109. Control of *Diels-Alder* Addition, Stereo- and Regioselectivity by Remote Substituents and Tricarbonyl(diene)iron Moieties[1])

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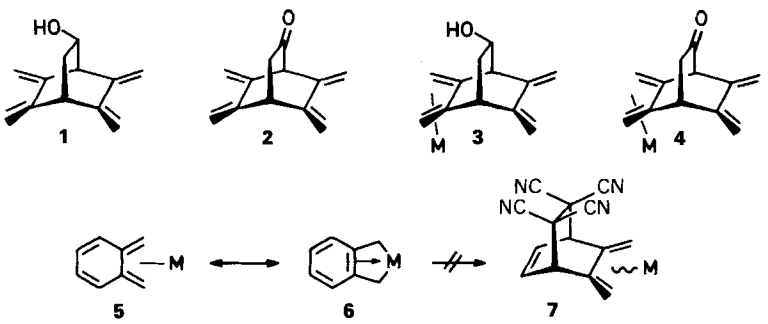
A stereoselective synthesis of tricarbonyl-[(1*RS*,2*RS*,4*RS*,5*RS*,6*SR*)-*C*-5,6,*C*-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-ol)]iron (**11**) and of its tosylate **12** and benzoate **13** is reported. The bulk of the *'endo'*-Fe(CO)$_3$ moiety and of the ester groups in **13** renders its *Diels-Alder* additions to methyl propynoate (**15**), butynone (**16**), and 1-cyanovinyl acetate highly *'para'* regioselective. The cycloadditions of diene-alcohol **11** are either *'meta'*- or *'para'*-regioselective depending on the nature of the dienophile. In the presence of $BF_3 \cdot Et_2O$, the addition of **11** to methyl vinyl ketone is highly stereo- (*Alder* mode) and *'para'*-regioselective, giving adduct **52** (tricarbonyl-[(1*RS*,4*RS*,8*RS*,9*SR*,10*RS*,12*RS*)-*C*,9,10,*C*-η-(12-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-en-4-yl methyl ketone)]iron) whose structure has been established by single-crystal X-ray crystallography.

Introduction. – The *Diels-Alder* additions of tetraenol **1** and tetraenone **2** were found to be little stereo- and regioselective, giving mixtures of mono- and bis-adducts when 1 mol-equiv. of dienophile was used for the reaction [1]. The corresponding *'endo,syn'*-tricarbonyliron monocomplexes **3** and **4** could be prepared readily, thus allowing one to obtain pure mono-adducts of the corresponding tetraenes. Unfortunately, the regioselectivity was very poor for the cycloadditions of **3**. In the case of **4**, it was a little better, *e.g.* the addition of methyl propynoate to **4** gave a 3:1 mixture of the corresponding *'para'*/*'meta'* adducts [1].



[1]) Part of the Ph. D. thesis of *J.-C. Zwick*, Ecole Polytechnique Fédérale de Lausanne, 1987. Part of this work has been presented at the fall meeeting of the Swiss Chemical Society in Bern, Oct. 10, 1986.

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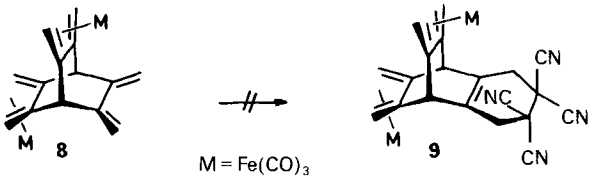
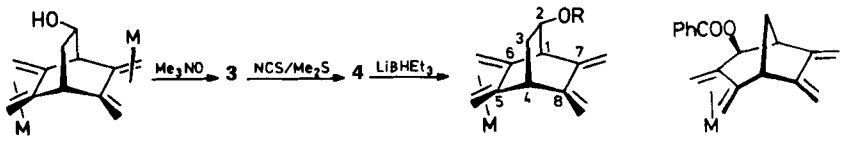
Coordination of a diene with a tricarbonyliron group can perturb significantly the chemical properties of a conjugated [2] [3] or homoconjugated function [4] [5]. For instance, the tricarbonyl (*o*-xylylene)iron complex **5** does not react with ethylenetetracarbonitrile to give the expected adduct **7**. The iron complex of the exocyclic diene moiety confers some aromatic character to the conjugated endocyclic diene function. This property can be interpreted in terms of the limiting structures **5**↔**6**. A $Fe(CO)_3$ group may also influence the reactivity of a remote function because of its inductive and polarizability effects [4b] [5] or/and because of its bulk (steric effect) [6]. Such an effect was invoked to interprete the lack of *Diels-Alder* reactivity of the doubly complexed [2.2.2]-hericene derivative **8** (*e.g.* ↛**9**) [7]. We thus predicted that monocomplexation of **1** by a $Fe(CO)_3$ group onto the *'endo'* face of the diene moiety *'anti'* with respect to the OH function should force the attack of a dienophile onto the *'exo'* face of the uncomplexed diene unit, *'syn'* with respect to the OH group. Under these circumstances, the OH group or its esters should be able to control the stereo- and regioselectivity of the *Diels-Alder* additions of non-symmetrical dienophiles. We report on the synthesis of such complexes (**11**–**13**) and shall show that the above concept can lead to good selectivities for the cycloadditions. Furthermore, we have found that the regioselectivity depends on the nature of the substituents at C(2) in the 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl derivatives and on that of the dienophile.



Results. – Oxidation of the doubly complexed tetraenol **10** with Me_3NO in acetone removed selectively the *'exo'*-$Fe(CO)_3$ moiety, giving the *'endo'*-monocomplexed tetraenol **3** [1]. *Collins'* oxidation of alcohol **3** into the corresponding ketone **4** has already been reported [1]. We have found that the *Corey* and *Kim*'s method [8] using *N*-chlorosuccinimide (NCS) and dimethylsulfide gave a better yield of **4** (65%) and was easier to scale up. Although it has been reported that desulfurization can be carried out with $Fe(CO)_5$ [9], we did not observe any products resulting from the decomplexation of **3** or **4** under these conditions.



10

11 R = H
12 R = $SO_2C_6H_4Me$
13 R = COC_6H_5

14

M = $Fe(CO)_3$

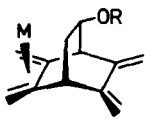
Attempts to invert the configuration at C(2) in **3** *via* S_N2-displacement reactions of the corresponding tosylate or mesylate failed using cesium carboxylates [10] or potassium carboxylates and [18]crown-6 [11]. Under these conditions, only products of decomposition were obtained. The *Mitsunobu*'s [12] technique applied to alcohol **3** (the modification of *Volante* [13] was used to avoid cycloaddition of the diene to diethyl azodicarboxylate) did not

give products of S_N2 displacement. Instead, products of homoallylic rearrangement, giving the corresponding bicyclo[3.2.1]oct-2-yl derivatives were observed [5c]. For instance, the reaction of diethyl azodicarboxylate and benzoic acid with the triphenylphosphine complex of alcohol **3** led to the rearranged benzoate **14**; no trace of any other isomeric product could be detected, thus indicating the facile heterolysis of the C–O bond in the phosphorus complex of **3** (S_N1 process with homoconjugative participation by the uncoordinated s-*cis*-butadiene moiety) [5c].

The base-catalyzed H/D exchange of H–C(3) in the *'endo'*-$Fe(CO)_3$-monocomplexed **4** was found to be highly stereoselective [14]. The addition of MeMgI to **4** was only slightly stereoselective, the nucleophile preferring (2:1) the face of the ketone *'syn'* with respect to the diene-$Fe(CO)_3$ moiety [14]. We found that the hydride reductions of **4** can also be stereoselective. For instance, when using $LiBH(Et)_3$ in anh. THF (–78°), the desired alcohol **11** was isolated in 88% yield. In this case, the *'syn' vs. 'anti'* facial selectivity for the hydride attack onto the ketone function was *ca.* 21:1 [5a]. The origin of these selectivities is not established yet [15]. The tosylate **12** and benzoate **13** were derived from alcohol **11** using standard methods (see *Exper. Part*).

The structure of **11** was deduced from its mode of formation, its elemental analysis, and its spectral data. In particular, the relative configuration of the alcohol at C(2) was established by 360-MHz ^{1}H-NMR and lanthanide-induced shifts (see *Exper. Part*) and by comparison with data obtained for **3**. The structures of **4** [15] and **10** [16] had been established unambiguously by X-ray diffraction studies.

The *Diels-Alder* additions of **12** to methyl 2-propynoate (**15**), and of **11** and **13** to **15**, 3-butyn-2-one (**16**), 2,3-didehydroanisole (**17**), 1-cyanovinyl acetate (CVA) and methyl vinyl ketone (MVK) have been carried out. Our results (see adducts and their dehydrogenation products **18–55**) are summarized in *Table 1* and compared with those (see **57–60**) obtained for the cycloadditions of **15** to the *'exo'*-$Fe(CO)_3$ monocomplex **56** which was prepared by benzoylation of the corresponding alcohol **61**.



56 R = OCOPh
61 R = H

The alcohol **61** was obtained by oxidation of the dinuclear complex **10** with *o*-chloranil in CH_2Cl_2 containing AcONa and silica gel (20°, ultra-sounds). Thus, we have demonstrated the high versatility of the dicomplex **10** since, depending on the nature of the oxidant, either the *'exo'*-$Fe(CO)_3$ (with Me_3NO) or the *'endo'*-$Fe(CO)_3$ moiety (with *o*-chloranil) can be removed selectively.

The adduct mixtures obtained for the reactions with the acetylenic dienophiles **15–17** were not very stable and contained significant amounts of the corresponding aromatized derivatives. On treatment of these mixtures with DDQ (= 4,5-dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitrile) in benzene at 60–80°, oxidation was complete, and mixtures of the corresponding aromatized adducts were isolated in good yield (see *Table 1*). The product ratios (regioselectivities) were determined by 360-MHz ^{1}H-NMR of the latter mixtures. In the case of reactions **12** + **15**, **13** + **15**, and **13** + **16**, the corresponding major products **28**, **32**, and **36**, respectively, were isolated pure by simple crystallization. The structures of the aromatized cyclo-adducts were deduced from their spectral data, and more specifically from their 360-MHz ^{1}H-NMR spectra with the help of nuclear *Overhauser* effect (NOE) measurements.

Table 1. *Regioselectivities of the* Diels-Alder *Additions of Dienes* **11**–**13** *and* **56** (M = $Fe(CO)_3$) *with the Dienophiles* $H-C\equiv C-E$ (E = COOMe, **15**; E = COMe, **16**)[a]), *2,3-Didehydroanisole* (**17**)[b]), *1-Cyanovinyl Acetate* (CVA), *and Methyl Vinyl Ketone* (MVK)

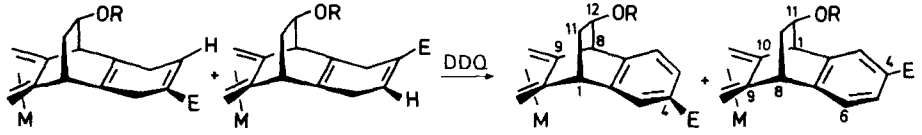
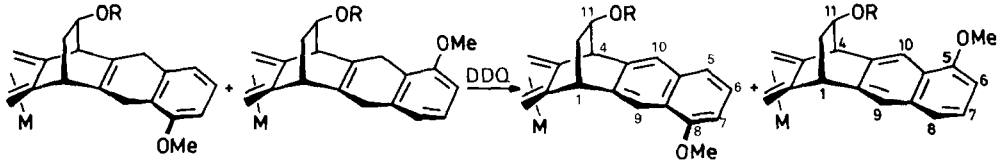
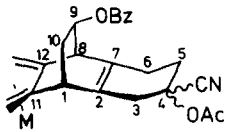
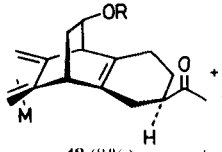
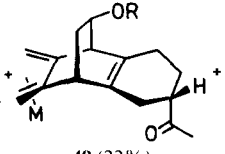
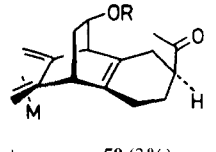
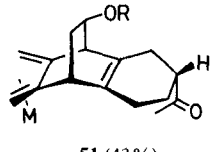
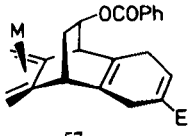
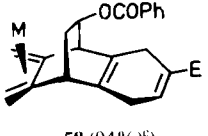
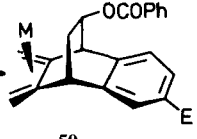
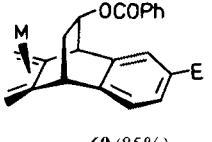
R	Cyclo-addents	Adducts (isolated yield)	Regioselectivity (ratio in % (± 2%))
			*para/meta*
H	**11** + **15**	→ **18** + **19** (97%)[c]) → **20** + **21** (97%)	37:63[d])
	11 + **16**	→ **22** + **23** (97%)[c]) → **24** + **25** (76%)	31:69[d])
Ts	**12** + **15**	→ **26** + **27** (90%)[c]) → **28**[e]) + **29** (80%)[e])	89:11[d])
PhCO	**13** + **15**	→ **30** + **31** (92%)[c]) → **32**[e]) + **33** (86%)[e])	94:6[d])
	13 + **16**	→ **34** + **35** (94%)[c]) → **36**[e]) + **37** (85%)[e])	92:8[d])
			*trans/cis*
H	**11** + **17**	→ **38** + **39** (71%) → **40** + **41** (75%)	28:72[d])
PhCO	**13** + **17**	→ **42** + **43** (76%)[c]) → **44** + **45** (70%)	29:71[d])
			*para/meta*
PhCO	**13** + CVA	→ **46** (63%) + **47** (17%)	> 98:2[f])

Table 1 (cont.)

R	Cyclo-addents	Adducts (isolated yield)								Regioselectivity (ratio in % (± 2%))	*para/meta*
			+		+		+				
PhCO	**13** + MVK	→ **48** (8%)	+	**49** (22%)	+	**50** (3%)	+	**51** (43%)		(13:14:5:58)[f])	37:63
PhCO	**13** + MVK + $BF_3 \cdot Et_2O$	→ **48**	+	**49**	+	**50**	+	**51** (92%)		(15:12:5:68)[f])	27:73
H	**11** + MVK	→ **52** (68%)	+	**53** (trace)	+	**54** (20%) or		**55** (20%)			77:23
H	**11** + MVK + $BF_3 \cdot Et_2O$	→ **52** (93%)									> 98:2[f])
			+		DDQ →		+				
	56 + **15**	→ **57**	+	**58** (94%)[c])	→	**59**	+	**60** (85%)			68:32[d])

[a]) At 80° in anh. C_6H_6.

