146. Face Selectivity of the *Diels-Alder* Reaction of Hexadienone Moieties Grafted onto the Bicyclo[2.2.2]octene Skeleton and Perturbed by a Remote Tricarbonylbutadieneiron Group

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(26.IV.85)

Selective oxidations of bis(tricarbonyliron) complexes of methyl (3,7,8-trimethylidenebicyclo[2.2.2]oct-5-en-2-ylidene)methyl ketones **15**–**17** afforded selectively the tricarbonyl{(1*RS*,4*SR*,7*SR*,8*RS*)-*C*,7,8,*C*-η-[methyl (3,7,8-trimethylidenebicyclo[2.2.2]oct-5-en-(2*Z*)-2-ylidene)methyl ketone]}iron (**12**), the corresponding (2*E*)-derivative **13** and the tricarbonyl{(1*RS*,2*RS*,3*SR*,4*SR*)-*C*,2,3,*C*-η-[methyl (3,7,8-trimethylidenebicyclo[2.2.2]oct-5-en-(2*Z*)-2-ylidene)methyl ketone]}iron (**18**). The stereoselectivity of the *Diels-Alder* reactions of the uncomplexed (*Z*)- and (*E*)-hexadienone **12** and **13**, respectively, was established. The face of the diene *syn* with respect to the C(5), C(6) etheno bridge was preferred for the cycloadditions of *N*-phenyltriazolinedione (NPTAD). In contrast, the reactions of dimethyl acetylenedicarboxylate (DMAD) and methyl propynoate showed a slight preference for addition to the face of the hexadienones *anti* with respect to the etheno bridges of **12** and **13**. The crystal structure of the adduct **25** resulting from the cycloaddition of NPTAD to **12** is reported.

Introduction. – Face selectivity can be observed for reactions of a π-function attached to a skeleton which is not symmetrical with respect to the 'π-plane' of this function [1–3]. The face selectivity of the *Diels-Alder* reactions of s-*cis*-butadiene moieties grafted onto bicyclo[2.2.1]heptanes **1** has been studied by several authors ($Z = CH_2$ [4–8], $Z = O$ [9] [10]). The reactions are either *endo*-face or *exo*-face selective depending on the nature of the dienophile, the substituents at the terminal diene C-atoms, and the nature of the bridges of the bicyclic skeleton [11]. The *endo*-face selectivity has been interpreted in terms of a kinetic stereoelectronic factor [6] [12] whereas the *exo*-face selectivity was attributed to steric hindrance between the cycloaddends [11] [13].

The perfluorinated triene **2** (a diene moiety grafted onto a bicyclo[2.2.2]oct-2-ene system) added to 2-butyne and dimethyl acetylenedicarboxylate (DMAD) preferentially onto the face *'anti'* with respect to the endocyclic double bond [14]. In contrast, the perfluorinated triene **3** added to 2-butyne and propyne preferentially onto the face *'syn'* with respect to the endocyclic double bond [15]. *Paquette* and coworkers [16] reported that dehydrobenzene, DMAD and methyl propynoate add preferentially onto the *'anti'* face of the cyclopentadiene derivative **4**, whereas *N*-methyltriazolinedione prefers the

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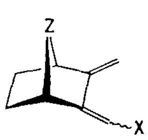
[1]) In part from the doctoral dissertation of *U. H.*, University of Lausanne, 1985.



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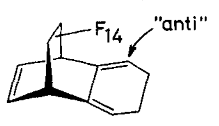

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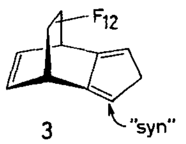

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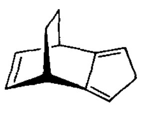

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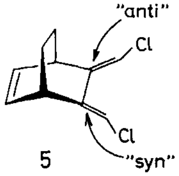

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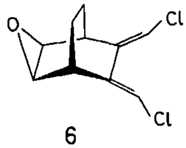

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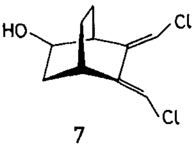

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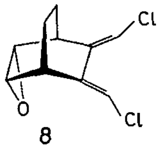

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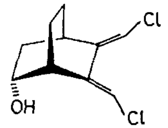

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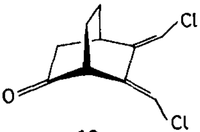

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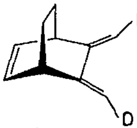

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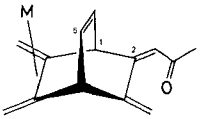
face *'syn'* with respect to the endocyclic double bond [17]. We found that ethylenetetracarbonitrile (TCE) adds preferentially onto the *'syn'* face of the dichlorodienes **5**–**7** and onto the *'anti'* face of derivatives **8**–**10** [18]. The *Diels-Alder* reactions of the dideuterated triene **11** were all *'syn'*-face selective with strong dienophiles such as *N*-phenyltriazolinedione (NPTAD), TCE, DMAD, and maleic anhydride [1]. An increase in the electrophilic character (*i.e.* in the electron affinity) increases the face selectivity, in agreement with the hypothesis that a differential polarizability factor (assistance of the endocyclic double bond to the stabilization of the transition state, or steric attractive effect) and steric repulsive effects are both present [1].

In order to test further the above hypotheses, we prepared the new exocyclic dienes **12** and **13** in which the s-*cis*-butadiene moiety is grafted onto a bicyclo[2.2.2]oct-2-ene system. The ethano bridge has been replaced by a s-*cis*-butadiene unit coordinated to a tricarbonyliron group. The position of the latter is *'syn'* with respect to the endocyclic double bond. It thus does not impede attack of dienophiles onto the face of the uncomplexed diene *'anti'* with respect to the endocyclic double bond. An acyl function substitutes the terminal C-atom of the free diene moiety. It serves as a stereochemical probe for the cycloadditions.



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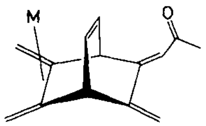

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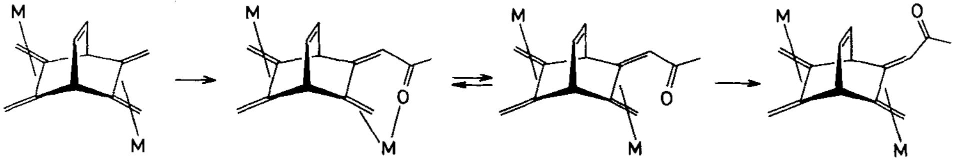
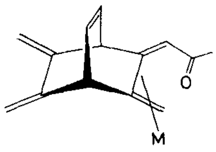
M = Fe(CO)$_3$

Results. – *Friedel-Crafts* acylation of the bis(tricarbonyliron) complex **14** of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene yielded the product of monoacylation **15** with high chemo- and stereoselectivity [19]. The latter could be equilibrated with **16**. On heating, **16** isomerized to the more stable derivative **17** [19]. The treatment of **14** with 1 equiv. of oxidant removed the tricarbonyliron moiety bounded to the *'syn'* face with respect to the etheno bridge [20]. We have found now that monodemetallation of the biscomplexes **15**–**17** were also highly selective.



14 15 16 17

The oxidation of **15** (in which the (*Z*)-hexadienone moiety is coordinated at one C=C bond and at the carbonyl group [19]) with 1 equiv. of $(NH_4)_2[Ce(NO_3)_6]$ in acetone gave exclusively **12** (98%). In contrast, the Me_3NO or Ce(IV) oxidation of **16** (in which the (*Z*)-hexadienone is coordinated at the two C=C bonds) led to the formation of the complexed hexadienone **18** (72%). The uncomplexed (*E*)-hexadienone **13** was obtained selectively (73%) on treating **17** with 1 equiv. of Me_3NO in DMF.



