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THERMAL *cis* → *trans* AND METAL SHIFT ISOMERIZATIONS IN ACYCLIC ELECTRON-DEFICIENT (TRIENE)TRICARBONYLIRON DERIVATIVES

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Summary

The synthesis of *cis/trans*-tricarbonyl[(4,5,6,7-η)-2,4,6-heptatriene]iron derivatives containing electron-withdrawing groups (COOR, COPh, CN) is reported. At 120 °C in toluene the isomeric esters and ketones undergo *cis* → *trans* isomerization and metal shift tautomerization to give an equilibrium mixture of isomers containing predominantly the *trans* shift isomers tricarbonyl[(2,3,4,5-η)-2,4,6-heptatriene]iron ester and ketone, respectively. The thermal *cis* → *trans* isomerization is faster than metal tautomerization. Tetracyanoethylene reacts readily in polar solvents only with the *trans* shift isomers, to give the corresponding 2 + 2 cycloaddition products.

Introduction

Thermally induced haptotropic shifts [1] are observed in numerous (polyene)M(CO)$_n$ complexes [2]. Fully conjugated cyclic polyolefins usually show fluxional behaviour at room temperature. For example, (cyclooctatetraene)Fe(CO)$_3$ (I) exhibits rapid fluxionality involving 1,2-metal shifts with a low energy of activation, E_a 8.3 kcal/mol [3]. Complexes of discontinuously conjugated cyclic polyenes and conjugated acyclic polyenes also show stereochemical non-rigidity, but their activation energies are much higher. Thus (cycloheptatriene)Fe(CO)$_3$ (II) undergoes a degenerate 1,3-metal shift with a free energy of activation $\Delta G^{\ddagger}$ 22.3 kcal/mol [4], while tautomerization of (1,6-diarylhexatriene)Fe(CO)$_3$ (III) required an activation energy of E_a 33 kcal/mol [5].

Recently we have reported on efficient metal transfer reactions and hydrogen shift isomerizations in (cycloheptatriene)tricarbonyliron derivatives which were shown to compete with metal shift isomerizations [6]. We now wish to report the results of a related study on the synthesis, thermal isomerizations, and reactivity of acyclic electron-deficient (triene)tricarbonyliron complexes.

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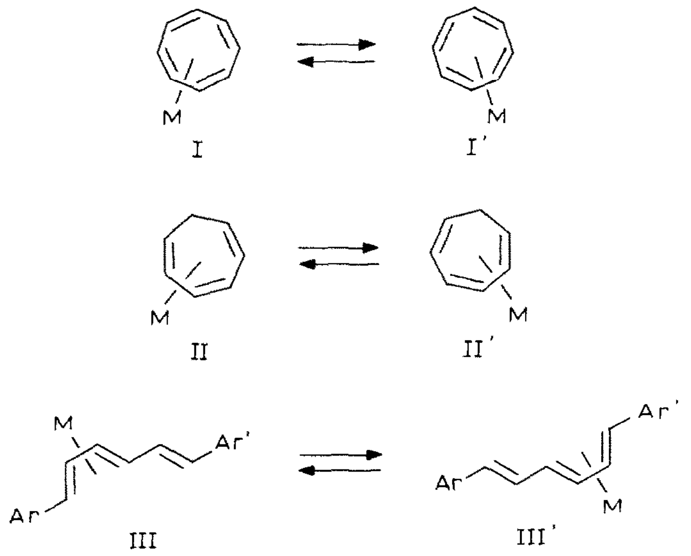


I ⇌ I'

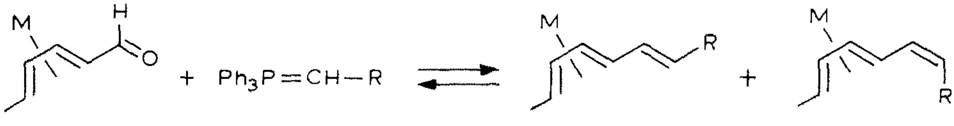
II ⇌ II'

III ⇌ III'