[b]) Prepared by decomposition of 3-methoxyanthranilic acid with isopentyl nitrite in anh. dioxane at 70°.

[c]) Yield of crude adduct mixtures containing some aromatized derivatives.

[d]) As given by 360-MHz ^{1}H-NMR spectra of the aromatized adducts; these product ratios do not differ from those observed before aromatization with DDQ.

[e]) IUPAC numbering shown for R = H; IUPAC numbering for R = Ts or PhCO, see *Exper. Part.*

[f]) Proportions in the crude reaction mixture as determined by ^{1}H-NMR.

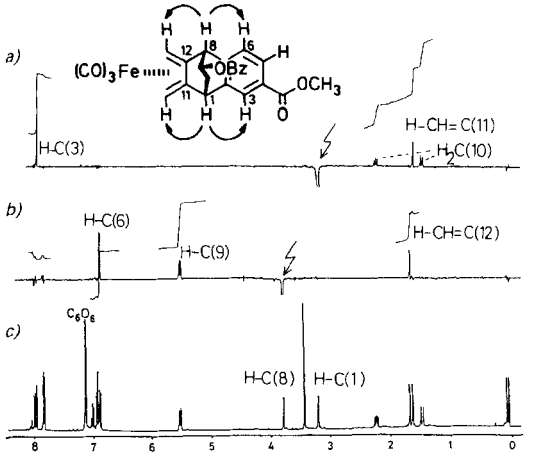


Fig. 1. *Nuclear* Overhauser *effect* (NOE) *measurements in the 360-MHz* ^{1}*H-NMR* (C_6D_6, 25°) *of* **32** (IUPAC numbering shown); *a)* irradiation of H–C(1) (3.23 ppm); *b)* irradiation of H–C(8) (3.82 ppm); *c)* without irradiation. Spectra *a)* and *b)* were obtained by substracting the spectrum *c)* from the irradiated spectra.

An illustrative example is shown in *Fig. 1* for **32**. The signals attributed to the bridgehead protons H–C(1) (3.23 ppm, *t*, ^3J(H–C(1), CH_2(10)) = 2.5 Hz) and H–C(8) (3.82 ppm, *d*, ^3J(H–C(8),H–C(9)) = 3.0 Hz) are identified unambiguously from their multiplicity. Irradiation of H–C(1) led to the observation of significant NOE's at 7.98 ppm (*d* attributed to H–C(3), vicinal to the ester group, ^4J(H–C(3),H–C(5)) = 1.5 Hz) and 1.62 ppm (*d* attributed to *H*–CH=C(11) *trans* to C(12), ^2J = 2.5 Hz): Irradiation of H–C(8) led to the observation of NOE's at 6.90 ppm (*d*, ^3J = 7.5 Hz) attributed to H–C(6) and at 1.67 ppm (*d*, ^3J = 2.5 Hz) attributed to *H*–CH=C(12) *trans* to C(11). Similar NOE measurements were made on the ^{1}H-NMR spectra of mixtures **20**/**21**, **24**/**25**, **28**/**29**, **32**/**33**, and **36**/**37**, allowing one to establish the relative configurations of these compounds unambiguously.

In the case of the 5-methoxy-1,4-ethanoanthracenol **41**, irradiation of the signals attributed to the bridgehead protons H–C(1) (3.33 ppm, *t*, *J* = 3.0 Hz) and H–C(4) (3.58, *d*, *J* = 3.0 Hz) allowed one to identify the signals attributed to the proximal protons H–C(9) (7.36 ppm, *s*) and H–C(10) (8.34 ppm, *s*) respectively (NOE measurements). Irradiation of the latter signals allowed one to establish their proximity with H–C(8) (7.40 ppm, *d*, *J* = 8.0 Hz) and the MeO group (3.44 ppm, *s*), respectively. The structure of **45** was determined in a similar way.

The reaction of diene-benzoate **13** with CVA under thermal conditions (C_6H_6, 80°) gave a 78:22 mixture of adducts **46** and **47** which were separated by chromatography on silica gel. The relative configuration at C(4) bearing the CN and AcO substituents could not be determined in these adducts. Nevertheless, their 360-MHz ^{1}H-NMR spectra together with NOE measurements allowed one to show that both products **46** and **47** resulted from the same *'para'* regiochemistry. In contrast with the good *'para'* regioselectivities observed for the *Diels-Alder* additions of **13** to methyl 2-propynoate (**15**), butynone **16** and CVA, the reaction of **13** with MVK under thermal conditions (C_6H_6, 60°) was slightly *'meta'*-regioselective, giving a 13:24:5:58 mixture of adducts **48**/**49**/**50**/**51**[3]). When MVK or **13** was precomplexed with $BF_3 \cdot Et_2O$ [17], the cycloaddition (−78°) was not much more selective, leading to a 15:12:5:68 mixture of **48**/**49**/**50**/**51** *(Table 1)*.

The thermal cycloaddition of MVK to the diene-alcohol **11** (C_6H_6, 60°, 4 h) gave a mixture of adducts from which the alcohols **52** and **54** (or **55**)[3]) were isolated pure in 68 and 20% yield, respectively. When **11** was precomplexed with 5 mol-equiv. of $BF_3 \cdot Et_2O$ in anh. CH_2Cl_2 at −78°, the cycloaddition of MVK (−78°, 90 min) gave a unique compound, the *'para'* adduct **52**, in 91% isolated yield. In this case, the stereo- and regioselectivity of *Diels-Alder* addition has been dramatically improved by the *Lewis*-acid

catalyst [18], in contrast with the cycloaddition of MVK to **13**. It is interesting to note that the reaction of 3-butyn-2-one (**16**) with the diene-alcohol **11** precomplexed with 5 equiv. of $BF_3 \cdot Et_2O$ (CH_2Cl_2, −55°, 50 h) gave a 1:1 mixture of adducts **24**/**25** (82% isolated yield), *i.e.* a lower regioselectivity than under thermal conditions (see *Table 1*). The same result was obtained when **16** was first precomplexed with $BF_3 \cdot Et_2O$.

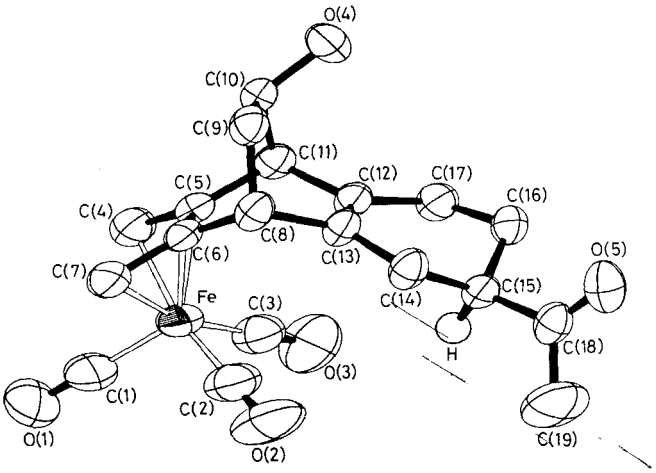


Fig. 2. *Perspective view of the molecular structure of* **52**. ORTEP program [29]; for reason of clarity, the H-atoms are not shown, except for H–C(15); the atom numbering does not correspond to the IUPAC numbering; atoms are reproduced with 50% thermal ellipsoids.

The structure of adduct **52** was established by X-ray-diffraction studies (see *Exper. Part* and *Fig. 2*). Benzoylation of **52** (PhCOCl, pyridine, 0°) gave **48**. Base-catalyzed isomerization of **52** (MeOH, K_2CO_3, 20°, 2 h) gave a mixture **52**/**53** which was separated by chromatography on silica gel. Benzoylation of **53** gave **49**. These experiments established the structure of **48**, **49**, and **53**. The *'meta'* regiochemistry of adducts **50**, **51**, **54**, and **55** was also established. However, the configuration *('exo' vs. 'endo')* at C(4) bearing the Ac group is arbitrary and could not be determined unambiguously.

Discussion. – The cycloadditions **12** + **15**, **13** + **15**, **13** + **16**, and **13** + CVA were all highly *'para'*-regioselective, in agreement with the hypothesis that the bulk of the *'endo'*-$Fe(CO)_3$ moiety and of the ester groups induce *'para'*-regioselective attacks of the dienophiles onto the face of the uncoordinated diene moieties *'syn'* with respect to C(2) of the tetramethylidenebicyclo[2.2.2]oct-2-yl esters. The two faces of the uncoordinated diene unit in the *'exo'*-$Fe(CO)_3$ monocomplex **56** are equally accessible to the dienophiles. Addition onto the face *'anti'* with respect to the benzoate group is not expected to be regioselective, thus explaining the relatively weak *'para'* regioselectivity observed for the cycloaddition **56** + **15**. This result confirms also the hypothesis of steric effects forcing the *'para'* regioselectivity in the reactions **12** + **15**, **13** + **15**, **13** + **16** and **13** + CVA.

The weak *'meta'* regioselectivity observed for the addition of MVK to diene-benzoate **13** could be explained in terms of favorable dipole-dipole interactions between the dienophile and **13** (see *Fig. 3*). This hypothesis is consistent with the fact that the cycloaddition of **13** to MVK was also *'meta'*-selective in the presence of an excess of $BF_3 \cdot Et_2O$.

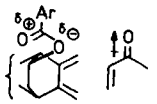


Fig. 3. *Dipole-dipole interaction between MKV and* **13**

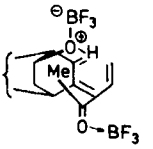
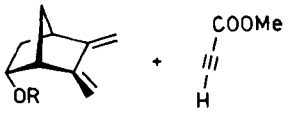


Fig. 4. *Steric repulsion between BF_3-complexed* **11** *and MVK*

This interpretation could be retained for both *Alder* and *anti-Alder (Fig. 3)* mode of addition[3]).

The *'meta'* regioselectivities observed for the *Diels-Alder* additions of the diene-alcohol **11** to methyl 2-propynoate (**15**) and 3-butyn-2-one (**16**) can be explained by invoking the formation of an H-bond between the carbonyl group of the acetylenic dienophiles and the alcoholic function of **11**. This type of interaction had been proposed earlier to explain the *'meta'* regioselectivity of the cycloaddition of **15** to 5,6-dimethylidene-bicyclo[2.2.1]heptan-2-*endo*-ol (**62**) [20]. In the latter reaction, one implies the *endo* face of the diene moiety to be favored for the dienophile attack, a property which has been demonstrated for deuterium-substituted s-*cis*-butadienes grafted onto bicyclo[2.2.1]-heptane skeletons [21]. In contrast, and as for the cycloadditions **12** + **15**, **13** + **15**, **13** + **16**, and **13** + CVA, the *Diels-Alder* additions of **15** to the acetate **63** and brosylate **64** were *'para'*-regioselective, consistent with an *endo*-face attack of the diene which is perturbed by the bulk of the *endo* substituent at C(2).



62 R = H *'meta'*-selective addition
63 R = CH_3CO *'para'*-selective addition
64 R = p-$BrC_6H_4SO_2$ *'para'*-selective addition

The *'para'* regioselectivity of the *Diels-Alder* addition of **11** to MVK under thermal conditions is not easily explained. The very high *'para'* regioselectivity and stereoselectivity (*Alder* mode of addition giving exclusively adduct **52**) observed under the $BF_3 \cdot OEt_2$-catalyzed conditions can be attributed to steric repulsive effects between the BF_3-complexed alcohol **11** and dienophile, as shown in *Fig. 4*. Double coordination of BF_3 by **52** and MVK is also possible [22].

We do not have any satisfying interpretation to offer for the *'cis'* regioselectivity of the additions of 2,3-didehydroanisole (**17**) to both diene-alcohol **11** and diene-benzoate **13**. We did not expect any significant differentiation of the modes of attack *'cis' vs. 'trans'* due to steric effects. It is not excluded yet that the regioselectivity observed is the expression of the geometry of precomplexes between the dienes and the precursor of the dienophile, *i.e.* 2-diazonio-3-methoxybenzene-1-carboxylate, rather than the translation of an electronic or steric effect. It is interesting to recall here that **17** has already been found to add to dienes substituted at C(1) with arylthio groups with high *'cis'* regioselectivity [23].

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[3]) Distinction between structures **50** and **51** as well as between **54** and **55** is arbitrary, see *Exper. Part.*

Conclusion. – Stereoselective syntheses of tricarbonyliron monocomplexes of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl derivatives have been presented. In the case of complexes **11**–**13**, the bulk of the *'endo'*-$Fe(CO)_3$ moiety forces the *Diels-Alder* addition of the uncomplexed diene unit to occur onto the face *'syn'* with respect to the substituents at C(2). The bulk of the ester groups of **12** and **13** renders the *'para'* mode of addition favored for acetylenic dienophiles such as methyl 2-propynoate (**15**) and 3-butyn-2-one (**16**) and for 1,1-disubstituted olefinic dienophiles such as 1-cyanovinyl acetate (CVA). The cycloadditions of methyl vinyl ketone (MVK) and 2,3-dihydroanisole (**17**) are slightly *'meta'* regioselective. The use of $BF_3 \cdot Et_2O$ catalyst did not improve the selectivity of the *Diels-Alder* additions of diene-benzoate **13** to MVK. In contrast with the reactions of the diene-ester **12** and **13**, the diene-alcohol **11** added to acetylenic dienophiles with *'meta'* regioselectivity. The cycloaddition of **11** to MVK was slightly *'para'*-regioselective. In the presence of $BF_3 \cdot Et_2O$, however, the reaction was completely stereo- (*Alder* mode of addition) and *'para'*-regioselective. The possibility to control the stereo- and regioselectivity of *Diels-Alder* additions by remote substituents and $Fe(CO)_3$ moieties makes complexes **11**–**13** potential synthetic intermediates for the preparation of polyfunctional, linearly condensed six-membered ring systems. This potentiality is certainly enhanced by the fact that **11**–**13** can be obtained as optically pure materials [14].

We thank *F. Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for generous support.

Experimental Part

General. See [24].