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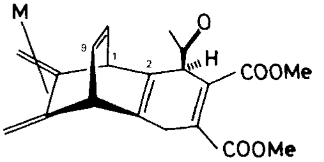
M = Fe(CO)$_3$

The structures of **12**, **13**, and **18** were determined by comparison of their ^{1}H- and ^{13}C-NMR data with those reported for tricarbonyliron complexes of **1** and analogs [20] [21] and of those of **15** for which a crystal structure has been obtained [19].

The addition of DMAD to **12** and **13** in benzene (45°C) gave a 76:24 and 33:66 mixture of adducts **19**/**20** (85%), respectively. The configuration of the acetyl group in **19** and **20** was assigned from the ^{1}H-NMR spectra using Eu(fod)$_3$ as a shift reagent (see *Exper. Part*). The lanthanide complex prefers the acetyl group of the adducts as coordination site. The lanthanide-induced shift (LIS) of the uncoordinated olefinic protons of the etheno bridge in **19** was about twice as large as those of the corresponding H-atoms in **20**.



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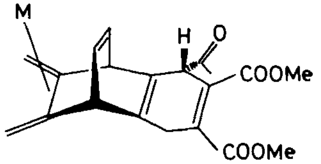

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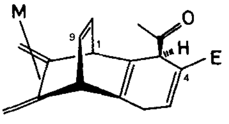
M = Fe(CO)$_3$

The reaction of **12** in methyl propynoate (65°C) gave, after chromatographic separation, a 9:1 mixture of the *'ortho'* adducts **21**/**22** (46%), the aromatized derivative **23** (25%), and an unidentified polymer exempt of iron. The **21**/**22** adducts ratio (9:1) did not vary during the reaction. No trace of the *'meta'* adducts **24** could be detected on monitoring the cycloaddition by TLC and 360-MHz-^{1}H-NMR. On heating the (*E*)-hexadienone **13** with methyl propynoate (65°C), a 2:3 mixture of adducts **21**/**22** (53%) and of **23** (11%) was isolated. The acetyl and methyl carboxylate substituents in **21** and **22** were located at C(3) and C(4), respectively, on the basis of the H,H coupling constants in the ^{1}H-NMR spectra (^4J(H–C(3), H–C(5)) < 0.5 Hz; ^3J(H–C(5), CH$_2$(6)) = 4.0 Hz) which were typical of analogous 1,4-cyclohexadienes reported in the literature [22]. The configu-



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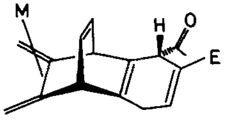

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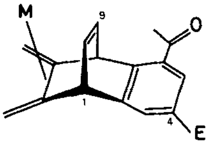

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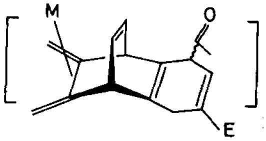

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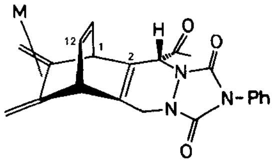
M = Fe(CO)$_3$ E = COOMe

ration of the acetyl group in **21** and **22** was assigned using Eu(fod)$_3$-induced shifts in the ^{1}H-NMR spectra (see *Exper. Part*).

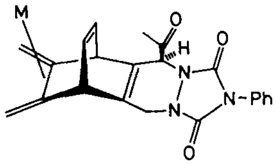
Prolonged heating of the *'ortho'* adducts **21**/**22** dit not aromatize these cyclohexadiene derivatives. Attempted dehydrogenation with dichlorodicyanobenzoquinone (DDQ) in benzene or with Pd/C (10%) in cyclohexane containing cyclohexene also failed to oxidize these adducts. It was thus postulated that **23** had been formed by dehydrogenation of the *'meta'* regioisomers **24**. The structure of **23** was assigned from its ^{1}H-NMR (^4J(H–C(3), H–C(5)) = 1.3 Hz; ^3J(H,H) in substituted benzenes are *ca.* 8 Hz [23]) and its ^{13}C-NMR spectra (^3J(C(6), *H*–C(5)) = 6 Hz, ^3J(C(5), *H*–C(3)) = 7 Hz) [24]. The *'ortho'* regioselectivity of the *Diels-Alder* reactions of hexadienones **12** and **13** with methyl propynoate is not definitive as the unobserved *'meta'* regioisomers **24** could well have decomposed to other, unidentified products besides **23**.

The (*Z*)-hexadienone **12** reacted 'instantaneously' with 1 equiv. of NPTAD (CH$_2$Cl$_2$, 20°C) and yielded only one adduct: **25** (85%, isolated). The (*E*)-hexadienone **13** reacted similarly and afforded a 1:9 mixture of adducts **25**/**26** (85%, isolated). Unfortunately, neither nuclear *Overhauser* effect nor LIS measurements could ascertain the configuration of the acetyl side chain in adducts **25** and **26**; thus, an X-ray crystallographic analysis of **25** was undertaken.



25

M = Fe(CO)$_3$



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Crystal Structure of 25. – The molecular structure of **25**, complete with the atom-numbering system, is illustrated in the *Figure*. Crystal data, atomic positional parameters and relevant bond lengths and angles are presented in *Tables 1–4*. The Fe(CO)$_3$ group is in

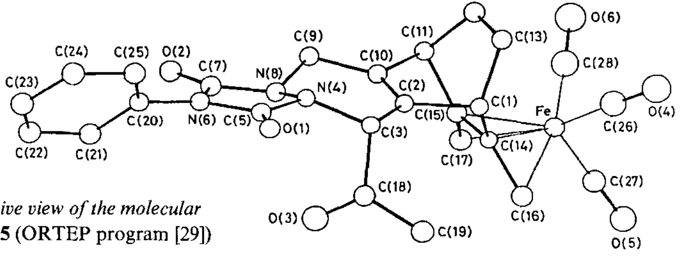


Fig. *Perspective view of the molecular structure of* **25** (ORTEP program [29])

Table 1. *Crystal Data of* **25**, *Intensity Collection, and Refinement*

Formula	$Fe(CO)_3(C_{22}H_{19}N_3O_3)$	F_{000}	528
Molecular mass	513.29	Min. and max. transmission	0.949 and 0.970
Crystal system	Triclinic	Scan type	$2\theta - \theta$
Space group	$P\bar{1}$	Scan width	$[2\theta(K\alpha_2) + 1.0]$
a [Å]	9.047(2)		$-(2\theta(K\alpha_1) - 1.0]^0$
b [Å]	10.578(3)	Scan speed	Variable (2 to 10 deg·min^{-1})
c [Å]	12.767(4)	$(\sin\theta/\lambda)_{max}$	0.995
α [°]	75.56(3)	Background from	Scan profile interpretation [28]
β [°]	78.41(2)	Standard reflections	3 remeasured after each 50
γ [°]	79.68(2)		reflections (2,0,0;0,2,0;0,0,3)
V [Å^3]	1148.3(7)	Data collected	$+h, \pm k, \pm l$
Z	2	No. of unique reflections	3029
$d_{obs.}$ [g cm^{-1}]	1.48 (1)	No. of reflections ($I < 3\sigma$)	1714
$d_{calc.}$ [g cm^{-1}]	1.485	Resolution method	*Patterson* and *Fourier*
μ [cm^{-1}]	7.2	Refinement method	Block-diagonal least-squares
Radiation	Mo-$K\alpha$, Nb-filtered	R	0.085
	(λ = 0.71069 Å)	R_w	0.071

Table 2. *List of Atomic Parameters for Complex* **25**[a])

