215. Preparation and *Diels-Alder* Reactivity of Tricarbonyliron Complexes of [2.2.2]Hericene

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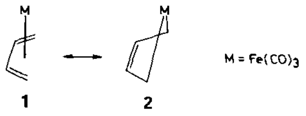
Summary

Treatment of [2.2.2]hericene **10** with $Fe_2(CO)_9$ in hexane gave a mixture of monometallic complex **14**, two isomeric dimetallic complexes **15** and **16**, and a trimetallic complex **19** in which all the three diene moieties of **10**, are coordinated. The rate constants of the *Diels-Alder* additions of tetracyanoethylene (TCE) and dimethyl acetylenedicarboxylate (DMAD) to the uncomplexed diene moieties of **14–16** have been evaluated and compared with those measured for the uncomplexed **10** and its monoadducts **11A, 11B** and bis-adducts **12A, 12B**. The tricarbonyldieneiron function retards the cycloaddition of an homoconjugated, exocyclic s-*cis*-butadiene. The effect is significantly larger for TCE- than for DMAD-additions. The origin of this effect is discussed briefly in terms of the valence-bond model which is usually assumed to describe the properties of a tricarbonyldieneiron complex, and in terms of the inductive and steric factors of the $Fe(CO)_3$-group.

Introduction. – The structural [1] and chemical properties [2] of tricarbonyldieneiron complexes can be described by invoking the limiting structures **1**↔**2** [3] (*Scheme 1*). The σ-bonded $Fe(CO)_3$-structure **2** interprets the property of the transition metal to retrodonate electrons into the LUMO of the π-system [4]. The rate constants for

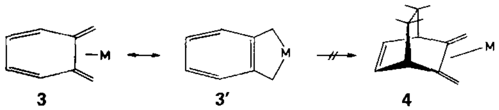
Schema 1



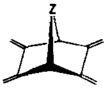
S_N1-solvolyses of esters *β* to a diene-Fe$(CO)_3$-group [2] has been rationalized by a simple *Electrostatic Field Model* [5]. The long-range substituent effect of the diene-Fe$(CO)_3$-group on the stability of a forming carbenium ion intermediate arises from two competing effects, *i.e.*, the dipole-charge destabilizing (inductive effect [6]) and the induced-dipole-charge stabilizing effect (polarizability effect). The latter effect has been interpreted in terms of the PMO theory [7] and also by the valence-bond model **1**↔**2** [2].

No trace of adduct **4** could be detected after prolonged heating (24 h, 60°) of tricarbonyl(*o*-xylylene)iron complex (**3**) [8] *(Scheme 2)* with strong dienophile such as ethylenetetracarbonitrile [9] (TCE, tetracyanoethylene)¹). This observation is consistent with the representation by limiting structure **3′** which confers some aromatic character to the uncoordinated cyclohexadiene and as a consequence, decreases its *Diels-Alder* reactivity. However, one cannot exclude the possibility that the inductive effect of the Fe$(CO)_3$-group also plays a role in decreasing the *Diels-Alder* reactivity of **3** towards strong dienophiles.

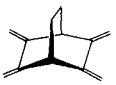
Scheme 2



The spectroscopic [10] and chemical properties of an exocyclic s-*cis*-butadiene moiety of a bicyclic skeleton can be modified by remote substitution [11]. We have recently discussed the *Diels-Alder* reactivity of 2,3,5,6-tetramethylidenebicyclo[2.2.n]-alkanes **5**–**9** [12–14] and of [2.2.2]hericene **10** [14]. We have found that the rate-constant



5 Z = CH_2
6 O
7 $(CH_3)_2C{=}C$



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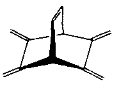

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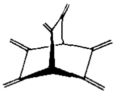

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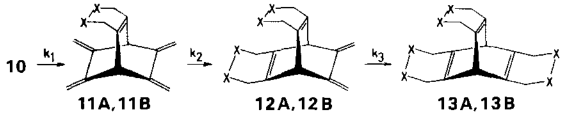
ratio k_1/k_2 for the two consecutive *Diels-Alder* additions to polyenes **5**–**10** was dependent on the nature of both the bridge Z, and of the dienophile [15]. For **10**, the rate constants k_1, k_2 and k_3 for the three consecutive cycloadditions **10**→**11**, **11**→**12** and **12**→**13**, respectively, have been evaluated [14] *(Scheme 3)*.