Tricarbonyl[(1RS,4RS,5RS,6SR)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-one)]iron (**4**). Me_2S (3 ml, 2.54 g, 41 mmol) was added slowly to a soln. of *N*-chlorosuccinimide (4.11 g, 30.8 mmol) in anh. toluene (100 ml) at 0° within 15 min until appearance of a precipitate. A soln. of alcohol **3** [1] (334 mg, 1.06 mmol) in anh. toluene (10 ml) was added dropwise under stirring at 0°. After the addition of Et_3N (4.5 ml) in anh. toluene (10 ml), the mixture was stirred for 10 more min. Et_2O (200 ml) was added, the soln. washed with 1N HCl (100 ml, twice), sat. aq. $NaNCO_3$ soln. (80 ml, 3 times), and H_2O (80 ml, 3 times), dried ($MgSO_4$), and evaporated. The crude **4** was filtered through a short column of silica gel (10 g, CH_2Cl_2), yielding 224 mg (68%) of yellow crystals [1].

Tricarbonyl[(1RS,2RS,4RS,5RS,6SR)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-ol)]iron (**11**). Complex **4** (113 mg, 0.362 mmol) was added to 1M $LiBH(Et)_3$ in THF (6 ml) stirred at −78°. After 5 h at −78°, $MeOH/H_2O$ 1:1 (20 ml) was added and the mixture allowed to warm to 20°. After the addition of H_2O (20 ml), the mixture was extracted with CH_2Cl_2 (50 ml, 3 times), the combined org. extract washed with H_2O (30 ml), and the combined aq. phase extracted with CH_2Cl_2 (50 ml). The combined org. phase was dried ($MgSO_4$) and evaporated and the residue filtered through a short column of silica gel (10 g, CH_2Cl_2). Recrystallization from CH_2Cl_2/hexane gave 99 mg (88%) of yellow crystals. M.p. 151.5–152°. UV (95% EtOH): 215 (sh, 19400), 282 (sh, 2200). IR (KBr): 3460 (br.), 3010, 2970, 2940, 2900, 2870, 2050*s*, 2000*s*, 1970*s*, 1630, 1060, 1040, 900, 635, 615. ^{1}H-NMR (360 MHz, $CDCl_3$, [LIS by $Eu(thd)_3$]): 5.5 (*s*, [19.7], *H*−CH=C(7) *cis* to C(8)); 5.28 (*s*, [16.1], *H*−CH=C(8) *cis* to C(7)); 4.93 (*s*, [25.0], *H*−CH=C(7) *trans* to C(8)); 4.82 (*s*, [15.2], *H*−CH=C(8) *trans* to C(7)); 4.35 (*m*, *J* = 9.0, 3.0, 2.5, [100], H−C(2)); 3.25 (*d*, *J* = 3.0, [53.8], H−C(1)); 3.18 (*t*, *J* = 3.0, [21.3], H−C(4)); 2.49 (*m*, *J* = 13.0, 9.0, 3.0, [36.2], H−C(3) *'anti'* to OH); 1.80 (*d*, *J* = 2.5, [9.4] and [10.4], *H*−CH=C(5) *trans* to C(6) and *H*−CH=C(6) *trans* to C(5), resp.); 1.71 (*m*, *J* = 13.0, 3.0, 2.5, [68.0], H−C(3) *'syn'* to OH); 0.25, 0.20 (2*d*, *J* = 2.5, [8.5] and [9.0], *H*−CH=C(5) *cis* to C(6) and *H*−CH=C(6) *cis* to C(5), resp.). MS (70 eV): 314 (1, $M^{+\cdot}$), 286 (23), 158 (60), 230 (100), 212 (9), 210 (6), 208 (3), 156 (18), 141 (11). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.52, H 4.47.

Tricarbonyl[(1RS,2RS,4RS,5RS,6SR)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl p-*toluenesulfonate)]iron* (**12**). A mixture of **11** (290 mg, 0.92 mmol), pyridine (4 ml), and TsCl (0.5 g, 2.64 mmol) was stirred

at 20° for 24 h. After addition of CH_2Cl_2 (150 ml), the soln. was washed successively with H_2O (50 ml), 1N HCl (50 ml, 3 times), H_2O (50 ml), aq. sat. $NaHCO_3$ soln. (50 ml), and H_2O (50 ml, twice), dried ($MgSO_4$), and evaporated and the residue filtered through a short column of *Florisil* (10 g, CH_2Cl_2). Recrystallization from CH_2Cl_2/hexane at −25° gave 320 mg (75%) of yellow crystals. M.p. 121–122°. UV (95% EtOH): 201 (40000), 223 (33500), 252 (sh, 10700), 296 (3750). IR (KBr): 3090, 3060, 3000, 2960, 2060, 1965, 1355, 1190, 1175, 1100, 1030, 930, 890, 825, 640. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.83, 7.37 (2*dt*, *J* = 8.0, 1.5, 4 arom. H); 5.42. 5.25 (2*s*, 2 H); 5.06 (*dt*, *J* = 9.5, 3.0, H–C(2)); 4.82, 4.79 (2*s*, 2 H); 3.40 (*d*, *J* = 3.0, H–C(1)); 3.14 (*t*, *J* = 3.0, H–C(4)); 2.47 (*s*, CH_3); 2.39 (*ddd*, *J* = 14.0, 9.5, 3.0, H–C(3) *'anti'* to TsO); 1.94 (*dt*, *J* = 14.0, 3.0, H–C(3) *'syn'* to TsO); 1.80, 1.78 (2*d*, *J* = 2.5, 2 H); 0.22, 0.16 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 468 (2, $M^{+\cdot}$), 440 (5), 412 (30), 384 (51), 252 (12), 235 (6), 212 (13), 156 (34), 141 (20), 128 (12), 115 (11), 105 (9), 91 (22), 58 (100). Anal. calc. for $C_{22}H_{20}FeO_6S$ (468.318): C 56.43, H 4.30; found: C 56.37, H 4.23.

*Tricarbonyl[(1*RS,*2*RS,*4*RS,*5*RS,*6*SR*)*-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl benzoate)]iron* (**13**). A mixture of **11** (102 mg, 0.325 mmol), pyridine (2 ml), and benzoyl chloride (73 mg, 60 µl, 0.52 mmol) was stirred at 20° for 100 min. After addition of CH_2Cl_2 (150 ml), the mixture was washed successively with H_2O (70 ml), 1N HCl (50 ml, 3 times), sat. aq. $NaHCO_3$ soln. (50 ml, twice), and H_2O (70 ml), dried ($MgSO_4$), and evaporated and the residue filtered through a short column of silica gel (10 g, CH_2Cl_2/hexane 1:1). Crystallization from hexane at −20° gave 126 mg (92%) of yellow crystals. M.p. 119.5–120°. UV (95% EtOH): 227 (34000), 260 (sh, 8500), 280 (3900). IR (KBr): 3100, 3070, 3000, 2980, 2960, 2060, 2000, 1985, 1970, 1940, 1715, 1330, 1280, 1120, 1035, 895, 715. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.07 (*m*, *J* = 8.5, 1.5, 2 H); 7.61 (*m*, *J* = 7.5, 1.5, 1 H); 7.49 (*m*, *J* = 8.5, 7.5, 1.5, arom. 2 H); 5.51 (*ddd*, *J* = 9.5, 3.5, 3.0, H–C(2)); 5.46, 5.34, 4.90, 4.88 (4*s*, olef. H); 3.59 (*d*, *J* = 3.5, H–C(1)); 3.29 (*t*, *J* = 3.0, H–C(4)); 2.65 (*ddd*, *J* = 14.0, 9.5, 3.0, 1 H), 2.04 (*dt*, *J* = 14.0, 3.0, 1 H, CH_2(3)); 1.91, 1.88, 0.32, 0.28 (4*d*, *J* = 2.5). MS (70 eV): 418 (1, $M^{+\cdot}$), 390 (9), 362 (56), 334 (100), 229 (6), 212 (26), 156 (18), 141 (15), 128 (11), 115 (13), 105 (60), 77 (57), 56 (55). Anal. calc. for $C_{22}H_{18}FeO_5$ (418.236): C 63.18, H 4.34; found: C 63.37, H 4.18.

*Mixture of Tricarbonyl[(1*RS,*8*RS,*9*RS,*10*SR,*11*RS*)*-C,9,10,C-η-(methyl 11-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate)]iron* (**19**) *and Tricarbonyl[(1*RS,*8*RS,*9*SR,*10*RS,*12*RS*)*-C,9,10,C-η-(methyl 12-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate)]iron* (**18**). A mixture of **11** (24.5 mg, 0.078 mmol), anh. C_6H_6 (0.5 ml), and methyl 2-propynoate (**15**; 66 µl, 66.4 mg) was heated to 80° for 2 h in a *Pyrex* tube sealed under vacuum. After solvent evaporation, an oily mixture was obtained whose ^{1}H-NMR (360 MHz, $CDCl_3$) showed a mixture of **18**/**19** and **20**/**21**.

*Mixture of Tricarbonyl[(1*RS,*8*RS,*9*RS,*10*SR,*11*RS*)*-C,9,10,C-η-(methyl 11-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene-4-carboxylate)]iron* (**21**) *and Tricarbonyl[(1*RS,*8*RS,*9*SR,*10*RS,*12*RS*)*-C,9,10,C-η-(methyl 12-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene-4-carboxylate)]iron* (**20**). A mixture of **18**/**19**/**20**/**21** (see above; 30 mg), anh. C_6H_6 (2 ml), DDQ (21 mg), and propene oxide (50 µl) was heated to 80° for 1 h under Ar. After cooling to 20°, CH_2Cl_2 (20 ml) was added, the soln. washed with aq. sat. $NaHCO_3$ soln. (15 ml, 3 times) and H_2O (15 ml), dried ($MgSO_4$), and evaporated, and the residue filtered through a short column of silica gel (CH_2Cl_2), yielding 29 mg (97%) of a 37:63 mixture **20**/**21** which was crystallized from CH_2Cl_2/hexane at −25°. M.p. 91–93°.

Data of **21**. IR ($CHCl_3$): 3620, 3040, 3000, 2960, 2050, 1975, 1720, 1440, 1320, 1300, 1280, 1170, 1120, 1100, 1050. ^{1}H-NMR (360 MHz, C_6D_6): 8.07 (*d*, *J* = 1.5, H–C(3)); 8.05 (*dd*, *J* = 7.5, 1.5, H–C(5)); 6.89 (*d*, *J* = 7.5, H–C(6)); 4.06 (*m*, H–C(11)); 3.45 (*s*, $COOCH_3$); 3.43 (*d*, *J* = 3.0, H–C(1)); 3.16 (*t*, *J* = 2.5, H–C(8)); 2.05 (*ddd*, *J* = 13.0, 8.5, 2.5, H–C(12) *'anti'* to OH); 1.64, 1.58 (2*d*, *J* = 2.5, *H*–CH=C(9) and *H*–CH=C(10) *trans* to C(10) and C(9), resp.); 1.28 (br. *s*, OH); 1.17 (*dt*, *J* = 13.0, 2.5, H–C(12) *'syn'* to OH); 0.04, 0.03 (2*d*, *J* = 2.5).

Data of **20**. ^{1}H-NMR (360 MHz, C_6D_6): 8.03 (*dd*, *J* = 7.5, 1.5, H–C(5)); 7.97 (*d*, *J* = 1.5, H–C(3)); 7.03 (*d*, *J* = 7.5, H–C(6)); 4.06 (*m*, H–C(12)); 3.47 (*s*, $COOCH_3$); 3.42 (*d*, *J* = 3.0, H–C(8)); 3.19 (*t*, *J* = 2.5, H–C(1)); 2.04 (*ddd*, *J* = 13.0, 8.5, 2.5, H–C(11) *'anti'* to OH); 1.62, 1.59 (2*d*, *J* = 2.5); 1.28 (br. *s*, OH); 1.16 (*dt*, *J* = 13.0, 2.5, H–C(11) *'syn'* to OH); 0.05, 0.01 (2*d*, *J* = 2.5.). MS (70 eV): 396 (2, $M^{+\cdot}$), 368 (16), 340 (56), 312 (100), 254 (29) 236 (39), 225 (8), 212 (43), 208 (52), 181 (40), 165 (35), 152 (59), 139 (8), 127 (15), 115 (12), 91 (4), 84 (20), 76 (7), 56 (39). Anal. calc. for $C_{19}H_{16}FeO_6$ (396.187): C 57.60, H 4.07; found: C 57.43, H 4.03.

*Mixture of Tricarbonyl[(1*RS,*8*RS,*9*SR,*10*RS,*12*RS*)*-C,9,10,C-η-(12-hydroxy-9,10-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2(7),4-dien-4-yl methyl ketone)]iron* (**22**) *and Tricarbonyl[(1*RS,*8*RS,*9*RS,*10*SR,*11*RS*)*-C,9,10,C-η-(11-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-dien-4-yl methyl ketone)]iron* (**23**). A mixture of **11** (22 mg, 0.07 mmol), C_6H_6 (0.5 ml), and 3-butyn-2-one (**16**; 47.7 mg, 55 µl) was heated to 80° for 75 min in a *Pyrex* tube degassed and sealed under vacuum. After solvent evaporation, one obtains 26 mg (97%) of a 32:68 mixture **22**/**23** contaminated with *ca.* 25% of **24**/**25**.

