VINYLFERROCENE AS PARADIGM FOR THE TWO-STEP REACTION MODE WITH KETENES. THE CASE OF *tert*-BUTYLCYANOKETENE (MOORE'S KETENE)

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The reaction of *tert*-butylcyanoketene (TBCK, Moore's ketene; **1**) with ethenylferrocene (**2**) yields four products: the cyclobutanone 2-*trans*-*tert*-butyl-2-cyano-3-ferrocenylcyclobutanone (**3**), two δ-lactones as 2:1 ketene:alkene *cis* and *trans* adducts 3-*cis*-*tert*-butyl-3-cyano-6-(1-cyano-2,2-dimethylpropylidene)-4-ferrocenyltetrahydro-2-pyrone (**4**) and 3-*trans*-*tert*-butyl-3-cyano-6-(1-cyano-2,2-dimethylpropylidene)-4-ferrocenyl-tetrahydro-2-pyrone (**5**), and an α,β-unsaturated ketone 3-cyano-1*E*-ferrocenyl-5,5-dimethylhex-1-en-3-one (**6**). The configuration of the bulky groups (*t*-Bu and ferrocenyl) in cyclobutanone **3** is *trans*. The two δ lactones are stereoisomers as a result of the *cis* and *trans* configuration of *t*-Bu and ferrocenyl groups. The cyclobutanone **3** isomerizes by heating or catalytically into the α,β-unsaturated ketone **6**. Assigned structures for the compounds were made based on IR, ^{1}H, ^{13}C NMR, and for **5** also by single-crystal X-ray diffraction.

Keywords: *t*-Butylcyanoketenes; Ethenylferrocenes; [2+2]-Cycloadditions; Non-concerted mechanism; Lactones.

Cycloaddition of ketenes to alkenes in general and to vinylderivatives in particular occurs either in concerted mode or as stepwise mode[1]. The concerted mode is regio- and stereospecific and provides cyclobutanones

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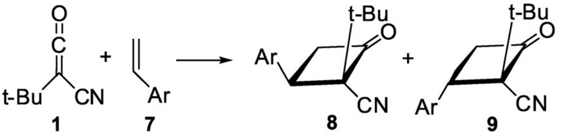
(ketene:alkene 1:1). The stepwise mode is regiospecific but not necessarily stereospecific and, in principle, could provide 1:1 adducts, and/or 1:2 adducts (cyclic and/or acyclic compounds). The outcome is controlled by the stereoelectronic factors on both alkene and ketene. We and others have illustrated both concerted and non-concerted cycloaddition modes of cycloaddition of *tert*-butylcyanoketene (TBCK; Moore's ketene[2]) to aromatic vinyl derivatives[3] displayed in Scheme 1.



7a: C_6H_5; **7b**: 4-Me-C_6H_4; **7c**: 4-*t*-Bu-C_6H_4; **7d**: 4-C_6H_5-C_6H_4; **7e**: α-naphtyl; **7f**: β-naphtyl; **7g**: 4-NO_2-C_6H_4; **7h**: 4-F-C_6H_4; **7i**: 4-Cl-C_6H_4; **7j**: 4-Br-C_6H_4; **7k**: 4-MeO-C_6H_4; **7l**: 9-anthryl.

SCHEME 1
Cycloaddition modes of *tert*-butylcyanoketene to aromatic vinyl derivatives

Styrene (**7a**), 4-substituted styrenes **7b**–**7g** [3a–3d], and vinylnaphthalenes **7e** and **7f** gave with TBCK the cyclobutanone **8** (as the sole reaction product) with *cis* configuration of the vicinal bulky groups aryl and *tert*-butyl. It is generally accepted that such a regio- and stereospecific reaction takes place by a concerted mechanism.

A different picture is provided by the reaction of halogenostyrenes[3h] and *p*-methoxystyrene[3e,3f] with TBCK yielding a mixture of two cyclobutanones **8** (*cis* configuration) and, preferentially, **9** (*trans* configuration). It is not so obvious how to reconcile the two-step process (*trans*-cyclobutanone) as operational simultaneously with what seems to be the outcome of the *cis*-cyclobutanone, resulting from a concerted process.