Scheme 3



A: X–X = $(NC)_2C{-}C(CN)_2$; B: X–X = $CH_3OOCC{\equiv}CCOOCH_3$

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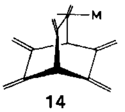
¹) We thank Prof. *H.-J. Hansen* for informing us about his unpublished work on this question.

The ratio k_1/k_2 is relatively small (*ca.* 8) as in the case of the cycloadditions of tetraene **8**, whereas k_2/k_3 is relatively large (*ca.* 320 for TCE in toluene at 25°) as for k_1/k_2 for the cycloadditions of pentaene **9**. These observations were attributed to a change in the *Diels-Alder* addition exothermicities, *i.e.*, while the reactions **10**→**11** and **11**→**12** have about the same exothermicity that of reaction **12**→**13** is significantly lower (*ca.* 10 kcal/mol) because of repulsive π-interactions [16] of the barrelene system generated in tris-adducts **13** [14].

If the valence-bond model **1**↔**2** describes the properties of a tricarbonyldieneiron complex and if the inductive effect of the $Fe(CO)_3$-group on the *Diels-Alder* reactivity of a remote diene moiety can be neglected, the cycloadditions of monocomplexed [2.2.2]hericene **14** would be predicted to have about the same reactivity as those of the uncomplexed **10**. Futhermore, the rate-constant ratios k_1/k_2 for the *Diels-Alder* additions of **14** should be relatively large, as in the case of the cycloadditions of pentaene **9** and as for k_2/k_3 in the case of the monoadduct **11**. According to the same model, the doubly complexed [2.2.2]hericenes **15** and **16** should be less reactive than **10** and **14** toward strong dienophiles as the corresponding adducts **17** might possess some barrelene character (limiting structure **18**).



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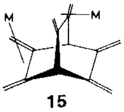

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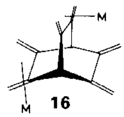

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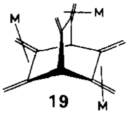

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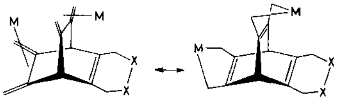


17A, 17B

18

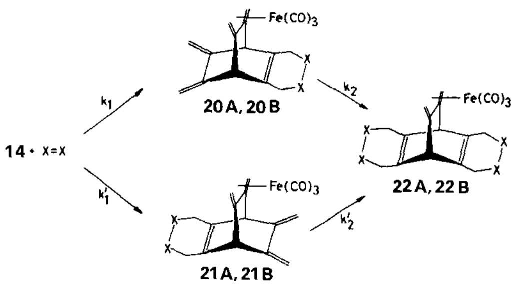
M = Fe(CO)3

17A: X–X = (NC)2C–C(CN)2 ; 17B: X–X = CH3OOCC≡CCOOCH3

We report here on the preparation of tricarbonyliron complexes of [2.2.2]hericene **14**–**16** and **19**. We present our preliminary results on the *Diels-Alder* reactivity of **14**–**16** which appear to be consistent, in part at least, with the above predictions.

Results and Discussion. – The preparation of the [2.2.2]hericene **10** has been described earlier [14]. When treated with $Fe_2(CO)_9$ in hexane at 20°, the hexaene **10** furnished a mixture of the monometallic complex **14**, dimetallic complexes **15** and **16**, and trimetallic complex **19**. The yields and relative proportions of these new compounds were a function of the initial [**10**]/[$Fe_2(CO)_9$]-ratio and reaction time. They could be readily separated by column chromatography on silica gel and purified by recrystallisation (see *Experimental*). Their structures were deduced from their mode of formation, their *Diels-Alder* reactivity toward TCE and dimethyl acetylenedicarboxylate (DMAD) (see *Tables 1* and *2*), and from their spectral data and elemental analysis. The difference in symmetry of the dimetallic isomeric complexes **15** (C_s, two different types of tricarbonyldieneiron groups) and **16** (C_{2v}, identical tricarbonyldieneiron groups) made for easy identification. The spectral characteristics of the complexes **14**–**16** and **19** were comparable to those of analogous tricarbonyldieneiron complexes [1] [2] [15] [17].