Mixture of Tricarbonyl[(1RS,8RS,9SR,10RS,12RS)-C,9,10,C-η-(12-hydroxy-9,10-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6-trien-4-yl methyl ketone)]iron (**24**) *and Tricarbonyl[(1RS,8RS,9RS,10SR,11RS)-C,9,10,C-η-(11-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-4-yl methyl ketone)]iron* (**25**). A mixture of **22**/**23**/**24**/**25** (see above; 37 mg, 0.097 mmol), C_6H_6 (1.5 ml), DDQ (41 mg), and propene oxide (3 drops) was heated to 80° for 90 min under Ar. After cooling to 20°, CH_2Cl_2 (50 ml) was added. The soln. was washed with sat. aq. $NaHCO_3$ soln. (30 ml, 3 times) and H_2O (30 ml), dried ($MgSO_4$), and evaporated and the residue filtered through a column of silica gel (10 g, AcOEt/hexane 1:1), yielding 28 mg (76%) of a 31:69 mixture **24**/**25**, which was crystallized from CH_2Cl_2/hexane at −25°. M.p. 141–142°. UV (95% EtOH): 206 (42000), 251 (16500). IR ($CHCl_3$): 3620, 3020, 2970, 2050, 1980, 1680, 1615, 1430, 1360, 1270, 1050. ^{1}H-NMR (360 MHz, C_6D_6) of **24**: 7.75 (*d*, *J* = 1.5, H–C(3)); 7.61 (*dd*, *J* = 7.5, 1.5, H–C(5)); 7.01 (*d*, *J* = 7.5, H–C(6)); 4.06 (*m*, H–C(12)); 3.42 (*d*, *J* = 3.0, H–C(8)); 3.16 (*t*, *J* = 3.0, H–C(1)); 2.12 (*s*, CH_3CO); 2.04 (*ddd*, *J* = 13.5, 9.0, 3.0, H–C(1) *'anti'* to OH); 1.62, 1.61 (2*d*, *J* = 2.5); 1.16 (*ddd*, *J* = 13.5, 3.0, 3.0, H–C(11) *'syn'* to OH); 1.1 (br. *s*, OH); 0.06, 0.02 (2*d*, *J* = 2.5). ^{1}H-NMR (360 MHz, C_6D_6) of **25**: 7.85 (*d*, *J* = 1.5, H–C(3)); 7.65 (*dd*, *J* = 7.5, 1.5, H–C(5)); 6.88 (*d*, *J* = 7.5, H–C(6)); 4.06 (*m*, H–C(11)); 3.40 (*d*, *J* = 3.0, H–C(1)); 3.17 (*t*, *J* = 3.0, H–C(8)); 2.10 (*s*, CH_3CO); 2.06 (*ddd*, *J* = 13.5, 9.0, 3.0, H–C(12) *'anti'* to OH); 1.66, 1.59 (2*d*, *J* = 2.5); 1.18 (*ddd*, *J* = 13.5, 3.0, 3.0, H–C(12) *'syn'* to OH); 1.1 (br. *s*, OH); 0.05, 0.04 (2*d*, *J* = 2.5). MS (70 eV): 380 (2, $M^{+\cdot}$), 352 (10), 324 (57), 296 (100), 278 (24), 263 (6), 252 (18), 207 (6), 196 (17), 181 (21), 165 (12), 152 (27), 142 (10), 127 (13), 115 (11), 105 (4), 91 (6). Anal. calc. for $C_{19}H_{16}FeO_5$ (380.187): C 60.03, H 4.24; found: C 60.12, H 4.28.

Mixture of Tricarbonyl[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-methoxycarbonyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-dien-9-yl p-*toluenesulfonate)]iron* (**26**) *and Tricarbonyl-[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(5-methoxycarbonyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-dien-9-yl* p-*toluenesulfonate)]iron* (**27**). A mixture of **12** (23 mg, 0.049 mmol), C_6H_6 (0.5 ml), and **15** (41.3 mg, 41.5 µl) was heated to 80° for 7 h in a *Pyrex* tube degassed and sealed under vacuum. After solvent evaporation, 25 mg (90%) of a 89:11 mixture **26**/**27** was obtained, contaminated by **28**/**29**. ^{1}H-NMR (360 MHz, $CDCl_3$) of **26**: 7.8 (*d*, *J* = 8.0, 2 H); 7.37 (*d*, *J* = 8.0, 2 H); 6.97 (br. *s*, H–C(5)); 5.11 (*ddd*, *J* = 8.0, 5.0, 3.0, H–C(9)); 3.75 (*s*, CH_3OOC); 3.5 (*d*, *J* = 3.0, H–C(8)); 3.01 (*t*, *J* = 2.5, H–C(1)); 2.98 (*m*, CH_2(3), CH_2(6)); 2.47 (*s*, CH_3); 2.26 (*ddd*, *J* = 13.5, 8.0, 2.5, H–C(10) *'anti'* to TsO); 1.98, 1.95 (2*d*, *J* = 2.5, 2 H); 1.68 (*ddd*, *J* = 13.5, 5.0, 2.5, H–C(10) *'syn'* to TsO); 0.38, 0.34 (2*d*, *J* = 2.5, 2 H). ^{1}H-NMR (360 MHz, $CDCl_3$) of **27**: 7.8, 7.37 (2*d*, *J* = 8.0, 4 H); 6.97 (br. *s*, H–C(4)); 5.11 (*ddd*, *J* = 8.0, 5.0, 3.0, H–C(9)); 3.75 (*s*, $COOCH_3$); 3.45 (*d*, *J* = 3.0, H–C(8)); 3.01 (*t*, *J* = 2.5, H–C(1)); 2.98 (*m*, CH_2(3), CH_2(6)); 2.47 (*s*, CH_3); 2.28 (*ddd*, *J* = 13.5, 8.0, 2.5, H–C(10) *'anti'* to TsO); 1.97, 1.93 (2*d*, *J* = 2.5, 2 H); 1.73 (*ddd*, *J* = 13.5, 5.0, 2.5, H–C(10) *'syn'* to TsO); 0.38, 0.34 (2*d*, *J* = 2.5, 2 H).

Tricarbonyl[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-methoxycarbonyl-11,12-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-yl p-*toluenesulfonate)]iron* (**28**). A mixture of **26**/**27** (25 mg, 0.05 mmol), anh. C_6H_6 (1 ml), DDQ (14.5 mg), and propene oxide (3 drops) was heated to 80° for 45 min under Ar. After cooling to 20°, CH_2Cl_2 (20 ml) was added. The soln. was washed with sat. aq. $NaHCO_3$ soln. (15 ml, 3 times) and H_2O (15 ml), dried ($MgSO_4$), and evaporated and the residue filtered through a short column of silica gel (CH_2Cl_2), yielding 20 mg (80%) of a 89:11 mixture **28**/**29**. Crystallization from CH_2Cl_2/hexane at −25° gave 17 mg (68%) of pure **28**, yellow crystals. M.p. 70–71°. UV (95% EtOH): 204 (57300), 225 (38300), 274 (4600). IR (KBr): 3060, 2960, 2050, 1970, 1720, 1440, 1365, 1295, 1275, 1190, 1180, 1100, 945. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.92 (*dd*, *J* = 7.5, 1.5, H–C(5)); 7.82 (*d*, *J* = 1.5, H–C(3)); 7.74 (*dt*, *J* = 8.0, 1.5, 2 H); 7.35 (br. *d*, *J* = 8.0, 2 H, TsO); 7.18 (*d*, *J* = 7.5, H–C(6)); 5.32 (*ddd*, *J* = 8.5, 3.0, 2.5, H–C(9)); 4.18 (*d*, *J* = 3.0, H–C(8)); 3.90 (*s*, CH_3OOC); 3.85 (*t*, *J* = 2.5, H–C(1)); 2.56 (*ddd*, *J* = 14.0, 8.5, 2.5, H–C(10) *'anti'* to TsO); 2.47 (*s*, CH_3); 1.98, 1.97 (2*d*, *J* = 2.5, 2 H); 1.76 (*dt*, *J* = 14.0, 2.5, H–C(10) *'syn'* to TsO); 0.39, 0.33 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 522 (4, $M^{+\cdot}$ − 28), 494 (6), 466 (54), 252 (13), 238 (13), 208 (100), 179 (48), 165 (36), 152 (24), 127 (23), 115 (5), 91 (18), 58 (28). Anal. calc. for $C_{26}H_{22}FeO_8S$ (550.378): C 56.74, H 4.03; found: C 56.81, H 4.07.

The mother liquor of the crystallization of **28** contained a mixture **28**/**29**. ^{1}H-NMR of **29**: 3.91 (*s*, CH_3COO); 2.48 (*s*, CH_3); the other signals were not distinguishable from those of **28**.

Mixture of Tricarbonyl[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-methoxycarbonyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-dien-9-yl benzoate)]iron (**30**) *and Tricarbonyl-[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(5-methoxycarbonyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-dien-9-yl benzoate)]iron* (**31**). A mixture of **13** (19 mg, 0.045 mmol), anh. C_6H_6 (0.5 ml), and **15** (40.2 mg, 40 µl) was degassed *in vacuo* and heated to 80° for 12 h in a *Pyrex* tube sealed *in vacuo*. After solvent evaporation, a 95:5 mixture **30**/**31** was obtained (21 mg, 92%), contaminated with **32**/**33**.

Tricarbonyl[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-methoxycarbonyl-11,12-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-yl benzoate)]iron (**32**). To a soln. of crude **30**/**31**/**32**/**33** (see above; 21 mg, 0.042 mmol) in anh. C_6H_6 (1 ml), DDQ (13 mg) and propene oxide (50 µl) were added. The mixture was heated to 80° for

90 min under Ar. After cooling to 20°, CH_2Cl_2 (20 ml) was added, the soln. washed with sat. aq. $NaHCO_3$ soln. (15 ml, 3 times) and H_2O (15 ml), dried ($MgSO_4$), and evaporated, and the residue filtered through silica gel (CH_2Cl_2), yielding 18 mg (86%) of a 94:6 mixture **32**/**33**. Crystallization from EtOH at −15° afforded 16 mg (76%) of pure **32**, yellow crystals. M.p. 144–145°. UV (95% EtOH): 228 (sh, 40500), 281 (12500). IR (KBr): 3070, 3000, 2950, 2050, 1985, 1960, 1720, 1440, 1320, 1270, 1215, 1030, 720. ^{1}H-NMR (360 MHz, C_6D_6): 8.01 (*dd*, *J* = 7.5, 1.5, H–C(5)); 7.98 (*d*, *J* = 1.5, H–C(3)); 7.85 (*dt*, *J* = 7.0, 1.5, 2 H, Bz); 7.03 (*tt*, *J* = 7.0, 1.5, 1 H, Bz); 6.94 (*tt*, *J* = 7.0, 1.5, 2 H, Bz); 6.90 (*d*, *J* = 7.5, H–C(6)); 5.54 (*ddd*, *J* = 8.5, 3.0, 2.5, H–C(9)); 3.82 (*d*, *J* = 3.0, H–C(8)); 3.46 (*s*, CH_3OOC); 3.23 (*t*, *J* = 2.5, H–C(1)); 2.24 (*ddd*, *J* = 13.0, 8.5, 2.5, H–C(10) *'anti'* to BzO); 1.67, 1.62 (2*d*, *J* = 2.5, 2 H); 1.46 (*dt*, *J* = 13.0, 2.5, H–C(10) *'syn'* to BzO); 0.09, 0.06 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 416 (15, $M^{+\cdot} - 3 \times 28$), 212 (25), 208 (32), 179 (31), 165 (31), 152 (34), 127 (20), 105 (100), 77 (56), 51 (31). Anal. calc. for $C_{26}H_{20}FeO_7$ (500.296): C 62.42, H 4.03; found: C 62.49, H 4.00.

^{1}H-NMR (360 MHz, C_6D_6) of **33** (crude reaction mixture): 5.41 (*m*, H–C(9)); 3.68 (*d*, *J* = 3.0, H–C(8)); 3.41 (*s*, $COOCH_3$); 3.13 (*t*, *J* = 2.5, H–C(1)); the other signals were not distinguishable from those of **32**.

Mixture of [(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-Acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]-dodeca-1(7),4-dien-9-yl benzoate)]tricarbonyliron (**34**) *and [(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(5-Acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-dien-9-yl benzoate)]tricarbonyliron* (**35**). A mixture of **13** (31 mg, 0.074 mmol), C_6H_6 (0.5 ml), and **16** (50.5 mg, 58 µl) was degassed *in vacuo* and heated to 80° for 8 h in a *Pyrex* tube sealed *in vacuo*. After solvent evaporation, 34 mg (94%) of a 92:8 mixture **34**/**35** was obtained, contaminated by *ca.* 20% of **36**/**37**. ^{1}H-NMR (360 MHz, C_6H_6) of **34**: 8.08 (*dt*, *J* = 7.0, 1.5, 2 H); 7.08 (*m*, 3 H, Bz); 6.21 (*m*, H–C(5)); 5.42 (*ddd*, *J* = 8.0, 3.0, 2.5, H–C(9)); 3.21 (*d*, *J* = 3.0, H–C(8)); 3.12 (*m*, CH_2(3)); 2.80 (*m*, CH_2(6)); 2.47 (*t*, *J* = 2.5, H–C(1)); 2.02 (*ddd*, *J* = 13.5, 8.0, 2.5, H–C(10) *'anti'* to BzO); 1.82 (*s*, CH_3CO); 1.73, 1.63 (2*d*, *J* = 2.5, 2 H); 1.40 (*ddd*, *J* = 13.5, 2.5, 2.5, H–C(10) *'syn'* to BzO); 0.13, 0.12 (2*d*, *J* = 2.5, 2 H). ^{1}H-NMR of **35** (crude reaction mixture): 1.84 (*s*, CH_3CO). MS (70 eV): 458 (7, $M^{+\cdot} - 28$), 430 (1), 402 (73), 280 (28), 252 (7), 222 (13), 207 (12), 198 (16), 179 (32), 165 (17), 155 (35), 141 (10), 122 (42), 105 (100).

[(1RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-Acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-yl benzoate)]tricarbonyliron (**36**). A 92:8 mixture **34**/**35** (34 mg, 0.07 mmol), anh. C_6H_6 (1 ml), DDQ (29 mg), and propene oxide (3 drops) was heated to 80° for 3 h under Ar. After cooling to 20°, CH_2Cl_2 (50 ml) was added, the soln. washed with sat. aq. $NaHCO_3$ soln. (30 ml, 3 times) and H_2O (30 ml), dried ($MgSO_4$), and evaporated, and the residue chromatographed on a column of silica gel (10 g, CH_2Cl_2), yielding 29 mg (85%) of 92:8 mixture **36**/**37**. Crystallization from EtOH at −25° gave 26 mg (76%) of pure **36**, yellow crystals. M.p. 131.5–132. UV (95% EtOH): 230 (36200), 259 (25000), 283 (20000). IR (KBr): 3060, 2990, 2970, 2940, 2050, 1970, 1955, 1715, 1680, 1450, 1360, 1315, 1280, 1265, 1120, 715. ^{1}H-NMR (360 MHz, C_6H_6): 7.90 (*dt*, *J* = 7.0, 1.5, 2 H, Bz); 7.76 (*d*, *J* = 1.5, H–C(3)); 7.61 (*dd*, *J* = 8.0, 1.5, H–C(5)); 7.03 (*tt*, *J* = 7.0, 1.5, 1 H, Bz); 6.94 (*tt*, *J* = 7.0, 1.5, 2 H, Bz); 6.88 (*d*, *J* = 8.0, H–C(6)); 5.54 (*ddd*, *J* = 9.0, 3.0, 3.0, H–C(9)); 3.82 (*d*, *J* = 3.0, H–C(8)); 3.16 (*t*, *J* = 2.8, H–C(1)); 2.24 (*ddd*, *J* = 13.5, 9.0, 2.8, H–C(10)); 2.08 (*s*, CH_3CO); 1.68, 1.63 (2*d*, *J* = 2.5, 2 H); 1.47 (*ddd*, *J* = 13.5, 3.0, 2.8, H–C(10)); 0.10, 0.07 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 456 (2, $M^{+\cdot} - 28$), 428 (5), 400 (47), 278 (19), 222 (11), 207 (10), 196 (16), 179 (26), 165 (9), 152 (17), 141 (7), 122 (24), 115 (4), 105 (100). Anal. calc. for $C_{26}H_{20}FeO_6$ (484.296): C 64.48, H 4.16; found: C 64.47, H 4.33.