M = Fe(CO)$_3$

Synthesis

Substituted (triene)tricarbonyliron esters, ketones and nitriles VI–IX were prepared by the Wittig reaction of (2,4-hexadienal)Fe(CO)$_3$ (IV) with the appropriate phosphoranes, V, in CH_2Cl_2 solutions, as previously described [6]. Addition of catalytic amounts of benzoic acid to the reaction mixture [7] reduced the reaction time and improved the yields. A *cis/trans* isomeric mixture was obtained which contained < 10% of the *cis* isomers. The isomers were separated by column chromatography and characterized by their ^{1}H NMR spectra (Table 1). The two low field vinyl protons H(2) and H(3) of the *cis* complexes couple with a characteristic J 11 Hz, whereas for the *trans* isomers, a coupling constant J 16 Hz was observed. In addition, the H(4) signals of the *cis* esters VIc and VIIc and ketone VIIIc shift down-field by ca. 2 ppm with respect to the corresponding H(4) resonances in the *trans* isomers VIt–VIIIt. This deshielding effect appears to be due to the anisotropy of the carbonyl group which lies in close proximity to H(4) in the preferred *s-trans* conformation of the *cis* isomers [8]. Further evidence that this paramagnetic shift is a



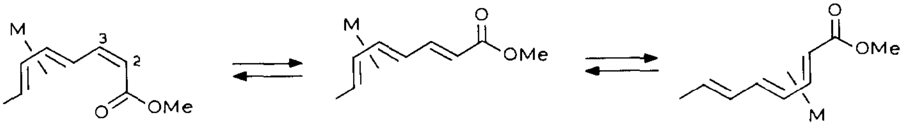
IV + V ⇌ *trans* + *cis*

VI , R = COOMe
VII , R = COOEt
VIII, R = COPh
IX , R = CN

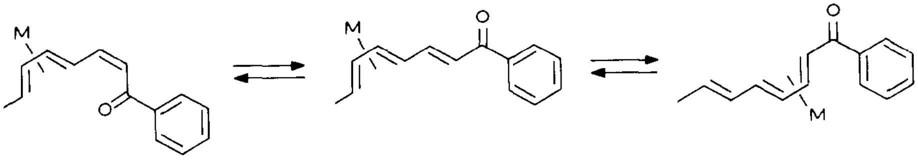
field effect and not an inductive effect is provided by the ^{13}C NMR spectra (Table 2), in which field effects are expected to be minor [9] and so the C(4) and C(7) signals in both the *cis* and *trans* isomers should appear in the same region ($\delta \sim 55.0$ ppm).

Thermolysis

When the *cis* methyl ester VIc was heated at 120 °C in toluene and the reaction monitored by TLC and ^{1}H NMR, isomerization to the *trans* isomer VIt was first observed, followed by further isomerization to the metal shift tautomer X. After 72 h there was obtained a mixture of VIc, VIt and X in a ratio of ca. 1/3/9, respectively. Prolonged heating of the reaction mixture caused considerable decomposition, but, the ratios of the isomers remained constant. Heating the *trans* isomer VIt under the same conditions gave the same equilibrium mixture.



VI*c* VI*t* X



VIII*c* VIII*t* XI

The structure of ester X was deduced from its ^{1}H NMR spectrum (Table 1). It is readily distinguished from the spectrum of the other isomers by a high-field doublet of the *anti* H(2) at δ 1.16 ppm which is coupled ($J_{2,3}$ 8 Hz) to the low-field H(3) at δ 5.70 ppm. In the ^{13}C NMR spectrum (Table 2) of X the C(2) resonance appears somewhat at a higher field (δ 45.3 ppm) than the corresponding C(4) and C(7) signals in VIIIt (δ 55.8 en 58.6 ppm).

Similarly the thermolysis of either the *cis* or *trans* ketones VIII led smoothly to an equilibrium mixture which contained VIIIc, VIIIt and XI in a ratio of 1/2/8, respectively. The ^{1}H and ^{13}C NMR spectra of the isomeric ketones are given in Tables 1 and 2, respectively. Here again, as in the ester series, the *cis* → *trans* isomerization is faster than metal tautomerization. If we assume the barrier for metal shift isomerization to be about 33 kcal/mol [5] then obviously the rotational barrier of the free double bond must be considerably lower. Compared to other push-pull ethylenes [10] of the acrylate series this barrier is significantly lower than that reported for *cis*-methyl crotonate (XII), E_a 58 kcal/mol [11] and methyl cinnamate (XIII), E_a 42 kcal/mol [12]. This is apparently due to the ability of the (diene)Fe(CO)$_3$ moiety than of a phenyl group to stabilize a positive charge in the zwitterionic twisted transition state XIV [10a].