Atom	x	y	z	U
Fe	0.7626(2)	0.7048(2)	0.5183(1)	4.42(7)*
C(1)	0.685(1)	0.5005(9)	0.7562(8)	3.5(3)
C(2)	0.522(1)	0.460(1)	0.8025(9)	3.8(3)
C(3)	0.502(1)	0.325(1)	0.8743(8)	3.7(3)
N(4)	0.341(1)	0.3368(8)	0.9293(7)	3.5(3)
C(5)	0.281(1)	0.231(1)	0.9935(9)	4.1(3)
N(6)	0.121(1)	0.2560(8)	0.9971(7)	4.1(3)
C(7)	0.091(1)	0.374(1)	0.9237(9)	4.5(3)
N(8)	0.228(1)	0.4168(8)	0.8699(7)	4.0(3)
C(9)	0.244(1)	0.556(1)	0.8250(8)	4.0(3)
C(10)	0.409(1)	0.560(1)	0.7801(8)	4.0(3)
C(11)	0.462(1)	0.692(1)	0.7113(9)	3.9(3)
C(12)	0.573(1)	0.725(1)	0.7734(9)	4.8(4)
C(13)	0.686(1)	0.624(1)	0.7997(9)	4.2(3)
C(14)	0.679(1)	0.547(1)	0.6336(8)	3.4(3)
C(15)	0.556(1)	0.646(1)	0.6088(9)	4.2(3)
C(16)	0.777(1)	0.497(1)	0.5453(9)	4.8(4)
C(17)	0.535(1)	0.698(1)	0.4957(9)	5.0(4)
C(18)	0.529(1)	0.223(1)	0.8002(9)	5.0(4)
C(19)	0.691(1)	0.173(1)	0.7603(9)	5.4(4)
C(20)	0.010(1)	0.178(1)	1.0670(9)	4.0(3)
C(21)	0.025(1)	0.133(1)	1.176(1)	5.1(4)
C(22)	−0.089(1)	0.058(1)	1.246(1)	5.6(4)
C(23)	−0.207(1)	0.031(1)	1.199(1)	5.7(4)
C(24)	−0.216(1)	0.078(1)	1.089(1)	5.6(4)
C(25)	−0.102(1)	0.152(1)	1.0159(9)	5.0(4)
C(26)	0.914(2)	0.698(1)	0.580(1)	7.3(4)
C(27)	0.847(1)	0.713(1)	0.381(1)	5.7(4)
C(28)	0.717(2)	0.863(1)	0.524(1)	7.8(5)
O(1)	0.3504(8)	0.1317(7)	1.0461(6)	4.5(2)
O(2)	−0.0356(9)	0.4317(7)	0.9062(6)	5.1(2)
O(3)	0.421(1)	0.1857(8)	0.7813(7)	7.6(3)
O(4)	1.026(1)	0.6943(8)	0.6181(7)	9.1(3)
O(5)	0.914(1)	0.7122(8)	0.2920(7)	7.4(3)
O(6)	0.680(1)	0.979(1)	0.5258(8)	10.1(3)

[a]) For the Fe-atom, the temperature factor has the form of e^{-T} where $T = 2\pi^2\Sigma h_i h_j U_{ij} a_i^* a_j^*$ with $U_{11} = 4.0(1)$, $U_{22} = 5.0(1)$, $U_{33} = 4.2(1)$, $U_{12} = 0.03(9)$, $U_{13} = -0.38(9)$, and $U_{23} = -0.95(9)$. For all other atoms, $T = 8\pi^2 U \cdot \sin^2\theta/\lambda^2$.

Table 3. *Bond Lengths (Å) in* **25**[a])

C(1)–C(2)	1.56(2)	C(7)–O(2)	1.23(1)	C(21)–C(22)	1.43(2)
C(1)–C(13)	1.55(2)	N(8)–C(9)	1.46(1)	C(22)–C(23)	1.41(2)
C(1)–C(14)	1.53(1)	C(9)–C(10)	1.49(2)	C(23)–C(24)	1.39(2)
C(2)–C(3)	1.51(1)	C(10)–C(11)	1.55(1)	C(24)–C(25)	1.45(2)
C(2)–C(10)	1.35(1)	C(11)–C(12)	1.53(2)	C(26)–O(4)	1.19(2)
C(3)–N(4)	1.48(1)	C(11)–C(15)	1.55(2)	C(27)–O(5)	1.17(2)
C(3)–C(18)	1.56(2)	C(12)–C(13)	1.36(1)	C(28)–O(6)	1.22(2)
N(4)–C(5)	1.34(1)	C(14)–C(15)	1.41(1)	Fe–C(14)	2.08(1)
N(4)–N(8)	1.42(1)	C(14)–C(16)	1.43(1)	Fe–C(15)	2.10(1)
C(5)–N(6)	1.42(1)	C(15)–C(17)	1.45(2)	Fe–C(16)	2.12(1)
C(5)–O(1)	1.24(1)	C(18)–C(19)	1.50(2)	Fe–C(17)	2.15(1)
N(6)–C(7)	1.38(1)	C(18)–O(3)	1.20(2)	Fe–C(26)	1.70(2)
N(6)–C(20)	1.44(1)	C(20)–C(21)	1.38(2)	Fe–C(27)	1.76(1)
C(7)–N(8)	1.38(1)	C(20)–C(25)	1.41(2)	Fe–C(28)	1.67(2)

[a]) The e.s.d. of the last significant digit is given in parentheses.

Table 4. *Bond Angles (°) in* **25**[a])

C(2)–C(1)–C(13)	105.1(8)	C(2)–C(10)–C(9)	125.5(9)
C(2)–C(1)–C(14)	101.7(9)	C(2)–C(10)–C(11)	115.0(10)
C(13)–C(1)–C(14)	107.1(8)	C(9)–C(10)–C(11)	119.2(9)
C(1)–C(2)–C(3)	120.6(9)	C(10)–C(11)–C(12)	106.0(9)
C(1)–C(2)–C(10)	113.4(9)	C(10)–C(11)–C(15)	100.2(9)
C(3)–C(2)–C(10)	125.7(9)	C(12)–C(11)–C(15)	107.7(9)
C(2)–C(3)–N(4)	105.1(8)	C(11)–C(12)–C(13)	114.0(11)
C(2)–C(3)–C(18)	109.0(9)	C(1)–C(13)–C(12)	114.4(11)
N(4)–C(3)–C(18)	109.1(10)	C(1)–C(14)–C(15)	113.7(9)
C(3)–N(4)–C(5)	121.0(8)	C(1)–C(14)–C(16)	127.9(9)
C(3)–N(4)–N(8)	119.1(8)	C(15)–C(14)–C(16)	118.4(10)
C(5)–N(4)–N(8)	108.0(9)	C(11)–C(15)–C(14)	113.0(12)
N(4)–C(5)–N(6)	108.1(9)	C(11)–C(15)–C(17)	127.2(9)
N(4)–C(5)–O(1)	126.7(11)	C(14)–C(15)–C(17)	119.7(10)
N(6)–C(5)–O(1)	125.1(10)	C(3)–C(18)–C(19)	116.9(12)
C(5)–N(6)–C(7)	107.1(9)	C(3)–C(18)–O(3)	119.6(11)
C(5)–N(6)–C(20)	127.1(8)	C(19)–C(18)–O(3)	123.5(12)
C(7)–N(6)–C(20)	125.8(9)	C(21)–C(20)–C(25)	126.1(10)
N(6)–C(7)–N(8)	108.3(10)	C(21)–C(20)–N(6)	117.8(12)
N(6)–C(7)–O(2)	126.8(11)	C(25)–C(20)–N(6)	116.0(10)
N(8)–C(7)–O(2)	124.9(9)	C(20)–C(21)–C(22)	117.4(12)
N(4)–N(8)–C(7)	106.0(8)	C(21)–C(22)–C(23)	119.0(11)
N(4)–N(8)–C(9)	117.9(9)	C(22)–C(23)–C(24)	121.9(11)
C(7)–N(8)–C(9)	122.9(9)	C(23)–C(24)–C(25)	120.6(13)
N(8)–C(9)–C(10)	106.0(8)	C(20)–C(25)–C(24)	115.0(10)
C(26)–Fe–C(27)	102.6(6)	Fe–C(26)–O(4)	176.2(11)
C(26)–Fe–C(28)	88.6(7)	Fe–C(27)–O(5)	174.6(11)
C(27)–Fe–C(28)	103.0(6)	Fe–C(28)–O(6)	177.9(14)