Schema 4



A: X-X = $(NC)_2C$-$C(CN)_2$; B: X-X = $CH_3OOCC{\equiv}CCOOCH_3$

The exocyclic diene moiety of the dimetallic complex **15** was added to strong dienophiles such as TCE and DMAD and gave the corresponding adducts **17A** and **17B**. Interestingly, the *Diels-Alder* reactivity of **15** toward TCE was about 540 times lower than that of the uncomplexed [2.2.2]hericene **10**. If the statistical factor of the number of mol-equiv. diene moieties is taken into account, a rate retardation factor of *ca.* 180 is estimated. Complex **15** has about the same reactivity as the bis-adduct **12A** toward TCE *(Table 1)*. However, the isomeric dimetallic complex **16** did not add to TCE or DMAD, and under forcing conditions (heating up to 60°) it only decomposed. This observation demonstrates the steric hindrance of the tricarbonyldieneiron group *syn* to the uncomplexed diene moiety.

The monometallic complex **14** added to one equivalent of TCE giving a 2.7:1 mixture of the monoadducts **21A** and **20A**. The dienophile had a slight preference for the diene *anti* to the $Fe(CO)_3$-group, which, in principle, has two faces available for the cycloaddition, whereas the diene *syn* to the $Fe(CO)_3$-group has one of its faces blocked by the complex. The *anti*-diene preference seems to be much greater when comparing the TCE-addition reactivities toward the monometallic monoadducts **20A** ($k_{rel} = 39$) and **21A** ($k_{rel} = 1$).

Table 1. *Kinetic Data for the Cycloaddition of TCE to* **10**, **11A**, **12A**, **14**, **15**, **16**, **20A** *and* **21A** *in* (D_6)*Acetone at 310 K*

Reactant	Product	$k \cdot 10^4 [l \cdot mol^{-1} s^{-1}]$	k_{rel}[a])
10	**11A**	5900[b])	1640
11A	**12A**	2950[b])	1250
12A	**13A**	13	11
14	**20A**	70	64
14	**21A**	190	173
20A	**22A**	43	39
21A	**22A**	1.2	1
15	**17A**	11	9
16	**17A'**[c])	< 0.01	< 0.01

[a]) Statistical factors of the number of mol-equiv. diene moieties are taken into account.

[b]) Measured by stopped-flow-^{1}H-FTNMR.

[c]) **17A'** is the isomer of **17A** with two $Fe(CO)_3$-groups in *syn*-positions.

The lower *Diels-Alder* reactivity of **15**, **20A** and **21A** compared with that of **10** and **11A** is consistent with the valence-bond model **17**↔**18** which leads to the prediction that, because of the 'barrelene character' in the adducts formed, the cycloadditions **15**→**17A**, **20A**→**22A** and **21A**→**22A** are less exothermic and consequently, because of the *Dimroth* [18] and *Bell-Evans-Polanyi* [19] principle, slower than the cycloadditions **10**→**11A**, **11A**→**12A**. Nevertheless, this hypothesis is not sufficient to interpret all our kinetic data. The inductive effect of the $Fe(CO)_3$-group must be invoked to explain the rate-retardation effect of 20 and 7 observed for the TCE additions **14**→**20A** and **14**→**21A**, respectively, as compared with **11A**→**12A**. According to the valence-bond model **1**↔**2** (and **17**↔**18**), we would have expected similar *Diels-Alder* reactivities for **10**, **11A** and the monometallic complex **14**. Our results deviate from that naïve prediction. The reactivity difference between cycloadditions **14**→**20A** ($k_{rel} = 64$) and **20A**→**22A** ($k_{rel} = 39$) militates against the hypothesis of the 'barrelene character' of the bisadduct **22A** which was proposed to render the addition **20A**→**22A** slower than **14**→**20A**. Contrastingly, however, the reactivity difference between reactions **14**→**21A** ($k_{rel} = 173$) and **21A**→**22A** ($k_{rel} = 1$) agrees with the latter hypothesis and the valence-bond model **1**↔**2**. In other words, the reaction sequence **14**→**21A**→**22A** imitates the sequence **11A**→**12A**→**13A** where $k_2/k_3 \approx 227$. This is not true for the reaction sequence **14**→**20A**→**22A**. The causes of this deviant behaviour can be numerous. At the moment, data are insufficient to delimit them. One recognizes, however, that the $Fe(CO)_3$-group has a retarding effect on the *Diels-Alder* reactivity of an homoconjugated uncomplexed diene. The size of this effect might depend upon the stereochemistry (attack of the dienophile onto the *syn*- or *anti*-face of the diene, $Fe(CO)_3$ *syn* or *anti* with respect to the reacting diene). We cannot exclude yet possible skeleton deformations upon complexation of the exocyclic dienes which could also influence the *Diels-Alder* reactivity of the homoconjugated, uncomplexed diene. The face selectivity of our cycloadditions should be investigated before a more elaborate analysis of the factors responsible for the reactivity changes observed can be made.

