d] Imidazodione or triazole ring for **9** and **11**, respectively, C-α/β/γ to N (**14**) or C=N/C=P/C−N carbon atoms (**16**) in the diene chain. [e] Triplet (C-2, C_{Ar}-1 and C_{Ar}-4)/dd (C_{Ar}-2,6 and C_{Ar}-3,5) split due to F,H-couplings, $^1J_{F,H}$ = 262.0 Hz , $^2J_{F,H}$ = 24.0 Hz (C_{Ar}-3,5), 14.4 (C_{Ar}-1), $^3J_{F,H}$ = 9.6 Hz (C_{Ar}-4), 3.8 (C-2), 4.8 (C_{Ar}-2,6), $^4J_{F,H}$ = 3.8 Hz (C_{Ar}-3,5). [f] Interchangeable assignments. Both signals of **14** are split into two lines (further maxima are at δ = 70.26 and 70.31). [g] Doublets, split due to P,C couplings, $^1J_{P,C}$ = 9 Hz (C=P), $^2J_{P,C}$ = 10.0 Hz (*ortho* C_{Ar}) and 7.4 (C=N), $^3J_{P,C}$ = 12.5 Hz (*meta* C_{Ar}) and $^4J_{P,C}$ ≈ 1 Hz (*para* C_{Ar}).

singlet is oppositely shifted (downfield) to a similar extent. This suggests that, in order to avoid the strong steric hindrance between the triazolo ring and the ferrocenyl moiety, the hetero ring adopts a position perpendicular to the olefinic C=C bond (coplanar with the substituted cyclopentadienate ring of the ferrocene moiety) in the preferred conformation. The upfield shift of the H-2′,5′ signal can be explained in terms of the anisotropic shielding effect of the perpendicular heteroaromatic ring and the downfield shift of the olefinic singlet may originate from the strong $-I$-effect of the hetero ring bearing the two electron-attracting ester groups. This effect is compensated for in the other compounds (**5, 8−10**) by the electron-releasing behaviour of the amine/imine N in the enamine/enimine moiety. (Another explanation, namely (*Z*) → (*E*) isomerization, may be discounted on the basis of X-ray measurements).

To answer this question, we carried out NOE measurements on compounds **11**. On saturation of either the olef-

Table 3. Characteristic IR frequencies [cm^{-1}] of compounds **5a − e**, **8 −11**, **14** and **16** in KBr discs

Compound	$\tilde{\nu}_{C=O}$(lactone)[a]	$\tilde{\nu}_{C=N}$	$\tilde{\nu}_{C-O}$	$\tilde{\nu}_{C(A)rH}$	$\tilde{\nu}_{as,Cp-Fe-Cp}$ & tilt of Cp
5a	1780, 1761	1650	1148	820	494, 478
5b	1780, 1757	1652	1262,[b] 1148	822	507, 485
5c	1782, 1762	1647	1149	818	513, 493, 476
5d	1774	1649	1655	702	498, 475
5e	1781, 1763	1640	1145	832	497, 479
8	1712	1652	1010	757	505, 489, ~ 470
9	1758, 1719	–	–	766	485
10	1651	1592 [c]	–	763	484
11	1735, 1720, 1632 [d]	–	1270, 1250, 1191	–	499, 479
14	1737, 1720, 1667 [d]	–	1255, 1244, 1192, 1182	–	499
16	1732, 1701, 1654 [d]	1548	1252, 1237, 1104	757, 746	512

Further bands: νNH: 3500−2500 (**10**), ν_{as,NH_2}: 3455, ν_{s,NH_2}: 3315 (**14**), ν_{as,NO_2}: 1527, ν_{s,NO_2}: 1350, $\nu_{C(Ar)N}$: 842 (**5d**); $\gamma_{C(Ar)C(Ar)}$: 693 (**10**), 691 (**16**), 697 (**8**, **9**).