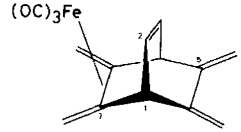
[a]) The e.s.d. of the last significant digit is given in parentheses.

the *'syn'* position with respect to the endocyclic double bond C(12),C(13). The arrangement of ligands about the Fe-atom is tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints of the outer C,C bonds of the diene moiety. The apex-to-base angles are 103° (mean) for the CO groups and 112° (mean) for the C,C bond midpoints. The basal angles are 92, 88, and 64°, the small angle being that subtended by the two outer C,C bonds of the diene. The diene is perpendicular to the basal plane, and the Fe-atom lies 0.5 Å above it. The geometrical features of the diene are quite comparable to those already discussed for analogous [Fe(CO)$_3$(exocyclic 1,3-diene)] complexes

[25]. The position of the acetyl group is *'anti'* with respect to the endocyclic double bond C(12),C(13) of the bicyclic skeleton.

The crystal structure of **25** shows a non-planar endocyclic double bond C(2),C(10) with the annulated diazacyclohexene moiety bent toward the face *'syn'* with respect to the C(12),C(13) etheno bridge. The torsion angles C(1)-C(2)-C(10)-C(9) and C(11)-C(10)-C(2)-C(3) are −171.9 and 175.3°, respectively. This is not too surprising in the light of a statistical analysis of the structures of other bicyclo[2.2.2]oct-2-ene derivatives taken from the *Cambridge Crystallographic Data File* [26] which confirmed that crystal-packing effects can engender non-planar endocyclic double bonds in these systems.

Discussion. – X-Ray crystallographic data on the tricarbonyliron monocomplex **27** showed that the two faces of the uncoordinated s-*cis*-butadiene moiety at C(5),C(6) are available for *Diels-Alder* additions. The diene unit is essentially planar and the bulks of the C(2),C(3) and C(7),C(8) bridges are not expected to differ significantly [21]. It should be noticed, however, that the angle between planes C(1),C(2),C(3),C(4) and C(1),C(6),C(5),C(4) is slightly larger (119.5°) than that between planes C(1),C(6),C(5),C(4) and C(1),C(7),C(8),C(4) (114.5°). If, because of that, there should be a differential steric effect contributing to the facial selectivity of the cycloadditions of hexadienones **12** and **13**, one would expect the face *'syn'* with respect to the endocyclic double bond (or etheno bridge) to be the preferred one. The high selectivity observed for the reactions NPTAD + **12** or **13** is in fact consistent with this hypothesis. However, this does not explain the reversal of face selectivity observed for the cycloadditions of the less reactive dienophiles DMAD and methyl propynoate, the latter showing a slight preference for the face of the hexadienone *'anti'* with respect to the etheno bridge.



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The tricarbonyliron group introduces a field effect [27] which could differentiate the two faces of the uncomplexed diene moiety. This could compete with the above steric factor. A third possible factor is a differential polarizability effect (attractive steric effect) between the etheno and tricarbonyl(diene)iron bridges. One would expect the NPTAD additions to be more prone to the latter factor than the other cycloadditions [1]. Our experimental results are not sufficient to decide which of the three factors (or others) mentioned above is the most important one in driving the facial selectivity of the *Diels-Alder* addition of hexadienones **12** and **13**. Nevertheless, they point out that the structure of the transition state of these reactions varies with the nature (structure and electron affinity) of the dienophiles. Most important is the observation that **12** and **13** can add strong dienophiles with high face selectivity. Our findings of the selective half-demetallations of the bis(tricarbonyliron) complexes **14**–**17** have synthetic significance.

We thank the *Swiss National Science Foundation* and the *Fonds Herbette*, Lausanne, for generous financial support.

Experimental Part

1. General Remarks. – See [30]. The preparation of **14–17** has been reported earlier [19].

2. Half-demetallation of Complexes 15–17. – a) $(NH_4)_2[Ce(NO_3)_6]$ (0.95 g, 1.74 mmol) was added portionwise to a well stirred soln. of **15** (0.40 g, 0.84 mmol) in acetone (10 ml) whose colour turned from red to yellow. Et_2O (50 ml) was added, and the mixture was extracted with H_2O (20 ml, 3×). The org. phase was dried over $MgSO_4$ and evaporated *i.v.* Crystallization from Et_2O/hexane at –25° gave **12** as yellow needles (0.28 g, 98%). *Tricarbonyl{(1*RS,*4*SR,*7*SR,*8*RS*)-C,7,8,C-η-[methyl(3,7,8-trimethylidenebicyclo[2.2.2]oct-5-en(2*Z*)-2-ylidene)methyl ketone]}iron* (**12**). M.p. 97–98°. IR: 2061, 1982, 1971 (CO), 1680 (C=O). ^{1}H-NMR (360 MHz, $CDCl_3$): 6.81 (*s*, CH=C(3) *cis* to C(2),C(3)); 6.58, 6.48 (2*m*, H–C(5), H–C(6)); 6.40 (*s*, CH=C(2)); 5.62 (*s*, CH=C(3) *trans* to C(2),C(3)); 3.95, 3.80 (2*dd*, H–C(1), H–C(4)); 2.30 (*s*, CH_3); 2.10, 2.07, 0.56, 0.52 (4*d*, CH_2=C(7), CH_2=C(8)); $J(1,5) = 1.4$, $J(1,6) = 6.0$, $J(4,5) \approx J(5,6) \approx 6.1$, $J(4,6) = 1.6$, $J_{gem} = 2.7$. ^{13}C-NMR (90.55 MHz, $CDCl_3$): 210.3 (*s*, CO); 198.3 (*s*, C=O); 148.4, 141.1 (2*s*, C(2), C(3)); 135.8, 133.3 (2*d*, $J = 172$, C(5), C(6)); 124.1 (*d*, $J = 155$, *C*H=C(2)); 118.5 (*t*, $J = 161$, *C*H_2=C(3)); 109.1, 106.5 (2*s*, C(7), C(8)); 53.6, 51.8 (2*d*, $J = 150$, 155, C(1), C(4)); 39.8 (*t*, $J = 160$, CH_2=); 31.7 (*q*, $J = 127$, CH_3). MS (70 eV): 338 (1, M^+), 310 (30), 282 (100), 254 (87, $M^+ - 3CO$), 198 (45), 56 (41). Anal. calc. for $C_{17}H_{14}FeO_4$ (338.15): C 60.38, H 4.17; found: C 60.35, H 4.21.