The rate constants for the cycloaddition of DMAD to the monometallic complex **14**, dimetallic complex **15** and of the monoadduct mixture **20B**–**21B** are summarized in *Table 2*. They are compared with those for the additions of DMAD to the uncom-

Table 2. *Kinetic Data for the Cycloaddition of DMAD to* **10**, **11B**, **12B**, **14**, **15**, **20B** *and* **21B** *in* (D_6)*Acetone at 310 K*

Reactant	Product	$k \cdot 10^4$ [$l \cdot mol^{-1} s^{-1}$]	k_{rel} [d])
10	**11B**	11.1[a])	4
11B	**12B**	9.8[a])	5
12B	**13B**	2.0[a])	2
14	**20B** + **21B**	6.0[b])	3
20B + **21B**	**22B**	1.0[c])	1
15	**17B**	0.5	0.5

[a]) In CD_2Cl_2 at 303 K the corresponding rate constants are 10, 6.5 and 1.0 $l \cdot mol^{-1} s^{-1}$ [14].

[b]) $k_1 + k_1'$.

[c]) $k_2 + k_2'$.

[d]) Statistical factors of the number of mol-equiv. diene moieties are taken into account.

plexed [2.2.2]hericene **10** and to the mono and bisadducts **11B** and **12B**, respectively. The *Diels-Alder* reactivity of DMAD to these polyenes follow a trend similar to that of TCE but at strong attenuated rate ratios. This difference in selectivity can be attributed to the higher exothermicity of the acetylenic dienophile cycloadditions (*e.g.* DMAD) compared to those of the ethylenic dienophile reactions (*e.g.* TCE) [14]. Thus, the transition states of the former reactions will be more cycloaddent-like, and consequently, less sensitive to a change in the exothermicity [19]. It is also consistent with the higher electronic demand of TCE as compared with that of DMAD [20].

Conclusion. – The *Diels-Alder* reactivity of the exocyclic s-*cis*-butadiene moieties of [2.2.2]hericene can be affected significantly by partial complexation of this polyene. The $Fe(CO)_3$-group retards the cycloadditions of the homoconjugated, uncomplexed diene toward strong dienophiles. This effect can be attributed to an inductive factor of the $Fe(CO)_3$-group, to a change in the exothermicity of the cycloadditions attributed to metaldiene backdonation, and to steric factors. When the two faces of an uncomplexed diene moiety are encombered by *syn*-$Fe(CO)_3$-functions, the cycloadditions can be stopped.

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Experimental. – *General Remarks.* All reactions were carried out under Ar and the solvents were dried and degassed by standard methods [21]. Melting points (m.p.; not corrected), *Tottoli* apparatus. IR spectra (ν [cm^{-1}]): in hexane, *Perkin-Elmer 577* spectrophotometer. Mass spectra (MS): in electron-ionization mode, *HP 5980-GC-MS Hewlett-Packard* spectrometer (*m/z* [amu] (% base peak), peaks corresponding to ^{56}Fe). ^1H-NMR spectra: *Bruker WH 360* (360 MHz) and *WP 80* (80 MHz) spectrometers; δ [ppm], number of protons, tentative attribution, apparent coupling constants J [Hz]. ^{13}C-NMR spectra: *Bruker WH 360* (90.55 MHz) spectrometer (D signal of $CDCl_3$ as lock signal, δ_C of $CDCl_3$ as internal reference (79.91 ppm)); δ ppm, apparent $^1J(C,H)$ coupling constant (± 1 Hz), tentative attribution; *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet. HPLC separations were made on a *Waters Associates 6000A* apparatus using 0.8 × 30 cm columns packed with *µ-Porasil* (10 µm). Elementary analyses were performed by the Mikrolabor of the ETH, Zürich (E. Manzer).