As anticipated, for large steric demands, like in the case of 9-vinylanthracene (**7l**)[3b], the cyclobutanone has the structure **9**, very probably resulted in a two-step process.

We report here our findings concerning the cycloaddition of vinylferrocene (**2**) to TBCK. Based on the reaction products (**3**, **4**, **5** and **6**), this reaction is very likely a stepwise process, more complex than, e.g., the reaction between 4-methoxystyrene and TBCK. Unfortunately, there are no available literature references concerning the cycloaddition of vinylferrocene to other ketenes to be compared to. Therefore, it is too early to sketch the chemistry pattern displayed by vinylferrocene in reaction with ketenes.

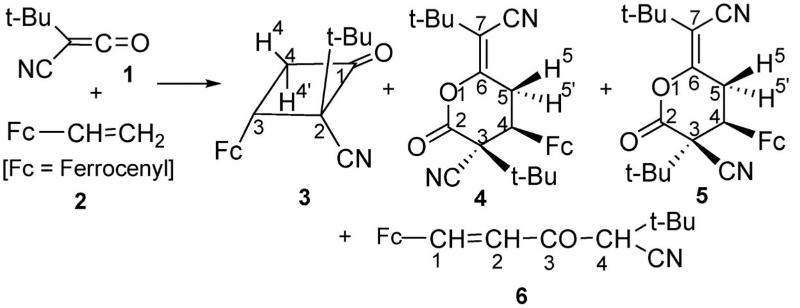
The complex outcome from cycloaddition of TBCK to vinylferrocene is, in part, anticipated. Firstly, the C=C bond has an enhanced nucleophilicity due to the electron rich vinylferocene double bond. McEwen et al.[4a] have noticed an unsual high reactivity of the vinylferrocene toward the addition of weak acids (electrophiles), and Kaufman et al.[4b] have signaled the ease to generate the α-ferrocenyl cation. Prakash et al.[4c] have noticed that if the α-ferrocenyl cation shares the positive charge with an adjacent cyclopropyl ring, the latter is not rearranging to an allylic cation.

Our computation of electrostatic charges (B3LYP/6-31G**, Spartan 06 [5]) reveals that the charge is of –0.47607 on the terminal vinyl CH_2 group in the vinyl group of ferrocene, compared with only –0.38872 from styrene and –0.46518 from 4-methoxystyrene. Therefore, vinylferrocene is a better ketenophile than either styrene or *p*-methoxystyrene. Secondly, in the zwitterionic intermediate, the carbocationic center is strongly stabilized by the adjacent ferrocenyl group[6].

In order to enrich the qualitative correlation of the reaction mechanism with the electronic effects of the substituents in the alkene, the vinylferrocene was chosen as an alkene of appreciable nucleophilicity[7].

RESULTS AND DISCUSSION

The reaction of vinylferrocene with TBCK occurs readily. The reaction product outcome is, however, more complex than for any of the other vinylaryl derivatives to TBCK studied so far. We have isolated the cyclobutanone **3**, two δ-lactones **4** and **5**, resulted as 2:1 ketene:alkene adducts, and, the α,β-unsaturated ketone **6** (Scheme 2).



SCHEME 2
The reaction of vinylferrocene with TBCK

The ratio of these products in the reaction products mixture varied according to the reaction parameters that have been considered, such as (i) the molar ratio (MR) of the reagents (1:1 vinylferrocene:TBCK, or up to 3:1 excess of TBCK over vinylferrocene), (ii) the temperature (room temperature or boiling benzene), (iii) the reaction time (from 3 min to 72 h) and (iv) the manner of addition (direct addition, i.e. vinylferrocene to TBCK, or inverse additon, namely TBCK addition to vinylferrocene). It was not our aim to run an analysis and parameter design optimization products distribution, nevertheles, we performed some cross-sections on this surface. Some results are displayed in Table I.

The conclusions regarding this reaction outcome are presented as follows: The cyclobutanone **3** is formed in refluxing benzene after ca. 3 min, if the reagents are introduced in equimolecular amounts. Immediately after the ketene is consumed, the reaction mixture proves to contain the cyclobutanone **3** as a major product and the 2:1 adduct **4**. At longer reaction time, a complete isomerization of the cyclobutanone to the α,β-unsaturated ketone **6** was observed. Also, this transformation occurs during the chromatography of the reaction mass or in the presence of polar solvents.