(Continued on p. 196)

TABLE 1

^{1}H NMR DATA FOR (TRIENE)TRICARBONYLIRON COMPLEXES[a]

	H(3)	H(4)	H(7)	H(2)	H(5)	H(6)	H(8)	Others	Coupling contants, J
VIc	6.06	3.05	1.70	5.47	5.16[c]		1.45	3.70 (OMe)	$J_{(23)} = J_{(34)} = 11$ Hz
VIIc	6.03	3.08	1.65	5.50	5.07, 5.25		1.45	1.28, 4.16 (OEt, $J = 7$ Hz)	$J_{(45)} = J_{(67)} = 8$ Hz
VIIIc	6.38	3.56	1.55	5.86	4.46, 4.72		1.07	7.1, 7.8 (aromatic)	$J_{(56)} = 5$ Hz; $J_{(78)} = 6$ Hz
IXc	6.26	1.93	1.70[b]	5.03	5.40[b]		1.53		
VIt	6.80	1.4–1.8[b]		5.86	5.10, 5.36		1.46	3.70 (OMe)	$J_{(23)} = 16$ Hz; $J_{(34)} = 10$ Hz
VIIt	6.78	1.4–1.8[b]		5.82	5.10, 5.35		1.45	1.26, 4.16 (OEt, J 7 Hz)	$J_{(45)} = 8$ Hz; $J_{(56)} = 5$ Hz
VIIIt	6.94[b]	1.4–1.9[b]		6.94[b]	5.13, 5.43		1.46	7.5, 7.9 (aromatic)	
IXt	6.35	1.4–1.9[b]		5.20	5.0–5.5		1.48		
X	5.70[c]	5.30	5.70[c]	1.16	2.15	5.70[c]	1.64	3.64 (OMe)	$J_{(23)} = 8$ Hz; $J_{(34)} = 5$ Hz
XI	6.0[c]	5.55[c]		2.12	2.48	6.0[c]	1.70	7.50, 7.95 (aromatic)	$J_{(45)} = J_{(56)} = 9$ Hz; $J_{(78)} = 6$ Hz
XVI[d]	5.80[c]		3.38[c]	1.35	2.46	3.38[c]	1.72	3 65 (OMe)	$J_{(23)} = 8$ Hz, $J_{(78)} = 6$ Hz
XVII[e]	6.34	6.09	3.31	2.02	2.72	3.65	1.68	7 50, 8.04 (aromatic)	$J_{(45)} = J_{(56)} = 9$ Hz; $J_{(67)} = 12$ Hz

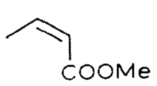
[a] 60 MHz, $CDCl_3$, δ ppm from TMS. [b] Obscured [c] Center of unresolved multiplet. [d] In nitromethane-d_3. [e] In acetone-d_6.

TABLE 2

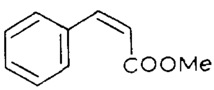
^{13}C NMR DATA OF (TRIENE)TRICARBONYLIRON COMPLEXES[a]

	C(3)	C(4)	C(7)	C(2)	C(5)	C(6)	C(8)	C(1)	CO	others
VIIc	149.7	54.3,	58.8	115.6	84.4,	87.0	19.1	166.6	211.2	14.3, 59.9 (OEt)
IXc	154.4	53.4,	59.5	94.1	82.4,	87.8	19.1	116.6	210.4	
VIt	149.1	55.8,	58.6	118.1	82.9,	87.2	19.1	166.9	211.0	51.3 (OMe)
VIIt	148.8	55.0	58.6	118.6	82.9,	87.2	19.1	166.4	211.1	14.3, 60.1 (OEt)
VIIIt	149.9	56.8,	58.8	122.9	83,	87.4	19.2	189.7	128.4,	128.5, 132.5, 137.9 (aromatic)
IXt	155.9	54.9,	59.3	95.2	82.1	87.6,	19.2	19.2	188.3	210.4
X	82.6,	84.3	129.3	45.3	64.7	131.7	18.3	172.7	209.9	51.6 (OMe)
XI	82.1,	85.3	129.5	49.7	64.9	131.8	18.4	195.3	210.6	127.7, 128.7, 132.8, 137.5 (aromatic)

[a] $CDCl_3$, δ ppm from TMS.