b) The same procedure as *a*) starting with **16** gave **18** as yellow needles (72%). *Tricarbonyl{(1*RS,*2*RS,*3*SR,*4*SR*)-C,2,3,C-η-[methyl(3,7,8-trimethylidenebicyclo[2.2.2]oct-5-en-(2*Z*)-2-ylidene)methyl ketone]}iron* (**18**). M.p. 110–112°. IR: 2062, 1986 (br., CO), 1673 (C=O). ^{1}H-NMR ($CDCl_3$): 6.82, 6.74 (2*m*, H–C(5), H–C(6)); 5.20, 5.19, 4.89, 4.88 (4*s*, CH_2=C(7), CH_2=C(8)); 4.12, 3.99 (2*dd*, H–C(1), H–C(4)); 3.42 (*s*, CH=C(2)); 2.33 (*d*, CH=C(3) *trans* to C(2), C(3)); 2.08 (*s*, CH_3); 1.35 (*d*, CH=C(3) *cis* to C(2), C(3)); $J_{gem} = 2.9$, other *J*'s as for **12**. ^{13}C-NMR ($CDCl_3$): 206.8 (*s*, CO); 199.1 (*s*, C=O); 144.6, 143.5 (2*s*, C(7), C(8)); 136.3, 135.3 (2*d*, $J = 174$, C(5), C(6)); 119.0, 114.0 (2*s*, C(2), C(3)); 104.0, 102.9 (2*t*, $J = 159$, CH_2=); 54.8 (*d*, $J = 152$, *C*H=C(2)); 52.5, 51.6 (2*d*, $J = 144$, C(1), C(4)); 41.1 (*t*, $J = 160$, *C*H_2=C(3)); 29.2 (*q*, $J = 127$, CH_3). MS: 338 (1, M^+), 310 (4), 282 (31), 254 (100, $M^+ - 3CO$), 224 (37), 198 (86), 56 (37). Anal. calc. for $C_{17}H_{14}FeO_4$ (338.15): C 60.38, H 4.17; found: C 60.39, H 4.24.

c) A soln. of **17** (346 mg, 0.73 mmol) and Me_3NO (0.2 g, 2.67 mmol) in DMF (10 ml) was stirred vigorously for 5 min. H_2O (50 ml) was added, and the mixture was extracted with AcOEt (50 ml, 2×). The org. extracts were dried over $MgSO_4$ and evaporated *i.v.* Column chromatography on silica gel with CH_2Cl_2 and crystallization from hexane at –25° gave **13** as yellow needles (181 mg, 73%). *Tricarbonyl{(1*RS,*4*SR,*7*SR,*8*RS)*-C,7,8,C-η-[methyl(3,7,8-trimethylidenebicyclo[2.2.2]oct-5-en-(2*E*)-2-ylidene)methyl ketone]}iron* (**13**). M.p. 106–108°. IR: 2060, 1983, 1972 (CO), 1690 (C=O). ^{1}H-NMR ($CDCl_3$): 6.64 (*s*, CH=C(3) *cis* to C(2), C(3)); 6.57, 6.54 (2*m*, H–C(5), H–C(6)); 5.78 (*dd*, H–C(1)); 5.64 (*s*, CH=C(2)); 5.26 (*s*, CH=C(3) *trans* to C(2), C(3)); 4.00 (*dd*, H–C(4)); 2.30 (*s*, CH_3); 2.17, 2.05, 0.51, 0.50 (4*d*, CH_2=C(7), CH_2=C(8)); $J(1,5) = 1.6$, $J(1,6) = 6.1$, $J(4,5) \approx J(5,6) = 6.2$, $J(4,6) = 1.4$, $J_{gem} = 2.5$. ^{13}C-NMR ($CDCl_3$): 210.0 (*s*, CO); 198.1 (*s*, C=O); 150.5, 144.3 (2*s*, C(2), C(3)); 135.8, 133.7 (2*d*, $J = 174$, C(5), C(6)); 117.2 (*d*, $J = 154$, *C*H=C(2)); 108.2 (*t*, $J = 160$, *C*H_2=C(3)); 108.7, 106.5 (2*s*, C(7), C(8)); 49.0, 42.5 (2*d*, $J = 145$, 142, C(1), C(4)); 40.6, 39.5 (2*t*, $J = 160$, CH_2=); 32.2 (*q*, $J = 127$, CH_3). MS: 338 (< 1, M^+), 310 (25), 282 (100), 254 (77, $M^+ - 3CO$), 224 (43), 198 (89), 56 (51). Anal. calc. for $C_{17}H_{14}FeO_4$ (338.15): C 60.38, H 4.17; found: C 60.21, H 4.15.

3. Addition of NPTD to 12 and 13. – a) A soln. of NPTD in CH_2Cl_2 was added dropwise to a soln. of **12** (0.2 g, 0.59 mmol) in CH_2Cl_2 (20 ml) at r.t. until persistence of the red colour. Evaporation *i.v.* and column chromatography (20 × 2 cm) on silica gel with CH_2Cl_2 brought down a yellow band containing a single isomer (HPLC, ^{1}H-NMR). Crystallization from CH_2Cl_2/hexane at –25° gave **25** as yellow microcrystals (0.255 g, 85%).

b) The same procedure as *a*) starting with **13** gave a 1:9 mixture of **25/26** (85%). *[(1*RS,*3*SR,*11*SR,*14*SR,*15*RS*)-C,14,15,C-η-(3-Acetyl-14,15-dimethylidene-6-phenyl-4,6,8-triazatetracyclo-[9.2.2.0*^{2,10}*.0*^{4,8}*]pentadec-2(10),12-diene-5,7-dione)]tricarbonyliron* (**25**). M.p. 158–159°. IR (Nujol): 2057, 1974, 1950 (CO), 1765, 1705 (C=O). ^{1}H-NMR ($CDCl_3$): 7.47 (*m*, C_6H_5); 6.89, 6.84 (2*m*, H–C(12), H–C(13)); 5.17 (*dd*, H–C(3)); 4.70, 4.27 (2*dd*, CH_2(9)); 4.66, 4.36 (2*dd*, H–C(1), H–C(11)); 2.33 (*s*, CH_3); 2.20, 2.16, 0.48, 0.43 (4*d*, CH_2=C(14), CH_2=C(15)); $J(1, 12) \approx J(12, 13) = 1.7$, $J(1, 13) = 6$, $J(3, 9) = 3.1$, 1.7, J_{gem} at C(9) = 17, $J(11, 12) = 6.1$, $J_{gem} = 2.7$. ^{13}C-NMR ($CDCl_3$; for numbering, see *Fig.*): 211.0 (br. *s*, CO); 199.3 (*s*, C(18)); 152.7, 151.9 (2*s*, C(5), C(7)); 138.4, 137.9 (2*d*, $J = 178$, C(12), C(13)); 142.6, 136.0 (2*s*, C(2), C(10)); 131.1 (*s*, C(20)); 129.2, 128.4, 125.6 (3*d*, $J = 160$, Ph); 112.9, 112.6 (2*s*, C(14), C(15)); 65.6 (*d*, $J = 148$, C(3)); 49.0 (2*d*, $J = 142$, 143, C(1), C(11)); 45.5 (*t*, $J = 142$, C(9)); 41.4, 40.6 (2*t*, $J = 160$, CH_2=); 29.7 (*q*, $J = 129$, CH_3). MS: 485 (11, $M^+ - CO$), 457 (58), 429 (100, $M^+ - 3\,CO$), 330 (42), 254 (14), 241 (40), 56 (62). Anal. calc. for $C_{25}H_{19}FeN_3O_6$ (513.29): C 58.50, H 3.73; found: C 58.56, H 3.72.