The cyclobutanone **3** was almost absent (traces) in the experiments in which the ketene was in excess or when the alkene was added to the ketene

TABLE I
The product distribution related to the syntheses parameters

Ketene:alkene molar ratio (MR)	Reaction temperature °C	Duration	Distribution of products **3**–**6** (molar ratios)			
			3	**6**	**4**	**5**
1:1	80 (refl. benzene	3 min	2.8	0	1	traces
		after 6 h	0	2.9	1	traces
ketene in excess (various MRs, up to 3:1)	80 (refl. benzene	2 h	0.2	0.2	1[a]	1.5[a]
		11 h	0	0.2	1[a]	1.5[a]
1:1	room temp.	10 min	0	1	8	0
		72 h	0	1	8	0
ketene in excess (various MRs, up to 3:1)	room temp.	11 h	0	0.3	1[a]	1.75[a]

[a] The amounts of **4** and **5** are almost constant, no matter how large the ketene excess or the duration of the reaction.

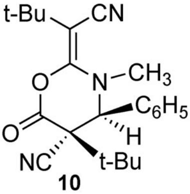
solution at room temperature. The ^{1}H NMR spectrum after 10-min reaction at this temperature showed the presence of the unreacted alkene (45%).

The structure of the cyclobutanone **3** was established based on IR, ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR, the *tert*-butyl group appears as a singlet at 1.15 ppm. This value is well correlated with the chemical shift values of the *t*-Bu groups in the cyclobutanones obtained in the reaction of TBCK with vinylanthracene and with *p*-methoxystyrene. If the bulky groups are in *cis* relation, the *t*-Bu group chemical shifts are less than 1 ppm [3a–3c]. The stereochemistry of the cyclobutanone **3** is also supported by the chemical shift value of the α-H related to the ferrocenyl group (H^3), of less than 4 ppm, as a result of the magnetic shielding of the vicinal and CN group. This value is only found in the case of the cyclobutanone formed in the reaction with the *p*-methoxystyrene It is worth to note that in all the cyclobutanones **8**, the chemical shift of this proton is greater than 4 ppm. In the ^{13}C NMR spectrum, the value of 115.97 ppm is assigned to the carbon of the cyano group, that also pleads for a *trans* configuration, because the CN group is shielded by the *cis*-ferrocenyl moiety. Comparable values are encountered in the cyclobutanones resulted in the reaction of TBCK with vinylanthracene and with *p*-methoxystyrene. If the configuration of the bulky groups is *cis*, the chemical shifts of CN carbon atom are close to 118 ppm [3c]).

The 2:1 ketene:alkene adducts (**4** and **5**) are formed even in experiments conducted at room temperature, when no traces of cyclobutanone were detected. Still, their occurence shows differences, since the *cis* adduct **4** is produced in all cases, even at a 1:1 ketene:alkene molar ratio. In the reactions performed with a ketene excess, the ratio of the *cis*:*trans* adducts is of ca. 2:3 and it does not seem to vary with temperature or reaction time. No equilibrium between the two isomers was observed.

The *cis* adduct **4** was isolated in all reactions, both at room temperature and in refluxing benzene. It accompanies the cyclobutanone **3** even in the case of reactions with alkene in excess, that should favor the formation of products **3** and **6**. By prolonged heating its decomposition was observed.

The *trans* adduct **5** is formed as a stable product in satisfactory yields in reactions with ketene excess. The spectral assignments have been made based on both ^{1}H, ^{13}C NMR and IR spectra. In the NMR spectra, the adduct **4** (named as the "*cis* adduct" due to the steric relationship of the two bulky groups, the *tert*-butyl and the ferrocenyl), presented two peaks, assigned to the *tert*-butyl protons, at 1.03 and 1.4 ppm. In the *trans* isomer **5**, the chemical shifts corresponding to the two *tert*-butyl groups are of 1.2 and 1.32 ppm, in accordance with a sterically less hindered structure. The NMR data for the two isomers were found to be close to those shown by two models reported in the literature[8], namely compounds **10** and **11**.