XII



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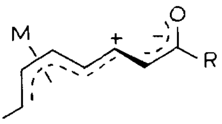
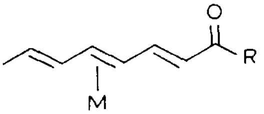


XIV



XV

R = OMe, Ph

Examination of the ratios of isomeric esters and ketones at equilibrium reveals that isomers X and XI, in which the metal is coordinated to an electron deficient diene moiety, are more stable than their alkyl-substituted counterparts VIt and VIIIt. From the 3/1 ratio between the pair of *trans* esters VIt and X we can estimate that X is more stable than VIt by ca. 0.8 kcal/mol at 120°C, whereas from the 4/1 ratio of ketones VIIIt and XI, XI appears to be about 1.0 kcal/mol more stable than VIIIt at this temperature. Frontier orbital approximations readily account for this site preference, predicting a lower energy for the LUMO of a diene conjugated to an electronegative group than for the LUMO energy of an alkyl-substituted diene [13]. Consequently, the energy difference between the high-lying double occupied $Fe(CO)_3$ HOMO [14] and the diene LUMO is smaller when the diene is substituted by electron-withdrawing groups than if the diene is alkyl substituted. This results in a stronger back-bonding interaction, which leads to a more stable complex.

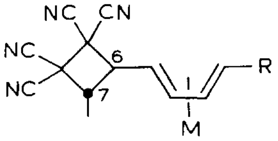
These results also support the proposal by Whitlock et al. that metal shift isomerizations in $(polyene)Fe(CO)_3$ complexes proceed via a common intermediate η^2 complex XV [5], which collapses to a mixture of η^4-diene complexes in a ratio depending on their relative thermodynamic stabilities.

Cycloadditions (with TCNE)

Although a wide variety of cycloaddition reactions of cyclic (triene)iron tricarbonyl complexes have been studied [15], there are relatively few reports on cycloadditions of the acyclic counterparts [15f,16]. Tetracyanoethylene (TCNE), perhaps the most versatile uniparticulate electrophile known, reacts with noncoordinated acyclic trienes to give a mixture of 2 + 2 and 2 + 4 (Diels–Alder adducts) [17]. With free cycloheptatriene only the 2 + 4 adducts were observed [18], whereas the corresponding complexed cyclic trienes gave predominantly 1,3-σ,π-allylic adducts [15].

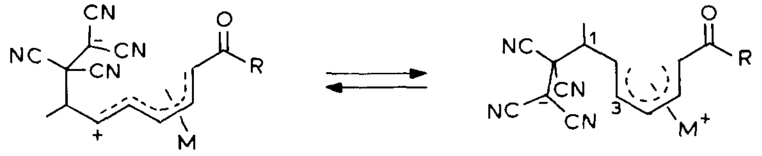
Ester VIt and ketone VIIIt were resistant to TCNE under a variety of conditions, including refluxing in the highly polar nitromethane. However, the rearranged isomers X and XI reacted readily with TCNE in nitromethane at room temperature to form the 2 + 2 adducts XVI and XVII, respectively, as the sole products. The reaction in less polar solvents such as benzene also gave the 2 + 2 adducts but more slowly and in poorer yields. The structures of the adducts were readily confirmed from their ^1H NMR spectra which closely resembled those of the corresponding starting trienes except that the low field signals of H(6) and H(7) are shifted upfield, as would be expected for cyclobutane protons (Table 1).

The ^1H NMR spectra (Table 1) of XVI and XVII also reveals the presence of only one cyclobutane isomer, whose stereochemistry at the C(6)–C(7) bond could not be



XVI , R = COOMe
XVII, R = COPh

unequivocally assigned. However, early reports on 2 + 2 cycloadditions of TCNE with electron-rich *trans* disubstituted ethylenes [19] show the predominance of the thermodynamically more stable trans isomer, obtained in a stepwise mechanism by way of a short lived dipolar intermediate XVIII. The significant solvent effect on the reaction rates appears to support the presence of such a zwitterionic intermediate [19,20] and further confirm the donor properties of the (diene)Fe(CO)$_3$ group [21]. However, the presence of an electron-withdrawing group at the other end of the free double bond, as in VIt and VIIt, is sufficient to prevent cycloaddition.