[a] Doubled for **5a−c**, **5e** and **9** due to split by Fermi resonance. Ester bands (**11**, **14**, **16**), amide-I-type band for **8** and **10**, imide bands for **9**. [b] $C_{Ar}OMe$ group. [c] Split band with the other maximum at 1569 cm^{-1}. [d] Internal group in the conjugated chain.

inic-H or the ester CH_2 signal, a strong response was observable in the DIFFNOE spectrum for the other signal, confirming the unchanged (*Z*) configuration of the olefinic C=C bond, and thus the perpendicular arrangement of the triazole ring. This stereo structure was also confirmed later by X-ray measurement (Figure 1).

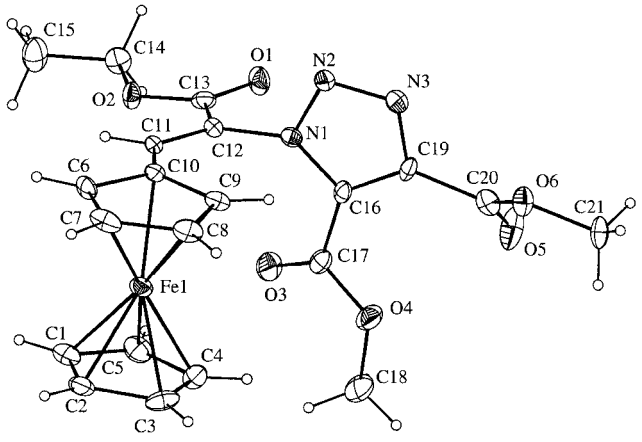


Figure 1. ORTEP diagram of compound **11**

Because of the apparent chemical equivalence of the H/C-2′,5′ and H/C-3′,4′ atom pairs and the downfield positions of their signals, it is plausible to suppose free rotation around the $Fc-C_{olefinic}$ axis and a preference for the coplanar rotamers in the conformational equilibrium. The only exception is compound **14**, in which the steric hindrance between the ferrocenyl and methoxycarbonyl groups (γ to the Fc substituent) produces hindered rotation and, as a consequence, the H-3′,4′ signal is split.

The structures of the two adducts **14** and **16** formed in the reaction between **2** and DMAD, were established by X-ray diffraction (Figure 2 and 3). The diene moiety in **14** has an *s-cis* (*E*,α,β)-(*Z*,γ,δ) stereostructure. In **16** the olefinic configuration is (*Z*).

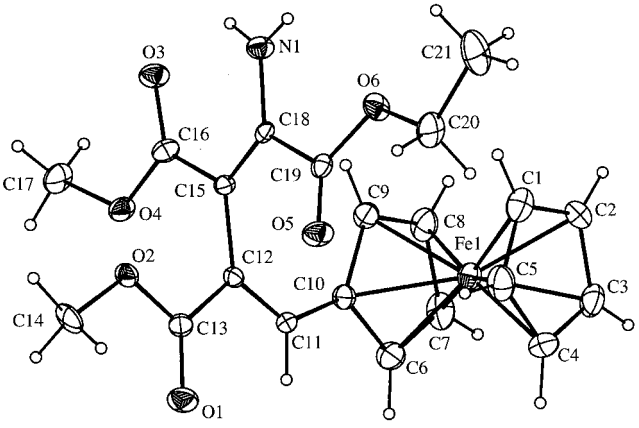


Figure 2. ORTEP diagram of compound **14**

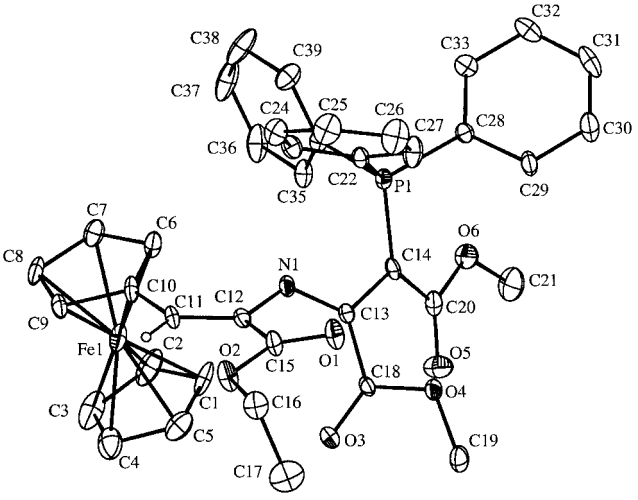


Figure 3. ORTEP diagram of compound **16**; hydrogen atoms are omitted for clarity