[(1RS,3RS,11SR,14SR,15RS)-C,14,15,C-η-(3-Acetyl-14,15-dimethylidene-6-phenyl-4,6,8-triazatetracyclo-[9.2.2.0^{2,10}.0^{4,8}]pentadec-2(10),12-diene-5,7-dione)]tricarbonyliron (**26**). M.p. 155° (dec.). IR (Nujol): 2060, 1980, 1970 (CO), 1770, 1710 (C=O). ^{1}H-NMR (CDCl$_3$): 7.50–7.41 (*m*, C$_6$H$_5$); 6.84 (*m*, H–C(12), H–C(13)); 5.29 (*dd*, H–C(3)); 4.60, 4.37 (2*dd*, H–C(1), H–C(11)); 4.55, 4.44 (2*dd*, CH$_2$(9)); 2.22 (*s*, CH$_3$); 2.20, 2.18, 0.49, 0.48 (4*d*, CH$_2$=C(14), CH$_2$=C(15)); $J(1, 12) = 1.5$, $J(1, 13) \approx J(11, 12) \approx J(12, 13) = 5$, $J(3, 9) = 2.9, 2.2$, J_{gem} at C(9) = 16, $J(11, 13) = 2$, $J_{\text{gem}} = 2.8$. ^{13}C-NMR (CDCl$_3$; numbering as for **25**, see *Fig.*): 211.5 (br. *s*, CO); 199.1 (*s*, C(18)); 152.7, 151.8 (2*s*, C(5), C(7)); 138.8, 137.8 (2*d*, $J = 177$, C(12), C(13)); 142.5, 136.1 (2*s*, C(2), C(10)); 131.1 (*s*, C(20)); 129.2, 128.4, 125.6 (3*d*, $J = 160$, Ph); 113.1, 112.9 (2*s*, C(14), C(15)); 65.0 (*d*, $J = 147$, C(3)); 49.0, 48.8 (2*d*, $J = 144$, C(1), C(11)); 45.3 (*t*, $J = 144$, C(9)); 39.9, 39.2 (2*t*, $J = 160$, CH$_2$=); 27.0 (*q*, $J = 129$, CH$_3$). MS: 485 (10, $M^+ - \text{CO}$), 457 (34), 429 (53, $M^+ - 3\,\text{CO}$), 373 (24), 330 (77), 56 (100). Anal. calc. for C$_{25}$H$_{19}$FeN$_3$O$_6$ (513.29): C 58.50, H 3.73; found: C 58.47, H 3.80.

4. Addition of DMAD to 12 and 13. – a) A soln. of **12** (0.3 g, 0.89 mmol) and DMAD (1 g, 7.1 mmol) in C$_6$H$_6$ (10 ml) was stirred at 45° for 2 days. Evaporation to dryness followed by column chromatography (25 × 2 cm) on silica gel, first with CH$_2$Cl$_2$, then CH$_2$Cl$_2$/Et$_2$O 9:1 gave a 1st fraction containing unreacted **12** (4%), and a 2nd fraction containing a 76:24 mixture of **19**/**20** (363 mg, 85%). This ratio was found to be constant on monitoring the reaction by ^{1}H-NMR between 10 and 60% completion. Several recrystallization from hexane/AcOEt at −25° gave pure **19** as yellow microcrystals.

b) The same procedure as *a*) starting with **13** gave a 33:66 mixture of **19**/**20** (85%). Performing the reaction in CH$_2$Cl$_2$ did not modify the proportion of isomers. Several recrystallizations from hexane/AcOEt gave pure **20** which was characterized only by its ^{1}H-NMR spectrum. *Tricarbonyl[(1RS,3SR,8SR,11SR,12RS)-C,11,12,C-η-(dimethyl-3-acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4,9-triene-4,5-dicarboxylate)]iron* (**19**). M.p. 158–159°. IR: 2045, 1980, 1952 (CO), 1720, 1708 (C=O). ^{1}H-NMR (CDCl$_3$)[2]): 6.69 (*m*, [10, 11], H–C(9), H–C(10)); 4.27, 4.26 (2*m*, 3H, [25 for H–C(1), 100 for H–C(3), 9 for H–C(8)]); 3.83, 3.77 (2*s*, [41, 28], 2 CH$_3$O); 3.55, 3.38 (2*dd*, [*ca.* 40], CH$_2$(6)); 2.13 (2*d*, 2H, [2], CH=C *trans* to C(11), C(12)); 1.98 (*s*, [57], CH$_3$); 0.43 (2*d*, 2H, [1], CH=C *cis* to C(11), C(12)); $J(3,6) = 7.0, 7.5$, J_{gem} at C(6) = 23.5, $J(9, 10) = 6.5$, $J_{\text{gem}} = 2.8$, $J(1, 9) \approx J(8, 10) < 2$. ^{13}C-NMR (CDCl$_3$): 210.0 (*s*, CO); 203.5 (*s*, C=O); 168.0, 166.7 (2*s*, COO); 142.0, 137.8, 130.3 (3*s*, C(2), C(4), C(5), C(7)); 137.8, 137.5 (2*d*, $J = 173, 179$, C(9), C(10)); 113.2, 113.1 (2*s*, C(11), C(12)); 56.3 (*d*, $J = 138$, C(3)); 52.7 (*q*, $J = 148$, CH$_3$O); 50.6, 48.5 (2*d*, $J = 143$, C(1), C(8)); 40.0, 39.9 (2*t*, $J = 160$, CH$_2$=); 31.3 (*t*, $J = 132$, C(6)); 26.3 (*q*, $J = 128$, CH$_3$). MS: 452 (18, $M^+ - \text{CO}$), 424 (53), 396 (100, $M^+ - 3\,\text{CO}$), 56 (75). Anal. calc. for C$_{23}$H$_{20}$FeO$_8$ (480.25): C 57.52, H 4.20; found: C 57.31, H 4.17.

Tricarbonyl[(1RS,3RS,8SR,11SR,12RS)-C,11,12,C-η-(dimethyl-3-acetyl-11,12-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2(7),4,9-triene-4,5-dicarboxylate)]iron (**20**). ^{1}H-NMR (CDCl$_3$)[2]): 6.72 (*m*, [6], H–C(9), H–C(10)); 4.31, 4.27 (2*m*, [*ca.* 30, 10], H–C(1), H–C(8)); 4.14 (*dd*, [100], H–C(3)); 3.81, 3.75 (2*s*, [43, 28], 2 CH$_3$O); 3.53, 3.40 (2*dd*, [*ca.* 40], CH$_2$(6)); 2.10 (2*d*, 2H, [5, 5.5], CH=C *trans* to C(11), C(12)); 2.00 (*s*, [56], CH$_3$); 0.38, 0.31 (2*d*, 2H, [6.5], CH=C *cis* to C(11), C(12)); same *J*'s as for **19**.

5. Addition of Methyl Propynoate to 12 and 13. – a) A soln. of **12** (0.30 g, 88.7 mmol) in methyl propynoate (2 ml) was stirred at 65° for 24 h, then excess propynoate was distilled off at 10^{-2} Torr. Column chromatography (60 × 1 cm) on *Florisil* with CH$_2$Cl$_2$ brought down 3 yellow bands. The 1st fraction contained an unidentified polymeric product. Crystallization of the 2nd fraction from Et$_2$O/hexane at −25° gave **23** as yellow microcrystals (95 mg, 25.4%). The 3rd fraction contained a 9:1 mixture (^{1}H-NMR) of **21**/**22** (174 mg, 46.4%). Several recrystallizations from Et$_2$O/hexane at −25° gave **21** as yellow needles. Prolonged heating of **21** in methyl propynoate at 65°, its reaction with DDQ in benzene or with 10% Pd/C in hexane containing cyclohexene failed to give any identified dehydrogenated product. The same 9:1 ratio of isomers was observed after *ca.* 30% completion of the reaction.