^{1}H-NMR of **37** (crude mixture **36**/**37**): 2.06 (*s*, CH_3CO); 3.73 (*d*, H–C(8)).

Mixture of Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4,9,10-hexahydro-8-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-ol)]iron (**38**) *and Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4,9,10-hexahydro-5-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-ol)]iron* (**39**). A soln. of 3-methoxyanthranilic acid (147 mg, 0.7 mmol) in anh. dioxane (0.25 ml) was added simultaneously with a soln. of isopentyl nitrite (120 µl, 0.7 mmol) in anh. dioxane (0.25 ml) to a stirred soln. of **11** (45 mg, 0.14 mmol) in anh. dioxane (0.25 ml) at 70°. After heating to 70° for 2 h, the mixture was cooled to 20°, 5% aq. NaOH soln. (30 ml) was added, the mixture extracted with CH_2Cl_2 (50 ml, 3 times), the org. phase dried ($MgSO_4$) and evaporated, and the residue filtered through a column of silica gel (5 g, AcOEt/hexane 1:3) yielding 43 mg (71%) of a 28:72 mixture **38**/**39** that crystallized from CH_2Cl_2/hexane at −25°. M.p. 54–56°. UV (95% EtOH): 221 (sh, 30000), 278 (6800). IR (KBr): 3440, 3050, 3000, 2950, 2860, 2840, 2050, 1960, 1580. ^{1}H-NMR (360 MHz, C_6D_6) of **38**: 7.04 (*t*, *J* = 8.0, H–C(6)); 6.74 (*d*, *J* = 8.0, H–C(5)); 6.40 (*d*, *J* = 8.0, H–C(7)); 4.01 (*m*, H–C(11)); 2.93 (*d*, *J* = 3.0, H–C(4)); 2.68 (*t*, *J* = 2.5, H–C(1)); 3.7 (*m*, CH_2(9), CH_2(10)); 3.34 (*s*, CH_3O); 1.90 (*ddd*, *J* = 13.0, 8.0, 2.5, 2.5, H–C(12)); 1.71, 1.62 (2*d*, *J* = 2.5, 2 H); 1.14 (*ddd*, *J* = 13.0, 2.5, 2.5, H–C(2)); 1.08 (*d*, *J* = 6.0, OH); 0.11, 0.09 (2*d*, *J* = 2.5, 2 H). ^{1}H-NMR (360 MHz, C_6D_6) of **39**: 7.06 (*t*, *J* = 8.0, H–C(7)); 6.76 (*d*, *J* = 8.0, H–C(8)); 6.40 (*d*, *J* = 8.0, H–C(6)); 4.01 (*m*, H–C(11)); 2.97 (*d*, *J* = 3.0, H–C(4)); 2.60 (*t*, *J* = 2.5, H–C(1)); 3.7 (*m*, CH_2(9), CH_2(10)); 3.32 (*s*, CH_3O); 1.92 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(12) *'anti'* to OH); 1.68, 1.64 (2*d*, *J* = 2.5, 2 H); 1.14 (*ddd*, *J* = 13.0, 2.5, 2.5,

H–C(12) *'syn'* to OH); 1.07 (*d*, *J* = 6.0, OH); 0.11, 0.09 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 392 (14, $M^{+\cdot} - 28$), 364 (27), 336 (100).

Mixture of Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4-tetrahydro-8-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-ol)]iron (**40**) *and Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4-tetrahydro-5-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-ol)]iron* (**41**). A mixture of **38**/**29** (see above; 24 mg, 0.057 mmol), anh. C_6H_6 (1 ml), DDQ (23 mg), and propene oxide (3 drops) was heated to 80° for 150 min under Ar. After cooling to 20°, CH_2Cl_2 (70 ml) was added. The soln. was washed with sat. aq. $NaHCO_3$ soln. (30 ml, 4 times) and H_2O (30 ml, twice), dried ($MgSO_4$), and evaporated, and the residue chromatographed on a column of silica gel (5 g, AcOEt/hexane 1:3), yielding 18 mg (75%) of a 28:72 mixture **40**/**41**. IR ($CHCl_3$): 3620, 3570, 3060, 3020, 2960, 2950, 2850, 2050, 1975, 1610, 1580. ^{1}H-NMR (360 MHz, C_6D_6) of **40**: 8.23 (*s*, H–C(9)); 7.48 (*s*, H–C(10)); 7.39 (*d*, *J* = 8.0, H–C(5)); 7.20 (*t*, *J* = 8.0, H–C(6)); 6.44 (*dd*, *J* = 8.0, 0.7, H–C(7)); 4.16 (*m*, H–C(11)); 3.56 (*d*, *J* = 3.0, H–C(4)); 3.45 (*s*, CH_3O); 3.38 (*t*, *J* = 3.0, H–C(1)); 2.16 (*ddd*, *J* = 13.5, 9.0, 3.0, H–C(12)); 1.66, 1.61 (2*d*, *J* = 2.5, 2 H); 1.25 (*ddd*, *J* = 13.5, 3.0, 3.0, H–C(12) *'syn'* to OH); 0.74 (br. *d*, *J* = 8.0, OH); 0.05, 0.03 (2*d*, *J* = 2.5, 2 H). ^{1}H-NMR (360 MHz, C_6H_6) of **41**: 8.34 (*s*, H–C(10)); 7.40 (*d*, *J* = 8.0, H–C(8)); 7.36 (*s*, H–C(9)); 7.22 (*t*, *J* = 8.0, H–C(7)); 6.43 (*dd*, *J* = 8.0, 0.7, H–C(6)); 4.16 (*m*, H–C(11)); 3.58 (*d*, *J* = 3.0, H–C(4)); 3.44 (*s*, CH_3O); 3.33 (*t*, *J* = 3.0, H–C(1)); 2.17 (*ddd*, *J* = 13.5, 9.0, 3.0, H–C(12) *'anti'* to OH); 1.64, 1.63 (2*d*, *J* = 2.5, 2 H); 1.26 (*ddd*, *J* = 13.5, 3.0, 3.0, H–C(12) *'syn'* to OH); 0.77 (br. *d*, *J* = 8.0, OH); 0.06, 0.02 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 390 (14, $M^{+\cdot} - 28$), 362 (35), 334 (100).

Mixture of Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4,9,10-hexahydro-8-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-yl benzoate)]iron (**42**) *and Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4,9,10-hexahydro-5-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-yl benzoate)]iron* (**43**). Same procedure as for the preparation of **38**/**39** using 61 mg (0.14 mmol) of **13** in 0.5 ml of anh. dioxane: 60 mg (76%) of yellow oil containing a 29:71 mixture **42**/**43** contaminated with **44**/**45**. ^{1}H-NMR (360 MHz, C_6D_6) of **42**: 8.03 (*m*, 2 H); 7.04 (*t*, *J* = 7.5, H–C(6)); 6.99 (*tt*, *J* = 8.0, 1.5, 1 H); 6.92 (*td*, *J* = 8.0, 1.5, 2 H); 6.71 (br. *d*, *J* = 7.5, H–C(5)); 6.38 (*d*, *J* = 7.5, H–C(7)); 5.53 (*ddd*, *J* = 8.0, 2.5, 2.5, H–C(11)); 3.3–3.9 (*m*, CH_2(9), CH_2(10)); 3.31 (*s*, CH_3O); 3.29 (*d*, *J* = 2.5, H–C(4)); 2.71 (*t*, *J* = 2.5, H–C(1)); 2.13 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(12)); 1.76, 1.64 (2*d*, *J* = 2.5, 2 H); 1.52 (*ddd*, *J* = 13.0, 2.5, 2.5, H–C(12)); 0.15, 0.14 (2*d*, *J* = 2.5, 2 H). ^{1}H-NMR (360 MHz, C_6D_6) of **43**: 8.03 (*m*, 2 H); 7.04 (*t*, *J* = 7.5, H–C(7)); 6.99 (*tt*, *J* = 8.0, 1.5, 1 H, Bz); 6.87 (*td*, *J* = 8.0, 1.5, 2 H, Bz); 6.75 (br. *d*, *J* = 7.5, H–C(8)); 6.38 (*d*, *J* = 7.5, H–C(6)); 5.50 (*ddd*, *J* = 8.0, 2.5, 2.5, H–C(11)); 3.3–3.9 (*m*, CH_2(9), CH_2(10)); 3.31 (*d*, *J* = 2.5, H–C(4)); 3.26 (*s*, CH_3O); 2.63 (*t*, *J* = 2.5, H–C(1)); 2.18 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(12) *'anti'* to BzO); 1.72, 1.67 (2*d*, *J* = 2.5, 2 H); 1.52 (*ddd*, *J* = 13.0, 2.5, 2.5, H–C(12)) *'syn'* to BzO); 0.16, 0.13 (2*d*, *J* = 2.5, 2 H).

Mixture of Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4-tetrahydro-8-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-yl benzoate)]iron (**44**) *and Tricarbonyl[(1RS,2RS,3SR,4RS,11RS)-C,2,3,C-η-(1,2,3,4-tetrahydro-5-methoxy-2,3-dimethylidene-1,4-ethanoanthracen-11-yl benzoate)]iron* (**45**). Same procedure as for the preparation of **40**/**41**, using 27 mg (0.052 mmol) of **42**/**43** (see above): 19 mg (70%) of 29:71 mixture **44**/**45**, yellow oil. IR ($CHCl_3$). 3060, 3020, 2960, 2940, 2850, 2050, 1975, 1710, 1610. ^{1}H-NMR (360 MHz, CD_2Cl_2) of **44**: 8.05 (*s*, H–C(9)); 7.74 (*dt*, *J* = 7.0, 1.5, 2 H, Bz); 7.62 (*s*, H–C(10)); 7.48 (*tt*, *J* = 7.0, 1.5, 1 H, Bz); 7.36 (*m*, 4 H, H–C(5), H–C(6), Bz); 6.84 (*dd*, *J* = 7.0, 1.0, H–C(7)); 5.74 (*ddd*, *J* = 9.0, 3.0, 3.0, H–C(11)); 4.33 (*d*, *J* = 3.0, H–C(4)); 4.07 (*t*, *J* = 3.0, H–C(1)); 3.99 (*s*, CH_3O); 2.87 (*ddd*, *J* = 13.5, 9.0, 3.0, H–C(12) *'anti'* to BzO); 2.12, 2.10 (2*d*, *J* = 2.5, 2 H); 1.92 (*ddd*, *J* = 13.5, 3.0, 3.0, H–C(12) *'syn'* to BzO); 0.51, 0.46 (2*d*, *J* = 2.5, 2 H). ^{1}H-NMR (360 MHz, CD_2Cl_2) of **45**: 8.07 (*s*, H–C(10)); 7.77 (*dt*, *J* = 7.0, 1.5, 2 H, Bz); 7.60 (*s*, H–C(9)); 7.49 (*tt*, *J* = 7.0, 1.5, 1 H, Bz); 7.36 (*m*, 4 H, H–C(7), H–C(8), Bz); 6.83 (*dd*, *J* = 7.0, 1.0, H–C(6)); 5.75 (*ddd*, *J* = 9.0, 3.0, 3.0, H–C(11)); 4.35 (*d*, *J* = 3.0, H–C(4)); 4.03 (*t*, *J* = 3.0, H–C(1)); 3.96 (*s*, CH_3O); 2.88 (*ddd*, *J* = 13.5, 9.0, 3.0, H–C(12) *'anti'* to BzO); 2.12, 2.10 (2*d*, *J* = 2.5, 2 H); 1.92 (*ddd*, *J* = 13.5, 3.0, 3.0, H–C(12) *'syn'* to BzO); 0.50, 0.46 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 494 (10, $M^{+\cdot} - 28$), 466 (43), 438 (100).

[(1RS,4RS,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-Acetoxy-4-cayno-11,12-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodec-2(7)-en-9-yl benzoate)]tricarbonyliron (**46**) *and [(1RS,4SR,8RS,9RS,11RS,12SR)-C,11,12,C-η-(4-Acetoxy-4-cyano-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-en-9-yl benzoate)]tricarbonyliron* (**47**). A mixture of **13** (55 mg, 0.132 mmol), C_6H_6 (0.3 ml), and 1-cyanovinyl acetate (1.5 ml, 1,6 g) was degassed *in vacuo* and heated, in a *Pyrex* tube sealed *in vacuo*, to 80° for 70 h. The mixture was filtered on a short column of silica gel (5 g, CH_2Cl_2). The yellow fraction was recovered, dried *in vacuo*, and separated by chromatography on silica gel (10 g, AcOEt/hexane 1:9). A 1st fraction (less polar) yielded 43 mg (63%) of **46** (arbitrary attribution) after crystallization from CH_2Cl_2/hexane at –25°. A 2nd fraction (more polar) yielded 12 mg (17%) of **47** after crystallization from CH_2Cl_2/hexane at –25°.

Data of **46**. Yellowish crystals. M.p. 161.5–162°. UV (95% EtOH): 226 (30800), 275 (4200), 283 (3900). IR (KBr): 3070, 2960, 2940, 2850, 2040, 1970, 1750, 1715, 1455, 1440, 1370, 1320, 1270, 1225, 1105, 1035, 720. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.08 (*dt*, *J* = 8.0, 1.5, 2 H); 7.57 (*tt*, *J* = 8.0, 1.5, 1 H); 7.45 (*tt*, *J* = 8.0, 1.5, 2 H, Bz); 5.62 (*ddd*, *J* = 8.0, 2.5, 2.5, H–C(9)); 3.60 (*d*, *J* = 2.5, H–C(8)); 3.20 (*ddd*, *J* = 17.5, 4.0, 1.5, H–C(3)); 3.16 (*t*, *J* = 2.5, H–C(1)); 2.75 (*dt*, *J* = 17.5, 3.0, H–C(3)); 2.54 (*ddd*, *J* = 13.5, 8.0, 2.5, H–C(10) *'anti'* to BzO); 2.44 (*m*, CH_2(5)); 2.33, 2.15 (2*m*, CH_2(6)); 2.11 (*s*, CH_3CO); 2.115, 2.04 (2*d*, *J* = 2.5, 2 H); 1.85 (*ddd*, *J* = 13.5, 2.5, 2.5, H–C(11) *'syn'* to BzO); 0.50, 0.48 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 473 (8, $M^{+\cdot}$ – 56), 445 (100), 385 (26). Anal. calc. for $C_{27}H_{23}FeNO_7$ (529.339): C 61.27, H 4.38; found: C 61.18, H 4.50.