The adduct **16**, unlike **14,** contains the ethoxycarbonyl group in an unchanged position in relation to the starting

compound **2**, on the β-carbon (β to the ferrocenyl moiety). This was supported by HMBC measurements, which demonstrate a vicinal (three bond length) coupling of the C=O carbon atom with its line at δ = 164.9 ppm with the hydrogen atoms of the olefinic-CH and the methylene groups, respectively.

X-ray crystal structure analysis of compound **14** revealed the structure depicted in Figure 2.

Extended conjugation including the butadiene moiety, cyclopentadienyl, amino and ester groups cannot be achieved because of the sterically crowded structure of the molecule. The conjugation breaks at the C12−C15 bond, resulting in two quasiplanar parts with an interplanar angle of 89.7° between them. The lone pair of the N1 is also conjugated. Both conjugated chains of the molecule are in extended conformations, with the two carbonyl oxygen atoms of the longer chain pointing in opposite directions. The bulkier ends of the two chains are farther apart from each other, resulting in more open C11−C12−C15 and C12−C15−C18 angles.

We found that the ethyl ester group was not in the plane of the other conjugated atoms because of the proximity of the π-electrons of the C11−C12 bond. The angle of the O5−C19−O6−C20 and the N1−C18−C15−C16−O4 planes is 24.1°. Because of conjugation the C18−C19 bond becomes elongated while the C19−O5 bond becomes shorter and the C19−O6 bond longer than the C16−O3 and C16−O4 bonds, respectively. The C20−O6 bond is also elongated as a result of the crowded stereostructure.

The interplane angle of the two cyclopentadienyl rings of the ferrocenyl group is 1.1(5)°, with Fe1 being 1.650(3) Å and 1.637(3) Å above the C1−C2−C3−C4−C5 ring and C6−C7−C8−C9−C10 ring, respectively.

The main crystal building forces are the dipole−dipole interactions. The distinct layers of the apolar ferrocenyl groups and the polar moieties run parallel to the ′ab′ plane of the unit cell. In the apolar layers the ring planes of the ferrocenes of symmetry equivalent molecules are perpendicular.

X-ray crystal structure analysis of compound **16** revealed the structure depicted in Figure 3.

The interplane angle of the two cyclopentadienyl rings of the ferrocenyl group is 4.9(5)°, with Fe1 being 1.638(6) Å and 1.641(6) Å above the C1−C2−C3−C4−C5 (Cp1) ring and C6−C7−C8−C9−C10 (Cp2) ring, respectively.

The conformation of the whole molecule is strongly influenced by the voluminous triphenylphosphoranylidene moiety. The C11−C12−N1−C13−C14−C20 chain is in an elongated but distorted conformation [C20−C14−C13−N1 −144.9(6)°, C13−N1−C12−C11 −140.1(7)°]. As a result of the steric crowding, the torsion angle of C14−P1−C22−C27 is 83.3(7)°, while those of C14−P1−C28−C29 and C14−P1−C34−C35 are 35.0(7)° and 25.8(7)°, respectively. The distorted position of the Ph3 (C34−C35−C36−C37−C38−C39) phenyl ring is caused by the proximity of the ferrocenyl group. The plane of the Ph3 phenyl ring is nearly perpendicular to the planes of the two cyclopentadienyl rings [82.4(3)° to Cp1, 86.5(3)° to Cp2]. The turning of the Ph1 (C22−C23−C24−C25−C26−C27) is to avoid interaction with the chain including the N1, C12, C15 and O1 atoms. The Ph2 (C28−C29−C30−C31−C32−C33) is rather close to O5−C20−O6−C21 methyl ester group, particularly to O6. In this conformation the hydrogen connected to C5 (member of Cp1 ring) is quite near to O3.