Preparation of Complexes. – *Preparation of* **14–16** *and* **19**. A suspension of $Fe_2(CO)_9$ (4.8 g; 13 mmol) and **10** (0.8 g; 4.5 mmol) in hexane (120 ml) was stirred at r.t. for 48 h. Acid alumina (grade I) was added to the green solution to decompose $Fe_3(CO)_{12}$. After filtration and evaporation to dryness, the Et_2O-extract was chromatographed on a 60 × 2 cm column packed with silica gel. Elution with hexane brought down 4 yellow bands which gave complex **14** (21%), **15** (33%), **16** (2%) and **19** (2%), respectively, after recrystallisation from hexane at −25°. Higher yields of the bi- and trimetallic complexes were obtained when using a higher ratio $Fe_2(CO)_9$/**1**. The same procedure, starting with **10** (1.1 mmol) and $Fe_2(CO)_9$ (6 mmol), gave **15** (21%), **16** (6%) and **19** (36%).

Tricarbonyl(C,2,3, C-η-2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane)iron (**14**). Yellow crystals, m.p. 131–133°. IR: 2067, 1987, 1976 (CO). ^1H-NMR (80 MHz, $CDCl_3$): 5.48, 5.28, 5.19 and 4.92 (4 *s*, each 2 H, uncoordinated $=CH_2$'s); 3.82 (*s*, 2 H, H(1,4)); 1.90 (*d*, 2 H, H of $CH_2=C(2)$ and $CH_2=C(3)$ *anti* to C(2,3), $J_{gem} = 3.0$); 0.25 (*d*, H of $CH_2=C(2)$ and $CH_2=C(3)$ *syn* to C(2,3), $J_{gem} = 3.0$). ^{13}C-NMR: 210.0 (*s*, CO); 144.8 and 143.7 (2 *s*); 108.1 (*s*); 106.4 (*t*, $^1J(C,H) = 162$); 104.3 (*t*, $^1J(C,H) = 158$); 55.7 (*d*, $^1J(C,H) = 143$, C(1,4));

35.9 (*t*, ^1J(C,H) = 158, CH_2=C(2) and CH_2=C(3)). MS (70 eV): 322 (1, M^+), 294 (20, $M^+ - CO$), 266 (55, $M^+ - 2\,CO$), 238 (100, $M^+ - 3CO$), 182 (35), 180 (30), 167 (27), 56 (Fe^+).

$C_{17}H_{14}O_3Fe$ (322.15) Calc. C 63.38 H 4.38% Found C 63.40 H 4.51%

trans-*μ-Bis(tricarbonyl)(C,2,3,C-η:C,5,6,C-η-2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane)diiron* (**15**). Yellow crystals, m.p. 145–146°. IR: 2063, 1987, 1976 (CO). ^{1}H-NMR (360 MHz, $CDCl_3$): 5.45 and 5.13 (2 *s*, each 2 H); 3.97 (*s*, 2 H, H–C(1), H–C(4)); 2.18 (*d*, 2 H, J_{gem} = 3.2); 1.96 (*d*, 2 H, J_{gem} = 3.0); 0.63 (*d*, 2 H, J_{gem} = 3.2); 0.38 (*d*, 2 H, J_{gem} = 3.0). ^{13}C-NMR: 210.0 (*s*, CO); 149.0, 110.0 and 107.5 (3 *s*); 105.5 (*t*, ^1J(C,H) = 160); 52.5 (*d*, ^1J(C,H) = 143, C(1,4)); 38.4 (*t*, ^1J(C,H) = 160); 35.9 (*t*, ^1J(C,H) = 160). MS: 462 (1, M^+), 434 (10), 406 (35), 378 (20), 350 (10), 322 (40), 294 (100, $M^+ - 6CO$), 56 (Fe^+).

$C_{20}H_{14}O_6Fe_2$ (462.03) Calc. C 51.99 H 3.05% Found C 52.14 H 3.06%

cis-*μ-Bis(tricarbonyl)(C,2,3,C-η:C,5,6,C-η-2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane)diiron* (**16**). Yellow crystals, m.p. 154–156°. IR: 2065, 1989, 1984 (CO). ^{1}H-NMR (360 MHz, $CDCl_3$): 5.22 and 4.85 (2 *s*, each 2 H); 4.03 (*s*, 2 H, H–C(1), H–C(4)); 2.13 (*d*, 4 H, J_{gem} = 3.2); 0.45 (*d*, 4 H, J_{gem} = 3.2). ^{13}C-NMR: 210.0 (*s*, CO); 146.4 and 113.7 (2 *s*); 102.6 (*t*, ^1J(C,H) = 158); 53.5 (*d*, ^1J(C,H) = 137, C(1,4)); 35.9 (*t*, ^1J(C,H) = 160). MS: 434 (0.5, $M^+ - CO$), 406 (3), 378 (2), 322 (5), 294 (15), 95 (100), 56 (70).