Data of **47**. Yellowish crystals. M.p. 138–140°. IR (KBr): 3060, 2980, 2960, 2930, 2860, 2045, 1965, 1750, 1715, 1455, 1440, 1370, 1350, 1320, 1270, 1230, 1110, 1035. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.97 (*dt*, *J* = 8.0, 1.5, 2 H); 7.60 (*tt*, *J* = 8.0, 1.5, 1 H); 7.46 (*tt*, *J* = 8.0, 1.5, 2 H, Bz); 5.53 (*ddd*, *J* = 8.0, 2.5, 2.5, H–C(9)); 3.60 (*d*, *J* = 2.5, H–C(8)); 3.14 (*t*, *J* = 2.5, H–C(1)); 3.09 (*dt*, *J* = 17.5, 2.5, H–C(3)); 2.86 (*ddd*, *J* = 17.5, 3.5, 1.5, H–C(3)); 2.58 (*ddd*, *J* = 13.5, 8.0, 2.5, H–C(10) *'anti'* to BzO); 2.56, 2.38 (2*m*, CH_2(6)); 2.38, 2.24 (2*m*, CH_2(5)); 2.07, 2.00 (2*d*, *J* = 2.5, 2 H); 1.95 (*s*, CH_3CO); 1.70 (*ddd*, *J* = 13.5, 2.5, 2.5, H–C(10) *'syn'* to BzO); 0.46, 0.44 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 473 (7, $M^{+\cdot}$ – 56), 445 (70), 376 (41), 254 (23), 190 (34), 105 (100). Anal. calc. for $C_{27}H_{23}FeNO_7$ (529.339): C 61.27, H 4.38; found: C 61.31, H 4.26.

*[(1*RS,*4*RS,*8*RS,*9*RS,*11*RS,*12*SR*)- and (1*RS,*4*SR,*8*RS,*9*RS,*11*RS,*12*SR*)*-C,11,12,C-η-(4-Acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-en-9-yl benzoate)]tricarbonyliron* (**48** and **49**, resp. *and [(1*RS,*5*RS,*8*RS,*9*RS,*11*RS,*12*SR*)- and (1*RS,*5*SR,*8*RS,*9*RS,*11*RS,*12*SR*)*-C,11,12,C-η-(5-Acetyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-en-9-yl benzoate)]tricarbonyliron* (**50** and **51**, resp.). A mixture of **13** (24 mg, 0.057 mmol), anh. C_6H_6 (0.5 ml), and methyl vinyl ketone (MVK; 40 mg, 47 µl) was degassed *in vacuo* and heated to 60° for 18 h in a *Pyrex* tube sealed *in vacuo*. After solvent evaporation, the residue was separated by medium-pressure chromatography (*Lobar*, col. *A*, SiO_2, AcOEt/hexane 1:9) giving 3 fractions. The 1st fraction contained 3 mg (11%) of a 3:1 mixture **48**/**50**[3]), yellowish oil. Crystallization from CH_2Cl_2/hexane at –25° gave pure **48**. The 2nd fraction contained 12 mg (43%) of **51**[3]), crystallized from CH_2Cl_2/hexane at –25°. The 3rd fraction contained 6 mg (22%) of **49**, yellowish oil. ^{1}H-NMR of the crude reaction mixture: 13:24:5:58 ratio of **48**/**49**/**50**/**51**.

Data of **48**. Yellowish crystals. M.p. 122–123°. IR ($CHCl_3$): 3020, 2960, 2930, 2050, 1975, 1710, 1455, 1360, 1320, 1275. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.97 (*dt*, *J* = 7.0, 1.5, 2 H); 7.58 (*tt*, *J* = 7.0, 1.5, 1 H); 7.46 (*tt*, *J* = 7.0, 1.5, 2 H, Bz); 5.57 (*ddd*, *J* = 8.0, 3.0, 2.5, H–C(9)); 3.50 (*d*, *J* = 3.0, H–C(8)); 3.18 (*t*, *J* = 2.5, H–C(1)); 2.6, 2.5 (2*m*, 2 H), 2.3 (*m*, 3 H), 2.0 and 1.72 (2*m*, 2 H; CH_2(3), H–C(4), CH_2(5), CH_2(6)); 2.48 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(10) *'anti'* to BzO); 2.19 (*s*, CH_3CO); 2.09, 2.04 (2*d*, *J* = 2.5, 2 H); 1.81 (*dt*, *J* = 13.0, 2.5, H–C(10) *'syn'* to BzO); 0.48, 0.46 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 460 (1, $M^{+\cdot}$ – 28), 432 (36), 404 (76), 358 (11), 280 (38), 252 (49), 105 (100).

Data of **49**: Yellow oil. IR ($CHCl_3$): 3060, 2995, 2960, 2940, 2840, 2050, 1975, 1710, 1450, 1265. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.00 (*dt*, *J* = 7.0, 1.5, 2 H); 7.60 (*tt*, *J* = 7.0, 1.5, 1 H); 7.48 (*tt*, *J* = 7.0, 1.5, 2 H, Bz); 5.53 (*ddd*, *J* = 8.0, 3.0, 2.5, H–C(9)); 3.52 (*d*, *J* = 3.0, H–C(8)); 3.16 (*t*, *J* = 2.5, H–C(11)); 2.6 (*m*, 1 H); 2.3–2.4 (*m*, 3 H), 2.05 (*m*, 1 H), 1.6 (*m*, 2 H; CH_2(3), H–C(4), CH_2(5), CH_2(6)); 2.54 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(10) *'anti'* to BzO); 2.19 (*s*, CH_3CO); 2.06, 2.02 (2*d*, *J* = 2.5, 2 H); 1.75 (*dt*, *J* = 13.0, 2.5, H–C(10) *'syn'* to BzO); 0.46, 0.43 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 432 (4, $M^{+\cdot}$ – 56), 404 (99), 358 (23), 105 (100). Anal. calc. for $C_{26}H_{24}FeO_6$ (488.328): C 63.95, H 4.95; found: C 64.01, H 5.03.

Data of **51** (the relative configuration at C(5) is not established; we chose the major adduct to result from *anti-Alder, 'meta'* mode of attack, see *Fig. 3*). Yellow crystals. M.p. 103–104°. IR ($CHCl_3$): 3040, 2960, 2840, 2050, 1975, 1710, 1455, 1320, 1275. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.99 (*dt*, *J* = 7.0, 1.5, 2 H); 7.60 (*tt*, *J* = 7.0, 1.5, 1 H); 7.47 (*tt*, *J* = 7.0, 1.5, 2 H, Bz); 5.57 (*dd*, *J* = 8.0, 3.0, 2.5, H–C(9)); 3.52 (*d*, *J* = 3.0, H–C(8)); 3.18 (*t*, *J* = 2.5, H–C(1)); 2.6 (*m*, 1 H), 2.4–2.3 (*m*, 4 H), 2.05 (*m*, 1 H), 1.55 (*m*, 1 H; CH_2(3), CH_2(4), H–C(5), CH_2(6)); 2.50 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(10) *'anti'* to BzO); 2.11 (*s*, CH_3CO); 2.07, 2.01 (2*d*, *J* = 2.5, 2 H); 1.74 (*dt*, *J* = 13.0, 2.5, H–C(10) *'syn'* to BzO); 0.45, 0,43 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 432 (4, $M^{+\cdot}$ – 56), 404 (92), 358 (29), 141 (50), 129 (44), 122 (60), 105 (100).

Partial ^{1}H-NMR (360 MHz, $CDCl_3$) of **50**: 3.53 (*d*, *J* = 3.5, H–C(8)); 2.11 (*s*, CH_3CO); 2.07, 2.05 (2*d*, *J* = 2.5, 2 H); 0.45, 0.43 (2*d*, *J* = 2.5, 2 H).

Cycloaddition of **13** *to MVK Catalyzed by $BF_3 \cdot Et_2O$*. Freshly distilled $BF_3 \cdot Et_2O$ (75 µl, 85 mg, 0.6 mmol) was added to a stirred soln. of **13** (50 mg, 0.12 mmol) in anh. CH_2Cl_2 (2 ml) at –78° under Ar. After stirring at –78° for 15 min, MVK (49 µl, 41.9 mg, 0.6 mmol) was added and the mixture stirred at –78° for 150 min. The mixture was poured into a vigorously stirred mixture of sat. aq. $NaHCO_3$ soln. (100 ml) and Et_2O (200 ml). The org. phase was washed with sat. aq. $NaHCO_3$ soln. (60 ml, twice) and sat. aq. NaCl soln. (60 ml, twice), dried ($MgSO_4$), and

evaporated and the residue filtered through a short column of silica gel (5 g, CH_2Cl_2), yielding 54 mg (82%) of a 15:12:5:68 mixture of **48/49/50/51**[3]), by ^{1}H-NMR (360 MHz, C_6D_6).

Tricarbonyl[(1RS,4RS,8RS,9SR,10RS,12RS)-C,9,10,C-η-(12-hydroxy-9,10-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodec-2(7)-en-4-yl methyl ketone)]iron (**52**) *and Tricarbonyl[(1RS,4SR,8RS,9RS,10SR,11RS)-C,9,10,C-η-(11-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-en-4-yl methyl ketone)]iron* (**54**)[3]). A mixture of **11** (29 mg, 0.092 mmol), anh. C_6H_6 (0.5 ml), and MVK (76 µl, 65 mg) was degassed *in vacuo* and heated to 60° for 4 h in a *Pyrex* tube sealed *in vacuo*. After solvent evaporation, the residue was separated by medium-pressure chromatography (*Lobar*, col. *A*, SiO_2, AcOEt/hexane 3:7) yielding 2 yellowish fractions. The 1st gave 7 mg (20%) of **54** after crystallization from CH_2Cl_2/hexane at −25°. The 2nd, more polar fraction gave 24 mg (68%) of **52**, after crystallization from CH_2Cl_2/hexane at −25° (see below).

Data of **52**. Yellow crystals. M.p. 126.5–127°. UV (95% EtOH): 223 (sh, 23400), 288 (3000). IR (KBr): 3520, 2960, 2930, 2900, 2860, 2840, 2040, 1975, 1950, 1700, 1460, 1440, 1375, 1355, 1295, 1215, 1170, 1055. ^{1}H-NMR (360 MHz, C_6D_6): 4.12 (*m*, H–C(12)); 2.93 (*d*, *J* = 3.0, H–C(8)); 2.58 (*t*, *J* = 2.5, H–C(1)); 2.27 (*m*, H–C(4)); 2.17, 1.91 (2*m*, CH_2(6)); 2.11 (*m*, CH_2(3)); 1.98 (*ddd*, *J* = 13.0, 7.5, 2.5, H–C(11) *'anti'* to OH); 1.75, 1.66 (2*d*, *J* = 2.5, 2 H); 1.61 (*s*, CH_3CO); 1.61 (br. *s*, OH); 1.57, 1.53 (2*m*, CH_2(5)); 1.45 (*ddd*, *J* = 13.0, 3.0, 2.5, H–C(11) *'syn'* to OH); 0.14, 0.11 (2*d*, *J* = 2.5, 2 H). ^{13}C-NMR (90.6 MHz, C_6D_6): 211.7 ($Fe(CO)_3$); 210.5 (*C*O–C(4)); 136.6, 135.4 (C(2), C(7)); 111.4, 107.1 (C(9), C(10)); 71.8 (C(12)); 51.7 (C(4)); 45.9 (C(1)); 43.2 (C(8)); 40.3, 39.1 (*C*=C(9), *C*=C(10)); 38.1 (C(11)); 27.9 (C(3)); 27.6 (*C*H_3CO); 27.3 (C(6)); 24.8 (C(5)). MS (70 eV): 356 (28, $M^{+\cdot}$ − 28), 328 (53), 300 (59), 280 (100), 252 (29), 238 (18), 219 (9), 200 (14), 183 (37), 165 (22), 155 (51), 141 (41), 128 (43), 115 (34), 91 (23). Anal. calc. for $C_{19}H_{29}FeO_5$ (384.219): C 59.40, H 5.25; found: C 59.49, H 5.24.

Data of **54** (the configuration at C(4) is chosen like that at C(4) in **52**; we assume an *Alder* mode of addition and the probable intervention of H-bridging in the transition state). Yellow crystals. M.p. 125–126°. IR ($CHCl_3$): 3450, 3010, 2960, 2880, 2840, 2050, 1970, 1700, 1455, 1440, 1415, 1170. ^{1}H-NMR (360 MHz, C_6D_6): 4.43 (*m*, H–C(11)); 3.26 (*d*, *J* = 3.0, H–C(1)); 2.56 (*t*, *J* = 2.5, H–C(8)); 2.29 (*m*, 3 H), 2.03 (*m*, 1 H), 1.63 (*m*, 3 H; CH_2(3), H–C(4), CH_2(5), CH_2(6)); 2.09 (*ddd*, *J* = 13.0, 8.0, 2.5, H–C(12) *'anti'* to OH); 1.90, 1.76 (2*d*, *J* = 2.5, 2 H); 1.66 (*s*, CH_3CO); 1.50 (br. *s*, OH); 1.38 (*ddd*, *J* = 13.0, 2.5, 2.5, H–C(12) *'syn'* to OH); 0.27, 0.26 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 384 (1, $M^{+\cdot}$), 356 (50), 328 (63), 300 (66), 280 (100). Anal. calc. for $C_{19}H_{20}FeO_5$ (384.219): C 59.40, H 5.25; found: C 59.49, H 5.24.

Cycloaddition of **11** *to MVK Catalyzed by $BF_3 \cdot Et_2O$.* As above for the analogous addition of **13**, with 42 mg (0.134 mmol) of **11** (90 min reaction with MVK). Filtration through a short column of silica gel (5 g, AcOEt/hexane 1:1) yielded 47 mg (91%) of pure **52** after crystallization from CH_2Cl_2/hexane at −25°. When first MVK was complexed with $BF_3 \cdot Et_2O$ at −78°, the reaction gave also pure **52** in 93% yield.