Conclusion

The easily available ethyl α- (triphenylphosphoranylidene)amino-β-ferrocenylacrylate (**2**) is readily convertible into azoles (oxazolones, imidazolones) with potential biological activity through the use of carbonyl reagents. Because of the activation due to the ferrocenyl group, **2** can also be viewed as a good precursor for the preparation of differently substituted 1-amino-4-ferrocenyl-1,3-dienes and 1-ferrocenyl-5-triphenylphosphoranylidene-3-aza-1,3-pentadienes, which are suitable for versatile transformations including cycloadditions and cyclocondensations, if the reaction with DMAD is extended to other electron-deficient acetylenes. The extension of the 1,3-dipolar cycloaddition of ethyl α-azido-β-ferrocenylacrylate (**1**), the precursor of **2**, to the application of further electron-deficient acetylenes other than DMAD may also afford a series of 1-(2-ferrocenylvinyl)-*v*-triazoles of both synthetic and potential pharmacological interest.

Experimental Section

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or [D_6]DMSO solution in 5-mm tubes at room temperature, with a Bruker DRX 500 spectrometer at 500 (^{1}H) and 125 (^{13}C) MHz, with the deuterium signal of the solvent as the lock and TMS as internal standard. The standard Bruker micro program NOEMULT.AU to generate NOE was used with a selective pre-irradiation time. DEPT spectra were run in a standard manner, by the use of only the Θ = 135° pulse to separate CH/CH_3 and CH_2 lines phased "up" and "down", respectively. The 2D-HMQC and 2D-HMBC spectra were obtained by use of the standard Bruker pulse programs INV4GSSW and INV4GSLRNDSW, respectively. The IR spectra were recorded in KBr pellets with a Bruker IFS 55 spectrometer.

The X-ray measurements were made with a Rigaku AFC6S diffractometer with graphite-monochromated Cu-K_α radiation (λ = 1.54178 Å). The crystals were mounted on a glass fibre. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of carefully centred reflections. The data were collected at a temperature of 293 °C by the ω-2θ scan technique. An empirical absorption correction based on azimuthal scans of several reflections was applied. Data processing was carried out by use of the software supplied with the diffractometer.

Structure solutions with direct methods were carried out by use of the teXsan package.[23a] Refinements were carried out with the aid of the SHELXL-97 program[23b] by the full-matrix, least-squares method on F^2. All non-hydrogen atoms were refined aniso-

tropically. Hydrogen atoms were generated and their positions were refined with the riding model.

Melting points (uncorrected) were determined on a Boetius apparatus.

Azidoester **1** and ethyl α-triphenylphosphoranylidene-β-ferrocenylacrylate (**2**) were prepared from formylferrocene by the procedures we had employed previously.[3]

General Procedure for the Preparation of 2-Aryl-4-(ferrocenyl)methylidene-4*H*-oxazol-5-ones 5a−e: The corresponding acid chloride (2.14 mmol) and triethylamine (4.3 mmol) were added dropwise to a solution of **2** (1.0 g, 1.789 mmol) in acetonitrile (40 mL). The resulting mixture was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure and the crude solid was chromatographed on silica (Kieselgel type 9385; eluent: *n*-hexane/ethyl acetate, 5:1). Recrystallization from absolute ethanol gave the pure products (see Table 1−3).

4-(Ferrocenyl)methylidene-2-*p*-tolyl-4*H*-oxazol-5-one (5a): Violet plates, m.p. 222−224 °C, yield 42%. $C_{21}H_{17}FeNO_2$ (371.2): calcd. C 67.92, H 4.58, N 3.77; found C 68.12, H 4.47, N 3.71.