$C_{20}H_{14}O_6Fe_2$ (462.03) Calc. C 51.99 H 3.05% Found C 52.10 H 3.10%

Tris(tricarbonyl)(C,2,3,C-η:C,5,6,C-η:C,7,8,C-η-2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane)triiron (**19**). Yellow crystals, m.p. 158–159°. IR: 2067, 1993, 1979 (CO). ^{1}H-NMR (360 MHz, $CDCl_3$): 4.28 (*s*, 2 H, H–C(1), H–C(4)); 2.28 (*d*, 6 H, J_{gem} = 3.0); 0.75 (*d*, 6 H, J_{gem} = 3.0). ^{13}C-NMR: 210.0 (*s*, CO); 110.0 (*s*); 50.3 (*d*, ^1J(C,H) = 138, C(1,4)); 38.5 (*t*, ^1J(C,H) = 158). MS: 574 (35, $M^+ - CO$), 546 (75), 518 (23), 490 (20), 462 (100, $M^+ - 5\,CO$), 434 (65), 406 (30), 378 (35), 350 (40, $M^+ - 9\,CO$), 294 (83), 56 (Fe^+).

$C_{23}H_{14}O_9Fe_3$ (601.91) Calc. C 45.90 H 2.35% Found C 46.06 H 2.37%

Reaction of Complexes with TCE. A solution of **14** (0.17 g, 0.53 mmol) and TCE (0.068 g, 0.53 mmol) in acetone (10 ml) was stirred at r.t. for 3 days. TLC (SiO_2, hexane/AcOEt 9:1) showed the formation of 2 products followed by the slow appearance of a third one. Evaporation to dryness and chromatography on a 30 × 1 cm column packed with silica gel using the TLC eluent brought down a mixture of **20A** and **21A** (0.157 g, 65%) and then **22A** (0.028 g, 9%). Complexes **20A** and **21A** were separated by HPLC (30 × 0.8 cm column packed with 10 μm SiO_2, hexane/AcOEt 4:1, 2.8 ml · min^{-1}). The same procedure starting with **15** (0.06 g, 0.13 mmol) and TCE (0.035 g, 0.27 mmol) in 5 ml of CH_2Cl_2 (2 h, r.t., chromatography on a 20 × 1 cm column packed with silica gel using hexane/AcOEt 9:1) gave **17A** (0.065 g, 85%) after recrystallisation from hexane/AcOEt at −20°. No satisfactory elementary analyses could be obtained for these TCE adducts.

*Tricarbonyl(*syn*-C,9,10,C-η-9,10,11,12-tetramethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile)iron* (**20A**). Yellow crystals, m.p. 190° (dec.). IR (Nujol): 2060, 1990, 1955; 2260 (CN). ^{1}H-NMR (80 MHz, $CDCl_3$): 5.27 (*s*, 2 H); 4.92 (*s*, 2 H); 3.85 (*s*, 2 H); 3.39 (*m*, 4 H); 1.88 (*d*, 2 H, J_{gem} = 3.0); 0.22 (*d*, 2 H, J_{gem} = 3.0)). MS: 450 (1, M^+), 422 (4), 394 (25), 366 (100, $M^+ - 3\,CO$), 302 (10), 282 (5), 238 (2), 149 (10), 56 (Fe^+).

*Tricarbonyl(*anti*-C,9,10,C-η-9,10,11,12-tetramethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile)iron* (**21A**). Yellow crystals, m.p. 160° (dec.). IR (Nujol): 2060, 1983, 1971; 2260. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.79 (*s*, 2 H); 5.52 (*s*, 2 H); 4.04 (*s*, 2 H); 3.57 (*s*, 4 H); 2.43 (*d*, 2 H, J_{gem} = 3.0); 0.82 (*d*, 2 H, J_{gem} = 3.0). MS 450 (< 1, M^+), 422 (2), 394 (20), 366 (100, $M^+ - 3\,CO$), 302 (35), 279 (25), 56 (Fe).