Benzoylation of **52** *to* **48**. A mixture of **52** (32 mg, 0.08 mmol), pyridine (1 ml), and benzoyl chloride (17.6 mg, 15 µl) was stirred at 0° for 2 h. After addition of CH_2Cl_2 (50 ml), the soln. was washed with H_2O (20 ml), 1N HCl (20 ml, 3 times), sat. aq. $NaHCO_3$ soln. (20 ml, twice), and H_2O (20 ml), dried ($MgSO_4$), and evaporated and the residue crystallized from CH_2Cl_2/hexane at −25°: 39 mg (96%) of pure **48** (see above).

Tricarbonyl[(1RS,4SR,8RS,9SR,10RS,12RS)-C,9,10,C-η-(12-hydroxy-9,10-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodec-2(7)-en-4-yl methyl ketone)]iron (**53**) *by Base-Catalyzed Isomerization of* **52**. A mixture of **52** (34 mg, 0.09 mmol), anh. MeOH (1.5 ml), and anh. K_2CO_3 (40 mg) was stirred at 20° for 2 h. CH_2Cl_2/H_2O 1:1 (40 ml) was added the aq. layer extracted with CH_2Cl_2 (30 ml, 3 times), the combined org. phase dried ($MgSO_4$) and evaporated and the residue chromatographed on a column of silica gel (10 g, AcOEt/hexane 1:1). The 1st fraction contained 16 mg (47%) of pure **52**. The 2nd fraction yielded 16 mg (47%) of pure **53**, yellow oil. ^{1}H-NMR (360 MHz, C_6D_6): 3.92 (*m*, H–C(12)); 2.71 (*d*, *J* = 3.0, H–C(8)); 2.47 (*t*, *J* = 2.5, H–C(1)); 2.40 (*m*, 1 H), 2.13 (*m*, 2 H), 1.96 (*m*, 2 H), 1.72 (*m*, 1 H), 1.37 (*m*, 1 H; CH_2(3), H–C(4), CH_2(5), CH_2(6)); 1.87 (*ddd*, *J* = 13.0, 7.5, 2.5, H–C(11) *'anti'* to OH); 1.71 (*s*, CH_3CO); 1.67, 1.64 (2*d*, *J* = 2.5, 2 H); 1.45 (*dt*, *J* = 13.0, 2.5, H–C(11) *'syn'* to OH); 1.34 (*s*, OH); 0.11, 0.09 (2*d*, *J* = 2.5, 2 H). ^{13}C-NMR (90.6 MHz, C_6D_6): 211.8 ($Fe(CO)_3$); 208.3 (*C*O–C(4)); 136.9, 135.2 (C(2), C(7)); 110.6, 107.1 (C(9), C(10)); 71.3 (C(12)); 51.8 (C(8)); 48.2 (C(4)); 42.9 (C(1)); 39.4, 39.1 (*C*=C(9), *C*=C(10)); 37.7 (C(11)); 29.5 (C(3)); 27.2 (*C*H_3CO); 25.5 (C(5)).

Benzoylation of **53** (same procedure as for the benzoylation of **52**, see above) gave **49**.

Tricarbonyl[(1RS,2RS,4RS,5SR,6RS)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-ol)]iron (**61**). A mixture of anh. CH_2Cl_2 (25 ml), **10** (492 mg, 1.084 mmol), *o*-chloranil (480 mg, 1.95 mmol), AcONa (120 mg), and SiO_2 (7.9 g) was stirred in a ultrasounds water bath at 20° for 5 h 30 min. The mixture was filtered, the precipitate washed with CH_2Cl_2 (200 ml), the CH_2Cl_2 soln. washed with sat. aq. $NaHCO_3$ soln. (100 ml, 3 times), dried ($MgSO_4$) and evaporated, and the residue filtered through a short column of silica gel (10 g, CH_2Cl_2). After solvent evaporation, the oily residue was separated by medium-pressure chromatography (*Lobar*, col. *A*, SiO_2, AcOMe/pentane 3:97). A 1st fraction gave 118 mg (67% based on recovered **10**) of **61**, after crystallization from

CH_2Cl_2/hexane at −25°. A 2nd fraction gave 237 mg of **10.61**: Yellow crystals. M.p. 121.5–122°. UV (95% EtOH): 202 (24500), 217 (23000), 254 (10100), 304 (2600). IR (KBr): 3280, 3080, 3060, 2980, 2950, 2930, 2860, 2040, 1980, 1960, 1920, 1055. ^{1}H-NMR (360 MHz, $CDCl_3$, [LIS by $Eu(thd)_3$]): 5.77 (*s*, [16.3], 1 H, *H*–CH=C(7) *cis* to C(8)); 5.53 (*s*, [12.3], 1 H, *H*–CH=C(8) *cis* to C(7)); 5.23 (*s*, [11.9], 1 H, *H*–CH=C(8) *trans* to C(7)); 5.12 (*s*, [22.9], 1 H, *H*–CH=C(7) *trans* to C(8)); 4.02 (*m*, [100], J = 9.5, 6.0, 3.0, 2.5, H–C(2)); 3.26 (*d*, J = 3.5, [57.7], H–C(1)); 3.20 (*t*, J = 3.0, [18.9], H–C(4)); 2.26 (*ddd*, J = 14.0, 9.5, 3.0, [31.9], H–C(3) *'anti'* to OH); 1.87 (*d*, J = 6.0, OH); 1.86 (*d*, J = 2.5, [9.6], 1 H, *H*–CH=C(5) *trans* to C(6)); 1.80 (*d*, J = 2.5, [12.8], 1 H, *H*–CH=C(6) *trans* to C(5)); 1.62 (*ddd*, J = 14.0, 3.0, 2.5, [60.6], H–C(3) *'syn'* to OH); 0.32 (*d*, J = 2.5, [9.9], 1 H, *H*–CH=C(5) *cis* to C(6)); 0.29 (*d*, J = 2.5, [10.8], 1 H, *H*–CH=C(6) *cis* to C(5)). MS (70 eV): 314 (8, $M^{+\cdot}$), 286 (55), 258 (48), 230 (98), 212 (32), 174 (6), 156 (33), 141 (18), 128 (24), 115 (30), 105 (12), 91 (18), 84 (25), 77 (18), 56 (100). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.25, H 4.53.

*Tricarbonyl[(1*RS,*2*RS,*4*RS,*5*SR,*6*RS*)*-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl benzoate)]iron* (**56**). Same procedure as for the benzoylation of **52** (see above), using **61** (37 mg, 0.118 mmol): 45 mg (91%), yellow crystals. M.p. 154.5–155°. UV (isooctane): 225 (33300), 252 (sh, 12500), 280 (2700), 312 (2200). UV (95% EtOH): 227 (32000), 253 (sh, 12200), 281 (2700), 310 (2300). IR (KBr): 3070, 2990, 2960, 2040, 1985, 1965, 1935, 1720, 1450, 1330, 1290, 1270, 1115, 1025, 900. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.06 (*m*, J = 7.5, 1.5, 2 H); 7.59 (*m*, J = 7.5, 1.5, 1.0, 1 H); 7.47 (*m*, J = 7.5, 1.5, 1.0, 2 H, Bz); 5.70, 5.58, 5.17, 5.16 (4*s*, 4 H); 5.21 (*ddd*, ^3J(H–C(2),H_{anti}–C(3)) = 10.0, ^3J(H–C(2),H–C(1)) = 3.5, ^3J(H–C(2),H_{syn}–C(3)) = 3.5, H–C(2)); 3.60 (*d*, J = 3.5, H–C(1)); 3.30 (*t*, J = 3.0, H–C(4)); 2.39 (*ddd*, J = 14.0, 10.0, 3.0, H–C(3) *'anti'* to BzO); 1.94 (*ddd*, J = 14.0, 3.5, 3.0, H–C(3) *syn* to BzO); 1.91 (*d*, J = 2.5, 1 H); 1.87 (*d*, J = 3.0, 1 H); 0.37 (*d*, J = 2.5, 1 H); 0.32 (*d*, J = 3.0, 1 H). MS (70 eV): 418 (1, $M^{+\cdot}$), 390 (6), 362 (29), 334 (100), 229 (7), 212 (57), 156 (17), 141 (16), 128 (12), 115 (14), 105 (44). Anal. calc. for $C_{22}H_{18}FeO_5$ (418.236): C 63.18, H 4.34; found: C 63.29, H 4.43.

*Mixture of Tricarbonyl[(1*RS,*8*RS,*9*RS,*11*SR,*12*RS*)*-C,11,12,C-η-(4-methoxycarbonyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-yl benzoate)]iron* (**59**) *and Tricarbonyl[(1*RS,*8*RS,*9*RS,*11*SR,*12*RS*)*-C,11,12,C-η-(5-methoxycarbonyl-11,12-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-yl benzoate)]iron* (**60**). A mixture of **56** (22 mg, 0.053 mmol), anh. benzene (0.5 ml), and **15** (44.2 mg, 44 µl, 0.53 mmol) was degassed *in vacuo* and heated to 80° for 10 h in a *Pyrex* tube sealed *in vacuo*. After solvent evaporation, 25 mg (94%) of **57**/**58** were obtained. C_6H_6 (1 ml), DDQ (14 mg), and propene oxide (50 µl) were added. The mixture was heated to 80° for 30 min under Ar. After cooling to 20°, CH_2Cl_2 (20 ml) was added, the soln. washed with sat. aq. $NaHCO_3$ soln. (15 ml, 3 times) and H_2O (15 ml), dried ($MgSO_4$), and evaporated and the residue filtered on silica gel (5 g, CH_2Cl_2), yielding 21 mg (85%) of a 68:32 mixture **59**/**60**. IR ($CHCl_3$): 3020, 2960, 2055, 1980, 1970, 1715, 1600. ^{1}H-NMR (360 MHz, C_6D_6) of **59**: 8.03 (*d*, J = 1.5, H–C(3)); 7.93 (*dd*, J = 7.5, 1.5, H–C(5)); 7.85 (*dt*, J = 7.0, 1.5, 2 H, Bz); 6.93 (*m*, 4 H, H–C(4), Bz); 5.58 (*ddd*, J = 8.0, 3.0, 2.5, H–C(9)); 3.88 (*d*, J = 3.0, H–C(8)); 3.50 (*s*, CH_3OOC); 3.08 (*t*, J = 2.5, H–C(1)); 2.28 (*ddd*, J = 13.0, 8.0, 2.5, H–C(10)); 1.54, 1.49 (2*d*, J = 2.5, 2 H); 1.38 (*ddd*, J = 13.0, 2.5, 2.5, H–C(10)); −0.13, −0.02 (2*d*, J = 2.5, 2 H). ^{1}H-NMR (360 MHz, C_6D_6) of **60**: 8.11 (*d*, J = 1.5, H–C(6)); 8.04 (*dd*, J = 7.5, 1.5, H–C(4)); 7.86 (*dt*, J = 7.0, 1.5, 2 H); 7.02 (*tt*, J = 7.0, 1.5, 1 H, Bz); 6.93 (*m*, 3 H, H–C(3), Bz); 5.58 (*ddd*, J = 8.0, 3.0, 2.5, H–C(9)); 3.83 (*d*, J = 3.0, H–C(8)); 3.43 (*s*, CH_3OOC); 3.05 (*t*, J = 2.5, H–C(1)); 2.33 (*ddd*, J = 13.0, 8.0, 2.5, H–C(10)); 1.51 (*d*, J = 2.5, 2 H); 1.38 (*ddd*, J = 13.0, 2.5, 2.5, H–C(10)); −0.14, −0.18 (2*d*, J = 2.5, 2 H). MS (70 eV): 416 (32, $M^{+\cdot} - 3 \times 28$), 238 (12), 212 (33), 208 (40), 179 (42), 165 (48), 105 (100).

Crystal Structure of **52**. A single crystal of **52** was obtained by slow recrystallization from CH_2Cl_2/hexane at 20°. Single crystal diffraction intensities were collected on a *Enraf-Nonius-CAD-4* autodiffractometer. *Table 2* gives the crystallographic data and data-collection procedure using the 'X-ray 72 system' of programs [25]. Atomic scattering factors for neutral C, O, Fe [26], and H [27] and anomalous coefficients for Fe [28] were included in the structure-factor calculations. List of atomic parameters are given in *Table 3*. Bond lengths and bond angles are summarized in *Table 4*. A perspective view of the molecular structure of **52** was prepared by the programm ORTEP [29] *(Fig. 2)*. A list of the observed and calculated structure-factor amplitude are available on request from *G.C.*

Table 2. *Crystal Data of* **52**, *Intensity Collection, and Refinement*

Formula	$C_{19}H_{20}FeO_5$	Radiation	Mo-K_α (graphite monochromator)
Molecular mass	384.219	λ [nm]	7.1069
Crystal system	monoclinic	μ[cm^{-1}]	8.57
Space group	$P2_1/c$	Scan method	$2\Theta - \Theta$
a [Å]	10.385(4)	$(\sin/\lambda)_{max}$	0.35 Å^{-1}
b [Å]	12.246(6)	No. of unique reflections	1684
c [Å]	14.199(2)	No. of reflections ($I > 3\sigma$)	1382
β [°]	91.30(2)	No. of reflections *vs.* no. of variables	5.06
U [Å^3]	1805.3	Resolution method	MULTAN and *Fourier* [30]
Z	4	Refinement method	weighted block-diagonal least-squares (2 blocks)
d_{calc} [gcm^{-3}]	1.414	R	0.026
d_{obs} [gcm^{-3}]	1.424	R_w	0.023
F_{000}	800	Minimized quantity	$\Sigma\omega(F_o^2-F_c^2)^2$
		Weight	$1/\sigma^2(\neq)$
		Lattice constants	least-squares of 25 accurately centered reflections

Table 3. *Atomic Parameters for* **52**. Estimated errors are given in parentheses; numbering of the atoms according to *Fig. 2*.