b) The same procedure as *a*) starting with **13** gave a 2:3 mixture of **21**/**22** (53%) and **23** (11%). HPLC separation failed to yield pure **22** which was only characterized by ^{1}H-NMR. Regioisomers **24** were not observed on monitoring the reaction by TLC and ^{1}H-NMR. *Tricarbonyl[(1RS,3SR,8SR,11SR,12RS)-C,11,12,C-η-(methyl-3-acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4,9-triene-4-carboxylate)]iron* (**21**). M.p. 148–150°. IR: 2060, 1980, 1969 (CO), 1717 (C=O). ^{1}H-NMR (CDCl$_3$)[2]): 7.20 (br. *d*, [54], H–C(5)); 6.68, 6.67 (2*dd*, [10], H–C(9), H–C(10)); 4.31 (*m*, [23], H–C(1)); 4.27 (*s*, [100], H–C(3)); 4.18 (*m*, [7.5], H–C(8)); 3.75 (*s*, [38], CH$_3$O); 3.30 (*m*, [20], CH$_2$(6)); 2.15, 2.13 (2*d*, 2H, [3], CH=C *trans* to C(11), C(12)); 1.94 (*s*, [43], CH$_3$); 0.43, 0.42 (2*d*, [2], CH=C *cis* to C(11), C(12)); $J(1, 9) = 2.0$, $J(1, 10) = 5.0$, $J(3, 5) < 1$, $J(3, 6) = 8$, $J(5, 6) = 4.0$, $J(9, 10) = 5.3$, $J_{\text{gem}} = 2.6$. ^{13}C-NMR (CDCl$_3$): 210.7 (*s*, CO); 204.8 (*s*, C=O); 166.3 (*s*, COO); 142.3, 139.0 (2*s*, C(2),

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[2]) Numbers in brackets are rel. LIS in % as obtained upon addition of Eu(fod)$_3$.

C(7)); 138.6, 137.8 (2*d*, J = 175, C(9), C(10)); 137.6 (*d*, J = 153, C(5)); 128.3 (*s*, C(4)); 113.6, 113.4 (2*s*, C(11), C(12)); 54.3 (*d*, J = 128, C(3)); 52.0 (*q*, J = 147, CH_3O); 50.9, 48.9 (2*d*, J = 150, 142, C(1), C(8)); 40.9, 39.8 (2*t*, J = 160, CH_2=); 30.3 (*t*, J = 141, C(6)); 26.5 (*q*, J = 128, CH_3). MS: 422 (3, M^+), 394 (11), 366 (61), 338 (100, $M^+ - 3$ CO), 312 (5), 254 (19), 56 (10). Anal. calc. for $C_{21}H_{18}FeO_6$ (422.22): C 59.74, H 4.30; found: C 59.66, H 4.30.

*Tricarbonyl [(1*RS*,3*RS*,8*SR*,11*SR*,12*RS*)-C,11,12,C-η-(methyl-3-acetyl-11,12-dimethylidenetricyclo[6.2.2.0*^{2,7}*]dodeca-2(7),4,9-triene-4-carboxylate)]iron* (**22**). ^{1}H-NMR (80 MHz, $CDCl_3$)[2]): 7.20 (br. *s*, [55], H–C(5)); 6.70 (*dd*, [5], H–C(9), H–C(10)); 4.30 (*m*, [25], H–C(1)); 4.20 (*m*, 2H, [100 for H–C(3), 10 for H–C(8)]); 3.80 (*s*, [33], CH_3O); 3.30 (*m*, [21], CH_2(6)); 2.10 (*d*, 2H, [7], CH=C *trans* to C(11), C(12)); 1.95 (*s*, [45], CH_3); 0.40 (*d*, 2H, [9.5], CH=C *cis* to C(11), C(12)); same J's as for **21**.

*Tricarbonyl [(1*RS*,8*SR*,11*SR*,12*RS*)-C,11,12,C-η-(methyl-6-acetyl-11,12-dimethylidenetricyclo[6.2.2.0*^{2,7}*]dodeca-2(7),3,5,9-tetraene-4-carboxylate)]iron* (**23**). M.p. 145–148°. IR: 2060, 1982, 1971 (CO), 1720 (br., C=O). ^{1}H-NMR ($CDCl_3$): 8.20, 8.09 (2*d*, H–C(3), H–C(5)); 6.92, 6.85 (2*m*, H–C(9), H–C(10)); 5.88 (*dd*, H–C(8)); 4.71 (*dd*, H–C(1)); 3.95 (*s*, CH_3O); 2.71 (*s*, CH_3); 2.27, 2.18 (2*d*, 2H, CH=C *trans* to C(11), C(12)); 0.45 (*d*, 2H, CH=C *cis* to C(11), C(12)); $J(1, 9) \approx J(8, 10) = 1.4$, $J(1, 10) \approx J(9, 10) = 5.8$, $J(3, 5) = 1.3$, $J_{gem} = 2.6$. ^{13}C-NMR ($CDCl_3$): 210.2 (*s*, CO); 199.9 (*s*, C=O); 166.1 (*s*, COO); 151.4, 148.7 (2*s*, C(4), C(6)); 138.9, 138.8 (2*d*, J = 176, C(9), C(10)); 133.9 (*s*, C(7)); 127.6, 127.2 (2*d*, J = 167, 161, ^3J(C, H) = 6, 7, C(3), C(5)); 127.0 (*s*, C(2)); 113.1, 111.8 (2*s*, C(11), C(12)); 52.3 (*q*, J = 148, CH_3O); 49.6, 45.8 (2*d*, J = 145, C(1), C(8)); 40.5, 39.9 (2*t*, J = 160, CH_2=); 29.0 (*q*, J = 128, CH_3). MS: 420 (1, M^+), 392 (10), 364 (54), 336 (100, $M^+ - 3$ CO), 226 (53), 56 (Fe^+). Anal. calc. for $C_{21}H_{16}FeO_6$ (420.20): C 60.03, H 3.84; found: C 59.34, H 3.73.

6. Collection of X-Ray Data for 25. – A well formed single crystal of approximate dimensions 0.18 × 0.07 × 0.05 mm was mounted on a *Syntex P2$_1$* auto-diffractometer. Unit-cell parameters were determined from 22 accurately centered reflections with 2θ values greater than 4.0°. Information on data collection appears in *Table 1*. All 3029 unique reflections were corrected for absorption (*Gaussian* integration), *Lorentz*, and polarization effects.

Solution and Refinement. All calculations were performed with the X-ray 72 system of programs [31]. Atomic scattering factors calculated by *Cromer* and *Mann* [32] were assigned to the non-H-atoms. Anomalous dispersion corrections [33] were applied to the Fe-atoms which were located from a *Patterson* map. The remaining non-H-atoms could be identified on successive *Fourier* maps. Location of H-atoms was not attempted. Subsequent refinement with anisotropic thermal coefficients for Fe and isotropic thermal coefficients for C-, N-, and O-atoms gave the final $R = 8.5\%$, $R_w = 7.1\%$, and GOF = 2.40 for 146 variables refined against 2162 reflections. The function minimized during full-matrix least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ with $w = 1/\sigma^2$. Final positional parameters are shown in *Table 2*. A list of observed and calculated structure factor amplitudes and least-squares planes data are deposited as *Table 2-S* (supplementary material, available from *R.R.*).

REFERENCES

[1] M. Avenati, P. Vogel, *Helv. Chim. Acta* **1983**, *66*, 1279, and ref. cit. therein.

[2] J.-C. Zwick, P. Vogel, submitted.