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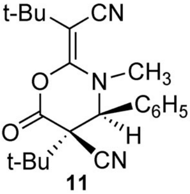

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Single-crystal X-ray diffraction study of the *trans* adduct **5** ellucidated the structure of this product confirming not only the *trans* relationship between the bulky ferrocenyl and *tert*-butyl groups, but also the *trans* configuration of CN and O as substituents of the C^6=C^7 double bond (Fig. 1).

The α,β-unsaturated ketone **6** has been isolated in the reaction of TBCK with vinylferrocene at an equimolecular ratio of the reagents, in refluxing benzene after 6-h reaction time, as the major product (70%) together with the *cis* 2:1 adduct **4**. The α,β-unsaturated ketone **6** could not be observed in the ^{1}H NMR spectra at the moment when the cyclobutanone was formed, i.e. at 3-min reaction time. It started to progressively form out of cyclo-

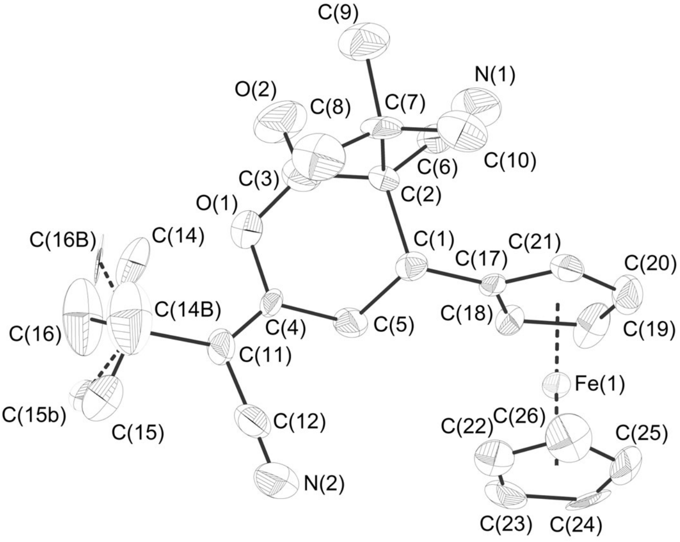
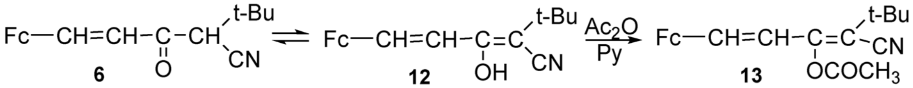


FIG. 1

ORTEP representation at 50% probability and atom-numbering scheme for the isomer of the *trans* adduct **5**. Hydrogen atoms have been omitted for clarity butanone **3** in the experiments intending the synthesis of **3** even during the subsequent chromatography separation step. The same transformation **3** → **6** was observed when trifluoroacetic acid (TFA) was added to the solution of the cyclobutanone **3**.

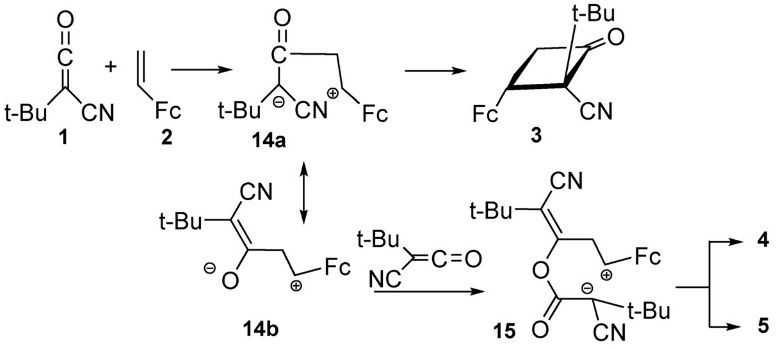
tert-Butylcyanoketene is documented, as it results from Becker et al.[9] findings, to give α,β-unsaturated ketones upon treatment with vinyl ethers. A structurally related α,β-unsaturated ketone is reported by England and Krespan[10] to be formed in the reaction of bis(trifluoromethyl)ketene with vinyl esters and ethers. It is worth to notice that such an α,β-unsaturated ketone was not isolated as reaction product between *p*-methoxystyrene and *tert*-butylcyanoketene[3f,3g,3i] or by isomerization of the corresponding cyclobutanone. Heated to 120 °C, the above mentioned cyclobutanone undergoes cycloreversion[3i].