XVIII XIX

R = OMe , Ph

Finally, we should point out that although geometric constraints prevent ring closure of the *syn-anti* bipolar intermediate XVIII to a 1,3-σ,π-allylic cycloadduct, facile isomerization of *syn-anti* to the *syn-syn* form XIX is expected [22], and this would enable a 1,3-cycloaddition. Since none was observed, it appears that the 2 + 2 ring closure to XVI and XVII is faster than *syn* to *anti* isomerization. An unequivocal confirmation of this assumption must however await further studies with the corresponding *syn-syn* hexatriene complexes in which the central double bond has the *cis* configuration and 1,3-cycloadditions are expected to be favored [15].

Experimental

General. ^1H NMR spectra were recorded on a Varian Model EM-360A spectrometer. ^{13}C NMR spectra were taken on a Varian CFT-20 instrument. IR spectra were measured with a Perkin–Elmer Model 257 spectrometer. Mass spectra were determined with a GC/MS Finnigan Model 4000 spectrometer using an EI source, with ionization energy of 70 eV. Column chromatographic separations were performed under a slight positive nitrogen pressure using Merck Kieselgel 60. Elemental analysis were determined at the analytical laboratories of the Hebrew University, Jerusalem. All reactions were conducted under nitrogen.

cis- and trans-tricarbonyl[ethyl(4,5,6,7-η)-octa-2,4,6-trienoate]iron (VII)

A solution of (hexadienal)Fe(CO)$_3$ (IV) [23] (2.36 g, 10 mmol) triphenyl(carboethoxymethylene)phosphorane (V, R = COOEt) [24] (5.22 g, 15 mmol) and benzoic acid (200 mg) in 100 ml CH_2Cl_2 was kept at room temperature for 3 days. Removal of solvent and chromatography of the residual brown oil using hexane as eluent gave first the *cis* ester VIIc (220 mg, 7% yield), m.p. 72°C (pentane); IR (Nujol): 2040, 1960 (CO) and 1680 (C=O) cm^{-1}; *m/e* 306 (M^+), 278, 250, 222, 166; Analysis. Found: C, 51.02; H, 4.65. $C_{13}H_{14}FeO_5$ calcd.: C, 50.97; H, 4.57%. For ^{1}H and ^{13}C NMR spectra see Tables 1 en 2.

The *trans* ester VIIt was eluted second (2.3 g, 75% yield), m.p. 76 °C (hexane); IR (Nujol): 2040, 1970 and 1690 cm^{-1}; *m/e* 306, 278, 250, 222, 166. Analysis. Found: C, 51.07; H, 4.63. $C_{13}H_{14}FeO_5$ calcd.: C, 50.97, H, 4.57%. For ^{1}H and ^{13}C NMR see Tables 1 and 2.

cis- and trans-tricarbonyl[methyl(4,5,6,7-η)-octa-2,4,6-trienoate]iron (VI)

These were made similarly by reaction of IV and triphenyl(carbomethoxymethylene)phosphorane (V, R = COOMe) [24]. The *cis*-isomer VIc was obtained as a yellow oil in 3% yield; IR (neat): 2040, 1965 and 1695 cm^{-1}; *m/e* 292 (M^+), 264, 236, 208. For the ^{1}H NMR spectrum see Table 1. The *trans*-isomer VIt was obtained in 65% yield, m.p. 81°C (hexane); IR (Nujol): 2045, 1970 and 1685 cm^{-1}; *m/e* 292, 264, 236, 208. Analysis. Found: C, 49.60; H, 4.15. $C_{12}H_{12}FeO_5$ calcd.: C, 49.34; H, 4.15%. For the ^{1}H and ^{13}C NMR spectra see Tables 1 and 2.

cis- and trans-tricarbonyl[(4,5,6,7-η)-1-phenyl-octa-2,4,6-trienone]iron (VIII)

These were similarly obtained from IV and triphenyl(benzoylmethylene)phosphorane (V, R = COPh) [25]. *cis*-Isomer VIIIc was isolated in 5% yield, m.p. 76 °C (pentane); IR (Nujol): 2040, 1980, 1640 cm^{-1}; *m/e* 338 (*M*), 310, 282, 254, 198. Analysis. Found: C, 60.20; H, 4.06. $C_{17}H_{14}FeO_4$ calcd.: C, 60.35; H, 4.14%. For the ^{1}H and ^{13}C NMR spectra see Tables 1 and 2.