Tricarbonyl(C,15,16,C-η-15,16-dimethylidenetetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile)iron (**22A**). Yellow crystals, m.p. 224–227°. IR (Nujol): 2057, 1958, 1946; 2260. ^{1}H-NMR (80 MHz, (D_6)acetone): 4.88 (*s*, 2 H, H–C(1), H–C(4)); 4.02 (*s*, 4 H); 3.90 (*m*, 4 H); 2.46 (*d*, 2 H, J_{gem} = 2.6); 0.74 (*d*, 2 H, J_{gem} = 2.6). MS: 578 (< 1, M^+), 550 (< 1), 522 (8), 494 (45, $M^+ - 3\,CO$), 468 (5), 446 (25), 442 (20), 430 (100), 56 (Fe^+).

trans-*μ-[C,9,10,C-η:C,11,12,C-η-9,10,11,12-Tetramethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile]bis(tricarbonyliron)* (**17A**). Yellow crystals, m.p. 220° (dec.). IR (Nujol): 2028, 1990, 1973, 1962; 2260. ^{1}H-NMR (80 MHz, $CDCl_3$): 4.17 (*s*, 2 H, H–C(1), H–C(4)); 3.53 (*m*, 4 H); 2.23 (*d*, 2 H, J_{gem} = 3.0); 2.17 (*d*, 2 H, J_{gem} = 2.6); 0.70 (*d*, 2 H, J_{gem} = 3.0); 0.58 (*d*, 2 H, J_{gem} = 2.6). ^{13}C-NMR: 213.0 and 209.0 (2 *s*, CO); 140.3, 111.1, 110.1, 110.0 and 108.9 (5 *s*); 51.9 (*d*, ^1J(C,H) = 146, C(1,4)); 39.6 (*t*, ^1J(C,H) = 161); 37.9 (*s*); 37.8 (*t*, ^1J(C,H) = 160); 34.5 (*t*, ^1J(C,H) = 149, CH_2). MS: 590 (< 1, M^+), 562 (< 1), 534 (15), 506 (25), 478 (8), 450 (65), 422 (45, $M^+ - 6\,CO$), 366 (30), 314 (100), 262 (90), 260 (55), 56 (Fe^+).

Reaction of Complexes with DMAD. A solution of **14** (0.03 g, 0.093 mmol) and DMAD (0.0265 g, 0.1864 mmol) in benzene (10 ml) was stirred at 37° under Ar for 12 h. Evaporation to dryness and recrystallisation from Et_2O/hexane at –20° gave **22B** (0.053 g, 94%). The same procedure starting with **15** (0.1 g, 0.22 mmol) and excess DMAD (0.16 g, 1.12 mmol) gave **17B** (91%).

Tricarbonyl[C,15,16,C-η-4,5,11,12-tetrakis(methoxycarbonyl)-15,16-dimethylidenetetracyclo-[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),4,9(14),11-tetraene]iron (**22B**). Yellow crystals, m.p. 198–200°. IR (Nujol): 2045, 1978, 1946; 1770. ^{1}H-NMR (360 MHz, $CDCl_3$): 3.94 (*s*, 2 H, H–C(1), H–C(4)); 3.80 and 3.75 (2*s*, each 6 H); 3.32 and 3.27 (2 *m*, each 4 H); 2.12 (*d*, 2 H, H(E), $J_{gem} = 3.0$); 0.40 (*d*, 2 H, $J_{gem} = 3.0$). ^{13}C-NMR: 210.2 (*s*, CO); 167.8 (*s*, C=O); 139.3, 138.1, 132.7, 132.6 and 114.3 (5 *s*); 53.4 (*d*, 141, C(1,4)); 52.4 and 52.3 (2 *q*, 147, CH_3O); 38.8 (*t*, 160, coordinated $=CH_2$); 30.9 and 30.4 (2 *t*, 131, CH_2). MS: 606 (< 1, M^+), 578 (5), 550 (10), 522 (100, $M^+ - 3$ CO), 56 (Fe^+).