For further structure confirmation, since a ketone of type **6** enolizes, the acetate of the enolic form has been synthesized from **6** at room temperature using acetic anhydride in pyridine (Scheme 3). Spectral data certified the structure of compounds **6** and **13**.



SCHEME 3
Enolization and acetate formation for the α,β-unsaturated ketone **6**

The distribution of products revealed by the TBCK cycloaddition to vinylferrocene is explained and summarized by Scheme 4.



SCHEME 4
The assumed reaction mechanism explaining the product distribution

As in the case of a concerted reaction, the cycloaddents are orthogonally approaching. A bond is formed between the spearhead carbonyl carbon atom from the ketene and the marginal CH_2 group of alkene. The zwitterion **14** is stabilized by double conjugation, the anionic center is stabilized by the CN and C=O groups and the cationic center by the α-ferrocenyl group.

Concerning the α,β-unsaturated ketone **6**, it is not a primary reaction product. Its occurence may be explained by the cyclobutanone **3** ring opening leading to the zwitterion intermediate **14**, followed by a proton migration from the CH_2 to the anionic center vicinal to the CN group.

A comparison of relative reactivity of ferrocene versus the nucleophilic styrenes substituted at C_4 by CH_3O and $N(CH_3)_2$ groups is available from the isodesmic reactions (B3LYP/6-31G(D); Spartan 06 [5]) shown in Scheme 5.

$$\mathrm{Fc{-}CH_2{-}CH_3 + p\text{-}X{-}C_6H_4{-}\overset{\oplus}{C}H{-}CH_3 \longrightarrow Fc{-}\overset{\oplus}{C}H{-}CH_3 + p\text{-}X{-}C_6H_4{-}CH_2{-}CH_3}$$

X	H	CH_3O	$(CH_3)_2N$
ΔE (kcal/mol)	-18.4	-3.7	-3.7

SCHEME 5
Isodesmic reactions to assess the relative stability of the ferrocenyl carbocation

All reactions are exothermic, however, the α-ferrocenyl carbocation is systematically more stable than the benzylic carbocation.

Unlike styrene, good donors like CH_3O and $(CH_3)_2N$ on the phenyl group render more stability to the benzyl carbocation, but it is slightly less than the ability of the α-ferrocenyl carbocation to stabilize the adjacent positively charged center.

CONCLUSIONS

In the reaction of vinylferrocene with *tert*-butylcyanoketene, four products were isolated: the cyclobutanone **3**, two 2:1 ketene:alkene adducts with δ-lactone structure (**4** and **5**) and the α,β-unsaturated ketone **6**. In cyclobutanone **3**, the bulky substituents Fc and *t*-Bu have *trans* configuration as a result of a stepwise reaction involving a zwitterion intermediate. The *cis* adduct **4** is formed in reactions with either equimolar or excess ratio ketene:alkene. The α,β-unsaturated ketone **6** results from the thermal or acid catalyzed isomerization of the cyclobutanone **3**.

EXPERIMENTAL

Anhydrous benzene (CHIMOPAR, S.A., Bucharest) was dried over sodium wire. The 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone has been synthesized starting from 2,5-di-*tert*-butylhydroquinone according to our reported protocol[11]. Vinylferrocene has been obtained by the acetylation of ferrocene with acetic anhydride in the presence of phosphoric acid[12], reduction of the acetyl derivative to the corresponding alcohol, its transformation in acetate[13] followed by vacuum distillation of this one. IR spectra (ν, cm^{-1}) were recorded on a Bruker Equinox 55 FTIR spectrometer. NMR spectra (δ, ppm; *J*, Hz) were recorded on a Varian Gemini 300 MHz spectrometer. For reported values of the assigned chemical shifts δ, the atoms placed in the substituted cyclopentadienyl ring of ferrocenyl moiety are indicated as H_{FcA}/C_{FcA} while the atoms belonging to the unsubstituted cyclopentadienyl ring are marked as H_{FcB}/C_{FcB} respectively; the broadened singlets (bs) are not resolved. Also, in the case of the two adducts **4** and **5**, bearing *tert*-butyl groups both in the 3 and in the 7 positions, the δ values are specified as (*t*-Bu^3) and (*t*-Bu^7).