Atom	x	y	z	Atom	x	y	z
Fe	0.15894(6)	0.12354(5)	0.64208(4)	H(1)	0.151(3)	−0.012(2)	0.491(2)
O(1)	0.0009(3)	0.2749(3)	0.5312(3)	H(2)	0.769(2)	−0.099(2)	0.527(2)
O(2)	0.1502(4)	0.2090(3)	0.8347(3)	H(3)	0.359(3)	0.270(2)	0.657(2)
O(3)	−0.0246(3)	−0.0457(3)	0.6943(3)	H(4)	0.321(3)	0.229(2)	0.544(2)
O(4)	0.5403(2)	−0.2005(2)	0.6391(2)	H(5)	0.479(2)	0.119(2)	0.758(2)
O(5)	0.3603(3)	−0.1377(2)	1.0756(2)	H(6)	0.615(3)	−0.047(3)	0.720(2)
C(1)	0.0616(5)	0.2156(4)	0.5773(4)	H(7)	0.596(2)	0.037(2)	0.633(2)
C(2)	0.1537(4)	0.1768(4)	0.7587(4)	H(8)	0.500(3)	−0.250(3)	0.611(3)
C(3)	0.0474(4)	0.0205(4)	0.6729(3)	H(9)	0.497(2)	−0.088(2)	0.546(2)
C(4)	0.2099(4)	0.0426(3)	0.5168(3)	H(10)	0.290(2)	−0.154(2)	0.595(2)
C(5)	0.2965(4)	0.0165(3)	0.5921(3)	H(11)	0.351(2)	0.061(2)	0.902(2)
C(6)	0.3570(3)	0.1018(3)	0.6424(3)	H(12)	0.464(3)	−0.031(3)	0.919(2)
C(7)	0.3304(4)	0.2114(3)	0.6154(3)	H(13)	0.186(2)	−0.063(2)	0.908(2)
C(8)	0.4446(4)	0.0599(3)	0.7211(3)	H(14)	0.383(2)	−0.219(2)	0.899(2)
C(9)	0.5493(4)	−0.0076(3)	0.6695(3)	H(15)	0.236(2)	−0.254(2)	0.915(2)
C(10)	0.4842(4)	−0.0988(3)	0.6119(2)	H(16)	0.288(3)	−0.269(2)	0.751(2)
C(11)	0.3358(3)	−0.0956(3)	0.6291(2)	H(17)	0.166(3)	−0.198(2)	0.766(2)
C(12)	0.3210(3)	−0.1037(3)	0.7344(3)	H(18)	0.211(5)	−0.019(4)	1.144(3)
C(13)	0.3743(4)	−0.0219(3)	0.7820(3)	H(19)	0.164(7)	0.031(5)	1.056(5)
C(14)	0.3707(4)	−0.0106(3)	0.8869(3)	H(20)	0.095(8)	−0.085(7)	1.093(6)
C(15)	0.2695(3)	−0.0889(3)	0.9270(2)				
C(16)	0.2899(3)	−0.2021(3)	0.8852(3)				
C(17)	0.2592(4)	−0.2005(3)	0.7798(3)				
C(18)	0.2791(4)	−0.0872(3)	1.0328(3)				
C(19)	0.1862(9)	−0.0161(9)	1.0835(6)				

Table 4. *Bond Lengths* (Å) *and Bond Angles* (°) *in* **52**. Atom numbering according to *Fig. 2.*

Bond lengths [Å]			
Fe–C(1)	1.760(5)	C(8)–C(9)	1.562
Fe–C(2)	1.782(5)	C(8)–C(13)	1.521(5)
Fe–C(3)	1.775(5)	C(9)–C(10)	1.533(5)
Fe–C(4)	2.114(4)	C(10)–O(4)	1.424(5)
Fe–C(5)	2.076(4)	C(10)–C(11)	1.566(5)
Fe–C(6)	2.074(4)	C(11)–C(12)	1.509(5)
Fe–C(7)	2.122(4)	C(12)–C(13)	1.323(5)
C(1)–O(1)	1.155(6)	C(12)–C(17)	1.501(5)
C(2)–O(2)	1.151(6)	C(13)–C(14)	1.496(5)
C(3)–O(3)	1.149(6)	C(14)–C(15)	1.541(5)
C(4)–C(5)	1.417(5)	C(15)–C(16)	1.525(5)
C(5)–C(6)	1.406(5)	C(15)–C(18)	1.504(5)
C(5)–C(11)	1.522(5)	C(16)–C(17)	1.523(5)
C(6)–C(7)	1.422(5)	C(18)–O(5)	1.200(5)
C(6)–C(8)	1.514(5)	C(18)–C(19)	1.50(1)
Bond angles [°]			
Fe–C(1)–O(1)	176.9(5)	C(6)–C(8)–C(9)	104.2(3)
Fe–C(2)–O(2)	178.6(5)	C(6)–C(8)–C(13)	110.8(3)
Fe–C(3)–O(3)	178.9(5)	C(7)–C(6)–C(8)	129.0(3)
C(1)–Fe–C(2)	102.8(2)	C(8)–C(9)–C(10)	109.4(3)
C(1)–Fe–C(3)	102.3(2)	C(8)–C(13)–C(12)	114.1(3)
C(1)–Fe–C(4)	90.7(2)	C(8)–C(13)–C(14)	121.8(3)
C(1)–Fe–C(5)	128.1(2)	C(9)–C(8)–C(13)	105.4(3)
C(1)–Fe–C(6)	129.9(2)	C(9)–C(10)–O(4)	108.6(3)
C(1)–Fe–C(7)	93.2(2)	C(9)–C(10)–C(11)	108.8(3)
C(2)–Fe–C(3)	89.8(2)	C(10)–C(11)–C(12)	106.0(3)
C(2)–Fe–C(4)	165.2(2)	C(11)–C(10)–O(4)	112.2(3)
C(2)–Fe–C(5)	125.8(2)	C(11)–C(12)–C(13)	114.0(3)
C(2)–Fe–C(6)	95.5(2)	C(11)–C(12)–C(17)	122.1(3)
C(2)–Fe–C(7)	91.4(2)	C(12)–C(13)–C(14)	124.0(3)
C(3)–Fe–C(4)	92.9(2)	C(12)–C(17)–C(16)	110.5(3)
C(3)–Fe–C(5)	95.4(2)	C(13)–C(12)–C(17)	123.8(3)
C(3)–Fe–C(6)	124.1(2)	C(13)–C(14)–C(15)	110.0(3)
C(3)–Fe–C(7)	163.7(2)	C(14)–C(15)–C(16)	108.7(3)
C(4)–C(5)–C(6)	119.0(3)	C(14)–C(15)–C(18)	109.3(3)
C(4)–C(5)–C(11)	128.6(3)	C(15)–C(16)–C(17)	110.1(3)
C(5)–C(6)–C(7)	118.9(3)	C(15)–C(18)–O(5)	121.9(4)
C(5)–C(6)–C(8)	112.2(3)	C(15)–C(18)–C(19)	117.4(4)
C(5)–C(11)–C(10)	103.0(3)	C(16)–C(15)–C(18)	113.3(3)
C(5)–C(11)–C(12)	111.7(3)	C(19)–C(18)–O(5)	120.7(5)
C(6)–C(5)–C(11)	112.4(3)		

REFERENCES

[1] R. Gabioud, P. Vogel, *Helv. Chim. Acta* **1983,** *66,* 1134.

[2] A.J. Pearson, *Acc. Chem. Res.* **1980,** *13,* 463; A. Monpert, J. Martelli, R. Gree, R. Carrie, *Tetrahedron Lett.* **1981,** *22,* 1961; M. Franck-Neumann, D. Martina, M.P. Heitz, *ibid.* **1982,** *23,* 3493; B.R. Bonazza, C.P. Lillya, G. Scholes, *Organometallics* **1982,** *1,* 137.

[3] E.O., Fischer, R.D. Fischer, *Angew. Chem.* **1960,** *72,* 919; A.J. Birch, A.J. Pearson, *J. Chem. Soc., Perkin Trans. 1* **1978,** 638; A.J. Birch, P.E. Cross, J. Lewis, D.A. White, S.B. Wild, *J. Chem. Soc. (A)* **1963,** 332; H.J. Dauben, D.J. Bertelli, *J. Am. Chem. Soc.* **1961,** *83,* 497; M.F. Semmelhack, *Pure Appl. Chem.* **1981,** *53,* 2379; M.F. Semmelhack, J.W. Herndon, J.L. Springer, *J. Am. Chem. Soc.* **1983,** *105,* 2497; M.F. Semmelhack, J.W. Herndon, J.K. Liu, *Organometallics* **1983,** *2,* 1885; R.C. Kerber, *J. Organomet. Chem.* **1983,** *254,* 131.

[4] a) D.F. Hunt, C.P. Lillya, M.D. Rausch, *J. Am. Chem. Soc.* **1968,** *980,* 2561; J. Wenger, N.H. Thuy, T. Boschi, R. Roulet, A. Chollet, P. Vogel, A.A. Pinkerton, D. Schwarzenbach, *J. Organomet. Chem.* **1979,** *174,* 89; b) C. Barras, L.G. Bell, R. Roulet, P. Vogel, *Tetrahedron Lett.* **1981,** *22,* 233; *Helv. Chim. Acta* **1981,** *64,* 2841; c) R. Roulet, E. Tagliaferri, P. Vogel, G. Chapuis, *J. Organomet. Chem.* **1981,** *208,* 353; d) A.A. Pinkerton, D. Schwarzenbach, R. Gabioud, P. Vogel, *Helv. Chim. Acta* **1986,** *69,* 305.

[5] J.-C. Zwick, P. Vogel, *Angew. Chem. Int. Ed.* **1985,** *24,* 787; b) P. Vioget, M. Bonivento, R. Roulet, P. Vogel, *Helv. Chim. Acta* **1984,** *67,* 1630; c) J.-C. Zwick, R. Gabioud, P. Vogel, *ibid.* **1987,** *70,* 1079.

[6] a) P. Narbel, A.A. Pinkerton, E. Tagliaferri, J. Wenger, R. Roulet, R. Gabioud, P. Vogel, D. Schwarzenbach, *J. Organomet. Chem.* **1981,** *208,* 335; b) A.J. Pearson, in 'Metallo-organic Chemistry', J. Wiley & Son, New York, 1985; c) D.H.R. Barton, H. Patin, *J. Chem. Soc., Perkin Trans. 1* **1976,** 829; M. Franck-Neumann, D. Martina, M.P. Heitz, *J. Organomet. Chem.* **1986,** *301,* 61.

[7] U. Hanisch, E. Tagliaferri, R. Roulet, P. Vogel, *Helv. Chim. Acta* **1983,** *66,* 2182.

[8] E.J. Corey, C.U. Kim, *J. Am. Chem. Soc.* **1972,** *94,* 7586.

[9] A.R. Koray, *J. Organomet. Chem.* **1983,** *243,* 191.

[10] W.H. Kruizinga, B. Strijtveen, R.M. Kellog, *J. Org. Chem.* **1981,** *46,* 4321; J.M. Huffman, R.C. Desai, *Synth. Commun.* **1983,** *13,* 553.

[11] C.L. Liotta, H.P. Harris, M. McDermott, T. Gonzales, K. Smith, *Tetrahedron Lett.* **1974,** 2417.

[12] O. Mitsonobu, *Synthesis* **1981,** 1.

[13] R.P. Volante, *Tetrahedron Lett.* **1981,** *22,* 3119.

[14] R. Gabioud, P. Vogel, *Tetrahedron Lett.* **1983,** *24,* 1983.

[15] R. Gabioud, P. Vogel, A.A. Pinkerton, D. Schwarzenbach, *Helv. Chim. Acta* **1986,** *69,* 271.

[16] E. Tagliaferri, P. Campiche, R. Roulet, R. Gabioud, P. Vogel, G. Chapuis, *Helv. Chim. Acta* **1985,** *68,* 126.

[17] F. Fringuelli, F. Pizzo, A. Taticchi, E. Wenkert, *J. Org. Chem.* **1983,** *48,* 2802; F. Fringuelli, F. Pizzo, A. Pizzo, A. Taticchi, T.D.J. Halls, E. Wenkert, *ibid.* **1982,** *47,* 5056.

[18] P. Yates, P. Eaton, *J. Am. Chem. Soc.* **1960,** *82,* 4436; T. Inukai, T. Kojima, *J. Org. Chem.* **1966,** *31,* 1121; N.T. Anh, J. Seyden-Penne, *Tetrahedron* **1973,** *29,* 3259; K.N. Houk, R.W. Strozier, *J. Am. Chem. Soc.* **1973,** *95,* 4094; P.V. Alston, R.M. Ottenbrite, *J. Org. Chem.* **1975,** *40,* 1111.

[19] K. Alder, G. Stein, *Justus Liebigs Ann. Chem.* **1933,** *504,* 22; *ibid.* **1934,** *514,* 1; R.B. Woodward, T.J. Katz, *Tetrahedron* **1959,** *5,* 70; T. Inukai, T. Kojima, *J. Org. Chem.* **1966,** *31,* 2032.

[20] M. Avenati, P.-A. Carrupt, D. Quarroz, P. Vogel, *Helv. Chim. Acta* **1982,** *65,* 188.

[21] P.-A. Carrupt, F. Berchier, P. Vogel, *Helv. Chim. Acta* **1985,** *68,* 1716.

[22] K. Naruyama, Y. Ishihara, Y. Yamamoto, *Tetrahedron Lett.* **1981,** *22,* 4235; see also: T. Takebayaski, N. Iwasawa, T. Mukaiyama, T. Hata, *Bull. Chem. Soc. Jpn.* **1983,** *56,* 1669; B.B. Snider, G.B. Philipps, *J. Am. Chem. Soc.* **1982,** *104,* 1113; W. Oppolzer, C. Chapuis, G. Bernardinelli, *Helv. Chim. Acta* **1984,** *67,* 1397.

[23] J.-M. Tornare, P. Vogel, *Helv. Chim. Acta* **1985,** *68,* 1069.

[24] J.-L. Métral, J. Lauterwein, P. Vogel, *Helv. Chim. Acta* **1986,** *69,* 1287; K.A. Black, P. Vogel, *J. Org. Chem.* **1986,** *51,* 5341.

[25] J.M. Stewart, I.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).

[26] D.T. Cromer, J.B. Mann, *Acta Crystallogr., Sect. A* **1968,** *24,* 321.

[27] R.F. Stewart, E.R. Davidson, W.T. Simpson, *J. Phys. Chem.* **1965,** *42,* 3175.

[28] International Tables of Crystallography, The Kynoch Press, Birmingham, 1974, p. 149.

[29] C.K. Johnson, ORNL-3794, Oak Ridge National Laboratory, 1971.

[30] P. Main, S.J. Fiske, S.E. Hull, J.-P. Declercq, G. Germain, M.M. Woolfson, MULTAN-a System of Computer Programs for the Automatic Solution of Crystal Structures, 1980.