$C_{29}H_{26}O_{11}Fe$ (606.37) Calc. C 57.44 H 4.32% Found C 57.37 H 4.29%

trans-*μ-[C,9,10,C-η:C,11,12,C-η-4,5-Bis(methoxycarbonyl)-9,10,11,12-tetramethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2(7),4-diene]bis(tricarbonyliron)* (**17B**). Yellow crystals, m.p. 206–209°. IR (hexane): 2044, 1977, 1962; 1724. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.05 (*s*, 2 H, H–C(1), H–C(4)); 3.78 (*s*, 6 H, OCH_3); 3.41 (*m*, 4 H, CH_2); 2.20 (*d*, 2 H, $J_{gem} = 3.0$); 2.15 (*d*, 2 H, $J_{gem} = 3.1$); 0.62 (*d*, 2 H); 0.52 (*d*, 2 H). ^{13}C-NMR: 210.0 (br. *s*, CO); 167.9 (*s*, C=O); 140.6, 132.5, 112.2 and 111.3 (4 *s*); 52.4 (*q*, $^1J(C,H) = 147$, OCH_3); 51.8 (*d*, $^1J(C,H) = 144$, C(1,4)); 39.5 (*t*, $^1J(C,H) = 161$); 38.2 (*t*, $^1J(C,H) = 159$); 30.2 (*t*, $^1J(C,H) = 131$, CH_2). MS 604 (< 1, M^+), 576 (< 1), 548 (< 1), 520 (35), 492 (3), 464 (10), 436 (30, $M^+ - 6$ CO), 408 (25), 102 (100), 56 (Fe^+).

Kinetic Measurement. An example is given for the reaction **14** + TCE: the ^{1}H-NMR spectrum (360 MHz) of a solution of **14** (0.093 mmol) and TCE (0.187 mmol) in (D_6)acetone (0.5 ml) was recorded at 310 K up to 90% completion of the first stage of the reaction (second-order conditons), and 3 pairs of signals characteristic of **14**, **20A** and **21A** were integrated at various time intervals within 3.5 h. Under these conditions the sum of rate constants $k_1 + k_1'$ is related to the rate of disappearance of **14**. A linear regression of the function $1/(b-a) \cdot \ln\{a(b-x)/b(a-x)\} = f(t)$ (where a and b are the initial concentrations of **14** and TCE, respectively, and x is the sum of the concentrations of **20A** and **21A**) gave $(k_1 + k_1') = (2.6 \pm 0.2) \cdot 10^{-2}\,l\,mol^{-1}\,s^{-1}$. The ratio $k_1/k_1' = 0.37 \pm 0.03$ was determined by averaging the ratios of the concentrations of **20A** and **21A** at different times before the appearance of **22A**. The second stage of the reaction was followed by the same procedure under pseudo-first-order conditions (0.031 mmol of **14**, 0.352 mmol of TCE, 0.5 ml (D_6)acetone, 310 K) up to 75% completion of the reaction. Treating the steps **20A**→**22A** and **21A**→**22A** as two independent reactions gave $k_2 = 4.3 \cdot 10^{-3}$ and $k_2' = 1.2 \cdot 10^{-4}\,l\,mol^{-1}\,s^{-1}$. Finally, the validity of the four rate constants was checked by a curve fitting procedure of the functions $[i] = f(t)$ (i = **14**, **20A**, **21A** or **22A**).

The reaction **10** + TCE is much faster and was followed by stopped-flow-^{1}H-NMR. The equipment and the technique used have been described elsewhere [22]: 20 μl of a solution of TCE in (D_6)acetone (0.384 g/ml) were injected in a NMR tube containing 300 μl of a solution of **10** in (D_6)acetone (0.0085 g/ml) at 310 K ($[\mathbf{10}]_0 = 4.38 \cdot 10^{-2}$M; $[TCE]_0 = 1.875 \cdot 10^{-1}$M). The consecutive cycloadditions **10**→**11A** and **11A**→**12A** were followed by recording 24 ^{1}H-NMR (360 MHz) spectra at various time intervals between 0.29 and 225 seconds. The ratio $r = k_2/k_1$ was determined in the range $0.1 < [\mathbf{12A}]/[\mathbf{10}] < 4$ by resolving the equation [23] $(r-1)[\mathbf{12A}]/[\mathbf{10}] + ([\mathbf{10}]/[\mathbf{10}]_0)^{r-1} - 1 = 0$.

Three kinetic runs gave an average $r = 0.50 \pm 0.01$. This special case has been treated by *Riggs* [24]: the time t when **11A** reaches its maximum concentration is related to k_1 by the equation $t = (4a - 2b)/k_1 \cdot \ln\{b/2b - 2a\}$ where a band b are the initial concentrations of **10** and TCE, respectively. Three kinetic runs gave an average $k_1 = 0.59 \pm 0.02\,l\,mol^{-1}\,s^{-1}$.

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