2-*trans*-*tert*-Butyl-2-cyano-3-ferrocenylcyclobutanone (**3**)

tert-Butylcyanoketene was generated in situ by thermolysis of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in anhydrous benzene. 2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (1.0 g, equivalent to 6.6 mmol ketene) was decomposed in anhydrous benzene (25 ml) at reflux. Under argon atmosphere, a solution of vinylferrocene (**2**; 1.2 g, 6 mmol) dissolved in anhydrous benzene (25 ml) was added dropwise over 2 min, followed by additional 3-min reflux. The reaction mixture was quickly cooled in order to be chromatographed and the ^{1}H NMR spectrum before chromatography was recorded (the spectrum showed the presence of both the cyclobutanone **3** and the *cis* 2:1 adduct **4** (2.8:1 molar ratio) and the absence of the α,β-unsaturated ketone **6**. The *trans* 2:1 adduct **5** was present only in traces). As resulted from chromatography on silica (Merck, Si 60), four fractions were collected (in order of elution): some unreacted alkene **2**, the cyclobutanone **3**, the 2:1 adduct **4** and the α,β-unsaturated ketone **6**. The benzene in the fraction containing the cyclobutanone **3** was partially evaporated (max. 40 °C). The crystals formed on cooling were filtered off and washed with methanol, 0.53 g (24%) of yellow crystals were obtained. Attempts to determine the melting point of the cyclobutanone failed. At 140 °C, the yellow crystals changed the colour and isomerized to a violet mass of α,β-unsaturated ketone **6**. IR ($CHCl_3$): 1780 s (characteristic for cyclobutanones); 2224 m (the signature of aliphatic nitriles); 2971 w, 3088 w. ^{1}H NMR (C_6D_6): 1.13 s, 9 H (*t*-Bu); 2.98 dd, 1 H, *J*(4′,3) = 10.0, *J*(4′,4) = 18.6 ($H^{4'}$); 3.17 dd, 1 H, *J*(4,3) = 7.8, *J*(4,4′) = 18.6 (H^4); 3.32 dd, 1 H, *J*(3,4) = 7.8, *J*(3,4′) = 10.0 (H^3); 4.10 m, 1 H (H_{FcA}); 4.12 s, 5 H (H_{FcB}); 4.18 m, 1 H (H_{FcA}); 4.22 m, 1 H (H_{FcA}); 4.30 m, 1 H (H_{FcA}). ^{13}C NMR (C_6D_6): 198.56 (C=O); 116.36 (C_{CN}); 86.63 (C_{qFcA}); 76.24 (C_2); 70.55 (C_{FcA}); 69.89 (C_{FcA}); 69.57 (5 C, C_{FcB} and 1 C, C_{FcA}); 67.85 (C_{FcA}); 52.25 (C_4); 36.38 (C_q *t*-Bu); 33.10 (C_3); 26.41 (CH_3 *t*-Bu). For $C_{19}H_{21}FeON$ (335.10) calculated: 68.07% C, 6.31% H, 4.17% N; found: 68.32% C, 6.59% H, 4.49% N.

3-*cis*-*tert*-Butyl-3-cyano-6-(1-cyano-2,2-dimethylpropylidene)-4-ferrocenyl-tetrahydro-2-pyrone (**4**)