4-(Ferrocenyl)methylidene-2-(4-methoxyphenyl)-4*H*-oxazol-5-one (5b): Violet powder, m.p. 213−214 °C, yield 31%. $C_{21}H_{17}FeNO_3$ (387.2): calcd. C 65.51, H 4.39, N 3.61; found C 66.01, H 4.18, N 3.53.

2-(4-Chlorophenyl)-4-(ferrocenyl)methylidene-4*H*-oxazol-5-one (5c): Violet powder, m.p. 235−236 °C, yield 41%. $C_{20}H_{14}ClFeNO_2$ (391.6): calcd. C 61.30, H 3.57, N 3.57; found C 61.24, H 3.61, N 3.53.

4-(Ferrocenyl)methylidene-2-(3-nitrophenyl)-4*H*-oxazol-5-one (5d): Violet powder, m.p. 221−223 °C, yield 28%. $C_{20}H_{14}FeN_2O_4$ (370.1): calcd. C 59.70, H 3.48, N 6.96; found C 59.75, H 3.55, N 7.03.

2-(2,6-Difluorophenyl)-4-(ferrocenyl)methylidene-4*H*-oxazol-5-one (5e): Violet powder, m.p. 127−128 °C, yield 18%. $C_{20}H_{13}F_2FeNO_2$ (393.1): calcd. C 61.06, H 3.30, N 3.56; found C 61.12, H 3.34, N 3.60.

2-Ethoxy-5-(ferrocenyl)methylidene-3-phenyl-3,5-dihydroimidazol-4-one (8): Phenyl isocyanate (0.89 mmol) was added to a solution of **2** (0.5 g, 0.89 mmol) in anhydrous pyridine (15 mL) and the mixture was stirred and heated at reflux for 30 min. After this period, absolute ethanol (1 mL) was added to the reaction mixture, which was then heated at reflux for 1.5 h. The solvent was removed under reduced pressure and the crude solid was chromatographed on silica (Kieselgel type 9385; eluent: *n*-hexane/ethyl acetate, 5:1). Recrystallization from anhydrous ethanol gave the pure product (see Table 1−3). Red plates, m.p. 140−141 °C, yield 63%. $C_{22}H_{20}FeN_2O_2$ (400.2): calcd. C 66.00, H 5.00, N 7.00; found C 66.19, H 5.04, N 7.11.

5-(Ferrocenyl)methylidene-3-(phenyl)imidazolidine-2,4-dione (9) and 5-(Ferrocenyl)methylidene-3-phenyl-2-phenylamino-3,5-dihydroimidazol-4-one (10). Procedure 1: The imidazolone compound **8** (0.1 g, 0.24 mmol) was heated at reflux under inert atmosphere in glacial acetic acid (20 mL) for 12 h, and the solvent was then removed under reduced pressure. The crude solid was chromatographed on silica (Kieselgel type 9385; eluent: dichloromethane/ethyl acetate, 25:1).

Procedure 2: Phenyl isocyanate (0.89 mmol) was added to a solution of **2** (0.5 g, 0.00089 mol) in anhydrous pyridine (15 mL) and the mixture was stirred and heated at reflux for 30 min. After this period, water (1 mL) was added to the reaction mixture, which was then heated at reflux for 1.5 h. The solvent was removed under reduced pressure and the crude solid was chromatographed on silica (Kieselgel type 9385; eluent: dichloromethane/ethyl acetate, 25:1). Recrystallization from anhydrous ethanol gave the pure product **9** (deep red crystals, m.p. > 310 °C, yield 64% in the case of Procedure 1 and 40% in the case of Procedure 2. $C_{20}H_{16}FeN_2O_2$ (372.2): calcd. C 67.06, H 4.50, N 3.91; found C 67.10, H 4.53, N 3.97. When Procedure 2 was used the imidazolone derivative **10** was always present as a more rapidly eluting by-product. Red plates, m.p. 148−150 °C, yield 30%. $C_{26}H_{21}FeN_3O$ (447.3): calcd. C 69.81, H 4.73, N 9.39; found C 69.88, H 4.70, N 9.42.