[3] F. Freeman, *Chem. Rev.* **1975**, *75*, 439; A. D. Allen, T. T. Tidwell, *J. Am. Chem. Soc.* **1982**, *104*, 3145; H. G. Richey, Jr., C. W. Wilkins, Jr., *J. Org. Chem.* **1980**, *45*, 5027; E. J. Corey, M. Shibasaki, K. C. Nicolaou, C. L. Malmsten, B. Samuelsson, *Tetrahedron Lett.* **1976**, 737; S. W. Baldwin, J. C. Tomesch, *J. Org. Chem.* **1974**, *39*, 2382; D. I. Davies, M. J. Parrott, *Tetrahedron Lett.* **1972**, 2719; N. G. Rondan, M. N. Paddon-Row, P. Caramella, K. N. Houk, *J. Am. Chem. Soc.* **1981**, *103*, 2436; N. G. Rondan, M. N. Paddon-Row, P. Caramella, J. Mareda, P. H. Mueller, K. N. Houk, *J. Am. Chem. Soc.* **1982**, *104*, 4974.

[4] K. Alder, F. H. Flock, P. Hansen, *Chem. Ber.* **1956**, *89*, 2689.

[5] T. Sugimoto, Y. Kobuke, J. Furukawa, *J. Org. Chem.* **1976**, *41*, 1457.

[6] M. C. Böhm, R. V. C. Carr, R. Gleiter, L. A. Paquette, *J. Am. Chem. Soc.* **1980**, *102*, 7218; R. Gleiter, L. A. Paquette, *Acc. Chem. Res.* **1983**, *16*, 338; L. A. Paquette, in 'Stereochemistry and Reactivity of Systems Containing π Electrons', Ed. W. H. Watson, Verlag Chemie International, Deerfield Beach, Florida, 1983, pp. 41–73; R. Gleiter, M. C. Böhm, *ibid.*, pp. 105–146; R. Gleiter, M. C. Böhm, *Pure Appl. Chem.* **1983**, *55*, 237; L. A. Paquette, K. E. Green, L. Y. Hsu, *J. Org. Chem.* **1984**, *49*, 3650.

[7] P. D. Bartlett, C. Wu, *J. Org. Chem.* **1984**, *49*, 1880; W. H. Watson, J. Galloy, P. D. Bartlett, A. A. M. Roof, *J. Am. Chem. Soc.* **1981**, *103*, 2022.

[8] J.P. Hagenbuch, P. Vogel, A.A. Pinkerton, D. Schwarzenbach, *Helv. Chim. Acta* **1981,** *64,* 1818.
[9] C. Mahaim, P. Vogel, *Helv. Chim. Acta* **1982,** *65,* 866.
[10] J.-M. Tornare, P. Vogel, *J. Org. Chem.* **1984,** *49,* 2510.
[11] P. Vogel, in 'Stereochemistry and Reactivity of Systems Containing π Electrons', Ed. W.H. Watson, Verlag Chemie International, Deerfield Beach, Florida, 1983, pp. 147–195.
[12] F.K. Brown, K.N. Houk, *Tetrahedron Lett.* **1984,** *25,* 4609.
[13] P.-A. Carrupt, F. Berchier, P. Vogel, submitted.
[14] W.J. Feast, R.R. Hughes, W.K.R. Musgrave, *J. Chem. Soc., Perkin Trans. I* **1977,** 152.
[15] W.J. Feast, W.K.R. Musgrave, W.E. Preston, *J. Chem. Soc., Perkin Trans. I* **1972,** 1830.
[16] L.A. Paquette, R.V.C. Carr, M.C. Böhm, R. Gleiter, *J. Am. Chem. Soc.* **1980,** *192,* 1186.
[17] L.A. Paquette, R.V.C. Carr, P. Charumilind, J.F. Blount, *J. Org. Chem.* **1980,** *45,* 4922.
[18] M. Avenati, P. Vogel, *Helv. Chim. Acta* **1982,** *65,* 204.
[19] R. Roulet, E. Tagliaferri, P. Vogel, G. Chapuis, *J. Organomet. Chem.* **1981,** *208,* 353.
[20] P. Narbel, T. Boschi, R. Roulet, P. Vogel, A.A. Pinkerton, D. Schwarzenbach, *J. Organomet. Chem.* **1980,** *194,* 103; see also: R. Gabioud, P. Vogel, *Helv. Chim. Acta* **1983,** *66,* 1134; R. Gabioud, P. Vogel, *Tetrahedron Lett.* **1983,** *24,* 1983.
[21] P. Narbel, T. Boschi, R. Roulet, P. Vogel, A.A. Pinkerton, D. Schwarzenbach, *Inorg. Chim. Acta* **1979,** *36,* 161.
[22] P.W. Rabideau, *Acc. Chem. Res.* **1978,** *11,* 141; M.C. Grossel, M.J. Perkins, *J. Chem. Soc., Perkin Trans. 2* **1975,** 1544; J.L. Marshall, T.K. Folsom, *J. Org. Chem.* **1971,** *36,* 2011; C. Mahaim, Thèse EPFL No. 426, 1981.
[23] J.M. Emsley, J. Feeney, L.H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon Press, Oxford, 1966, Vol. 2, pp. 770–773, and ref. therein.
[24] M. Avenati, P.-A. Carrupt, D. Quarroz, P. Vogel, *Helv. Chim. Acta* **1982,** *65,* 188; F.J. Weigert, J.D. Roberts, *J. Am. Chem. Soc.* **1967,** *89,* 2967; K. Tori, T. Tsushima, H. Tanida, K. Kushida, S. Satoh, *Org. Magn. Reson.* **1974,** *6,* 324; L.F. Johnson, W.C. Jankowski, '^{13}C-NMR Spectra', Wiley-Interscience, New York, 1972; G.C. Levy, G.L. Nelson, 'Carbon-13 NMR for Organic Chemists', Wiley-Interscience, New York, 1972; D.F. Ewing, *Org. Magn. Reson.* **1974,** *12,* 499; P.E. Hansen, *Progr. NMR Spectr.* **1981,** *14,* 175.
[25] A.A. Pinkerton, G. Chapuis, P. Vogel, U. Hänisch, P. Narbel, T. Boschi, R. Roulet, *Inorg. Chim. Acta* **1979,** *35,* 197.
[26] A.A. Pinkerton, D. Schwarzenbach, J.-L. Birbaum, P.-A. Carrupt, L. Schwager, P. Vogel, *Helv. Chim. Acta* **1984,** *67,* 1136.
[27] R. Pettit, G. Emerson, J. Mahler, *J. Chem. Educ.* **1963,** *40,* 175; H.D. Murdoch, E. Weiss, *Helv. Chim. Acta* **1962,** *45,* 1156; *ibid.* **1963,** *46,* 1588; Ch. Barras, L.G. Bell, R. Roulet, P. Vogel, *ibid.* **1981,** *64,* 2841.
[28] H. Blessing, P. Coppens, P. Becker, *J. Appl. Cryst.* **1972,** *7,* 488; D. Schwarzenbach, TWOTHLEH, a *Syntex P2$_1$* data collection program including scan profile interpretation, Abs. Fourth European Crystallographic Meeting, 1977, p. 134.
[29] C.K. Johnson, ORNL-3794, Oak Ridge National Laboratory, 1971.
[30] U. Hänisch, E. Tagliaferri, R. Roulet, P. Vogel, *Helv. Chim. Acta* **1983,** *66,* 2182.
[31] J.M. Stewart, F.A. Kundell, J.C. Baldwin, X-Ray 72, version of June 1972, Technical Report TR-192 of the Computing Science Center, University of Maryland (as modified by *D. Schwarzenbach*).
[32] D.T. Cromer, J.B. Mann, *Acta Crystallogr., Sect. A* **1968,** *24,* 321.
[33] D.T. Cromer, *Acta Crystallogr.* **1965,** *18,* 17.