2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (2.3 g, yielding 15.2 mmol ketene) was decomposed in refluxing anhydrous benzene (50 ml). Under argon atmosphere, a solution of vinylferrocene (**2**; 1.1 g, 5 mmol) dissolved in anhydrous benzene (20 ml) was added dropwise over 5 min, followed by additional 3-h reflux. The solvent was evaporated and the solid residue was chromatographed on silica (Merck, Si 60) with benzene as an eluent. After evaporation, the first fraction yielded 1.2 g (52%) of adduct **4** as yellow crystals, m.p. 131–132 °C (EtOH). (The second fraction contained the *trans* adduct **5**.) IR (CCl_4): 1162, 1619 s (C=C); 1761 s (C=O); 2206 s (CN attached to the double bond); 2238 m (the second CN). ^{1}H NMR ($CDCl_3$): 1.04 s, 9 H (*t*-Bu^3); 1.39 s, 9 H (*t*-Bu^7); 3.59 t, 1 H, *J*(4,5-5′) = 6.7 (H^4); 3.74 dd, 1 H, *J*(5′,5) = 18.7, *J*(5′,4) = 6.7 (H$^{5'}$); 3.86 dd, 1 H, *J*(5,5′) = 18.7, *J*(5,4) = 6.7 (H^5); 4.01 bs, 1 H (H_{FcA}); 4.23 s, 5 H (H_{FcB}); 4.25 bs, 2 H (H_{FcA}); 4.49 bs 1 H (H_{FcA}). ^{13}C NMR ($CDCl_3$): 159.04 (C=O); 158.90 (C_6); 117.58 (C_{CN}); 117.44 (C_{CN}); 106.64 (C_7); 86.38 (C_{qFcA}); 71.08 (C_{FcA}); 69.42 (5 C, C_{FcB}); 69.20 (C_{FcA}); 68.14 (C_{FcA}); 56.15 (C_3); 37.95 (C_4); 34.99 (C_q *t*-Bu^3); 34.92 (C_5); 34.39 (C_q *t*-Bu^7); 29.84 (CH_3 *t*-Bu); 28.11 (CH_3 *t*-Bu). For $C_{26}H_{30}FeO_2N_2$ (458.17) calculated: 68.13% C, 6.59% H, 6.11% N; found: 67.95% C, 6.86% H, 6.50% N.

3-*trans*-*tert*-Butyl-3-cyano-6-(1-cyano-2,2-dimethylpropylidene)-4-ferrocenyltetrahydro-2-pyrone (**5**)

Compound **5** was separated after the solvent evaporation of the second fraction in the previously described chromatography, yielding 0.8 g (35%) of yellow crystals, m.p. 217–218 °C (EtOH). IR (CCl_4): 1160, 1635 s (C=C); 1764 s (C=O); 2207 s (CN attached to the double bond); 2239 m (the second CN). ^{1}H NMR ($CDCl_3$): 1.23 s, 9 H (*t*-Bu^3); 1.34 s, 9 H (*t*-Bu^7); 3.17 dd, 1 H, *J*(5,4) = 9.6, *J*(5,5′) = 15.2 (H^5); 3.25 dd, 1 H, *J*(4,5′) = 4.3, *J*(4,5) = 9.6 (H^4); 3.81 dd, 1 H, *J*(5′,5) = 15.2, *J*(5′,4) = 4.3 (H$^{5'}$); 4.10 m, 1 H (H_{FcA}); 4.25 (5H_{FcB}); 4.27 t, 2 H, *J* = 1.9 (H_{FcA}); 4.31 m, 1 H (H_{FcA}). ^{13}C NMR ($CDCl_3$): 161.47 (C=O); 158.91 (C_6); 117.68 ($C_{CN}{}^3$); 115.79 ($C_{CN}{}^7$); 105.69 (C_7); 87.88 (C_{qFcA}); 70.58 (C_{FcA}); 69.17 (C_{FcB}); 68.89 (C_{FcA}); 68.18 (C_{FcA}); 66.65 (C_{FcA}); 61.85 (C_3); 40.53 (C_q *t*-Bu); 36.74 (C_4); 34.60 (C_5); 28.85 (CH_3 *t*-Bu); 27.37 (CH_3 *t*-Bu). For $C_{26}H_{30}FeO_2N_2$ (458.17) calculated: 68.13% C, 6.59% H, 12.19% Fe, 6.11% N; found: 68.31% C, 6.68% H, 12.33% Fe, 6.34% N.