Dimethyl 1-[(*Z*)-1-Ethoxycarbonyl-2-(ferrocenyl)vinyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate (11): Dimethyl acetylenedicarboxylate (0.218 g, 1.537 mmol) was added to a solution of **2** (0.5 g, 1.537 mmol) in acetonitrile (30 mL) and the mixture was stirred for 12 h at room temperature. The solvent was removed and the crude product was purified by column chromatography on silica (Kieselgel type 9385; eluent: dichloromethane/ethyl acetate, 40:1), providing a resinous mass that slowly solidified in about two weeks (deep red powder, m.p. 86−91 °C, yield 82%. $C_{21}H_{21}FeN_3O_6$ (467.2): calcd. C 53.98, H 4.53, N 8.99; found C 54.03, H 4.55, N 9.02.

1-Ethyl 2,3-Dimethyl (1*Z*)-1-Amino-4-(ferrocenyl)buta-1,3-diene-1,2,3-tricarboxylate (14) and Dimethyl (2*E*)-2-{[(*Z*)-2-Ferrocenyl-1-(ethoxycarbonyl)vinyl]imino}-3-(trimethylphosphoranylidene)-succinate (16): Dimethyl acetylenedicarboxylate (0.254 g, 1.789 mmol) was added to a solution of **2** (1.0 g, 1.789 mmol) in acetonitrile (30 mL) and the mixture was stirred at reflux temperature for 10 hours. The solvent was then removed and the crude product was chromatographed on silica [Kieselgel type 9385; elution was carried out with: *n*-hexane/ethyl acetate (3:1) for isolation of **16** and then with ethyl acetate to obtain **14**]. **14:** Red crystals, m.p. 69−70 °C, yield 42%. $C_{21}H_{23}FeNO_6$ (441.2): calcd. C 57.16, H 5.25, N 3.17; found C 57.20, H 5.26, N 3.21. **16:** Orange powder, m.p. 78−79 °C, yield 46%. $C_{39}H_{36}FeNO_6P$ (701.5): calcd. C 66.77, H 5.17, N 1.99; found C 66.80, H 5.15, N 2.02.

Crystallographic Data for Compound 14: $C_{21}H_{23}FeNO_6$, M_w = 441.25, red, plate crystal, 0.25 × 0.05 × 0.60 mm, orthorhombic space group *Pbca*, a = 15.666(3) Å, b = 10.853(3) Å, c = 23.617(4) Å, V = 4015.4(7) Å^3, Z = 8, $D_{calcd.}$ = 1.460 Mg/m^3, 8890 reflections were collected, 3956 were unique (R_{int} = 0.183), μ(Cu-K_α) = 6.356 mm^{-1}. Final R indices are R = 0.0632, R_w = 0.0936 for $I > 2\sigma(I)$ and R = 0.2703, R_w = 0.1419 for all data. Maximum and minimum peaks in the final difference map 0.35 and −0.40 e·Å^{-3}, respectively.

Crystallographic Data for Compound 16: $C_{39}H_{36}FeNO_6P$, M_w = 701.51, red, rhombohedral crystal, 0.75 × 0.55 × 0.32 mm, monoclinic space group *P*21/*c*, a = 9.49(3) Å, b = 18.49(5) Å, c = 19.93(3) Å, β = 102.45(16)°, V = 2060.5(6) Å^3, Z = 4, $D_{calcd.}$ = 1.365 Mg/m^3, 9886 reflections were collected, 4672 were unique (R_{int} = 0.1356), μ(Cu-K_α) = 4.383 mm^{-1}. Final R indices are R = 0.0611, R_w = 0.1249 for $I > 2\sigma(I)$ and R = 0.1933, R_w = 0.1659 for all data. Maximum and minimum peaks in the final difference map 0.39 and −0.35 e·Å^{-3}, respectively.

CCDC-186375, -219020 and -220792 for compounds **14**, **16** and **11**, respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge

CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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