The *trans*-isomer VIIIt was obtained in 37% yield; m.p. 86 °C (hexane); IR (Nujol) 2040, 1970, 1645 cm^{-1}; *m/e* 338, 310, 282, 254, 198. Analysis. Found: C, 60.15; H, 4.22. $C_{17}H_{14}FeO_4$ calcd.: C, 60.15; H, 4.14%. For the ^{1}H and ^{13}C spectra see Tables 1 and 2.

cis- and trans-tricarbonyl[(4,5,6,7-η)-octa-2,4,6-trienonitrile]iron (IX)

These were similarly prepared from IV and triphenyl(cyanomethylene)phosphorane (V, R = CN) [26] with 14 days reaction. The *cis*-isomer IXc was obtained in 6% yield, m.p. 97 °C (pentane). IR (Nujol): 2210 (CN), 2045, 1975 cm^{-1}; *m/e* 259 (M^+), 231, 203, 175. Analysis. Found: C, 51.10; H, 3.64. $C_{11}H_9FeNO_3$ calcd.: C, 50.97; H, 3.47%. For the ^{1}H and ^{13}C NMR spectrum see Tables 1 and 2. The *trans*-isomer IXt was obtained in 38% yield, m.p. 77 °C (hexane). IR (Nujol): 2210, 2040 and 1970 cm^{-1}; *m/e* 259, 231, 203 and 175. Analysis. Found: C, 51.02; H, 3.48. $C_{11}H_9FeNO_3$ calcd.: C, 50.97; H, 3.47%. For the ^{1}H and ^{13}C NMR spectra see Tables 1 and 2.

Tricarbonyl[methyl(2,3,4,5-η)-trans-octa-2,4,6-trienoate]iron (X)

A solution of *trans*-ester VIt (400 mg) in toluene (10 ml) was heated for 72 h then cooled and filtered. Preparative TLC (silica) gave VIc (20 mg, 5%), X (170 mg, 43%) and VIt (54 mg, 14%). This ratio of products was also obtained when *cis*-isomer VIc was heated under the same conditions. Complex X: m.p. 72 °C (hexane). IR (Nujol): 2040, 1980, 1685 cm^{-1}; *m/e* 292 (*M*), 264, 236, 208. Analysis. Found: C, 49.58; H, 4.27. $C_{12}H_{12}FeO_5$ calcd: C, 49.32; H, 4.15%. For ^1H and ^{13}C spectra see Tables 1 and 2.

Tricarbonyl[2,3,4,5-η)-trans-1-phenyl-octa-2,4,6-trienone]iron (XI)

This was similarly obtained as the major product upon heating VIII (*cis* or *trans*) (200 mg) in toluene at 120 °C. After 72 h there was obtained VIIIc (12 mg, 6%), XI (98 mg, 49%) and VIIIt (26 mg, 13%). Complex XI: m.p. 87 °C (pentane). IR (Nujol): 2050, 1985 and 1640 cm^{-1}; *m/e* 338 (M^+), 310, 282, 254, 198. Analysis. Found: C, 60.16; H, 4.20. $C_{17}H_{14}FeO_4$ calcd.: C, 60.35, H, 4.14%. ^1H and ^{13}C NMR spectra see Tables 1 and 2.

TCNE adduct XVI

To a solution of ester X (146 mg, 0.5 mmol) in nitromethane (5 ml) was added a solution of freshly sublimed TCNE (64 mg, 0.5 mmol) in nitromethane (5 ml). The mixture was stirred at room temperature for 6 h. Dry ether (25 ml) was added, and the bright yellow precipitate filtered off and recrystallized from CH_2Cl_2/hexane to give XVI (104 mg, 49% yield); m.p. 213 °C (dec.). IR (Nujol): 2055, 1980, 1700 cm^{-1}; *m/e* 392 ($M-\text{CO}$), 364, 336, 208. Analysis. Found: C, 51.43, H, 2.78; N 13.39. $C_{18}H_{12}FeN_4O_5$ calcd.: C, 51.40; H, 2.85; N, 13.33%. For ^1H NMR see Table 1.

TCNE adduct XVII

This was made similarly from XI and TCNE in nitromethane with reaction for 16 h, 32% yield; m.p. 192 °C (dec.); IR (Nujol): 2060, 2000, 1980 and 1640 cm^{-1}; *m/e* 410 ($M-2\text{CO}$), 382, 326. Analysis. Found: C, 59.17; H, 2.89; N, 12.07. $C_{12}H_{14}FeN_4O_4$ calcd.: C, 59.22; H, 3.02; N, 12.0%. For ^1H NMR spectrum see Table 1.

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