CCDC 769208 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

3-Cyano-1*E*-ferrocenyl-5,5-dimethylhex-1-en-3-one (**6**)

Cyclobutanone **3** (1 g, 3 mmol) was heated at 150–160 °C for 5 min. The obtained violet solid was chromatographed on silica (Merck, Si 60) with benzene as an eluent. After the solvent evaporation, 0.8 g (2.4 mmol; 80%) of violet crystals of the product **6** were obtained, m.p. 139–140 °C. IR (CCl_4): 1584 s (C=C); 1672 s (CO); 2233 m (CN). ^{1}H NMR ($CDCl_3$ + TFA): 1.19 s, 9 H (*t*-Bu); 3.50 s, 1 H (H^4); 4.23 s, 5 H (H_{FcB}); 4.66 s, 4 H (H_{FcA}); 6.59 d, 1 H, *J*(2,1) = 15.2 (H^2); 7.81 d, 1 H, *J*(1,2) = 15.2 (H^1). ^{13}C NMR ($CDCl_3$ + TFA): 190.63 (C=O); 151.82 (C_1); 128.31 (C_{qFcA}); 119.16 (C_2); 116.47 (CN); 73.23 (C_{FcA}); 70.31 (5 C, C_{FcB}); 70.13 (C_{FcA}); 69.99 (C_{FcA}); 54.54 (C_4); 35.87 (C_q *t*-Bu); 28.06 (CH_3 *t*-Bu).

(1*E*,3*Z*)-3-Acetoxy-4-cyano-1-ferrocenyl-5,5-dimethyl-1,3-hexadiene (**13**)

α,β-Unsaturated ketone **6** (1 g, 3 mmol) was treated with acetic anhydride (1 ml, 10 mmol) and pyridine (5 ml). After 24 h at room temperature, the solvent was evaporated and the residue was chromatographed with benzene on silica (Merck, Si 60), to give 0.9 g (2.4 mmol; 80%) of red crystals, m.p. 135–136 °C. IR ($CHCl_3$): 1600 s (C=C); 1773 s (CO); 2187, 2210 (CN, the two values prove both *cis* and *trans* configuration). For $C_{21}H_{23}FeO_2N$ (377.11) calculated: 66.95% C, 6.15% H, 3.71% N; found: 67.13% C, 5.93% H, 3.4% N.

X-ray Diffraction Studies

The crystal structure measurement and refinement data are given in Table II. Data collection and processing were carried out using a Bruker AXS SMART APEX system ("Babes-Bolyai" University, Cluj, Romania). Crystal of dimensions 0.24 × 0.23 × 0.02 mm, was mounted on

TABLE II
Crystal data and structure refinement for **5**

Empirical formula	$C_{26}H_{30}FeN_2O_2$
MW	458.37
Temperature, K	297(2)
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	*P2(1)/n*
a, Å	14.3253(17)
b, Å	7.0407(8)
c, Å	22.965(3)
β, °	100.563(2)
Volume, Å^3	2277.0(5)
Z	4
D_c, g cm^{-3}	1.337
Absorption coefficient, mm^{-1}	0.687
F(000)	968
Crystal size, mm	0.30 × 0.23 × 0.20
θ range for data collections, °	2.83 to 25.00
Reflections collected	15497
Independent reflections	3987 [R(int) = 0.0918]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3987/53/317
Goodness-of-fit on F^2	1.269
Final *R* indicies [$I > 2\sigma(I)$]	R = 0.1341, $wR2$ = 0.2502
R indicies (all data)	R = 1635, $wR2$ = 0.2632
Largest diff. peak and hole, e Å^{-3}	0.767 and –1.515

a cryo loop and optically centered. The data were collected on a Bruker AXS three-circle platform goniometer equipped with a CCD area detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å at 297(2) K). The structure was solved by direct methods SHELXS97[14] and successive difference Fourier syntheses and refined against F^2 on all data by full-matrix least-squares with SHELXL97. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed at idealized positions with isotropic thermal parameters set at 1.5 times for the methyl hydrogens and 1.2 for the rest, respectively, of the carbon atom to which they were attached. The methyl groups were allowed to rotate but not to tip. The methyl groups from a *t*-Bu fragment are disordered over two positions with 45:55 occupancy. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography[15]. The drawing was created with the ORTEP[16] program.

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