102. Remote Tricarbonyl(diene)iron Substituent Effect on Ester Heterolysis. The Solvolyses of 5,6,7,8-Tetramethylidenebicyclo[2.2.2]oct-2-yl Methanesulfonate and of its Tricarbonyliron Mono- and Dinuclear Complexes[1])

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Buffered acetolyses and hydrolyses of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl methanesulfonate (**17**), of its *'syn-endo'* (**18**), *'syn-exo'* (**19**), *'anti-endo'* (**20**), *'anti-exo'* (**21**) tricarbonyliron complexes and of its *'anti-exo,syn-endo'* (**22**) and *'anti-endo,syn-exo'* (**23**) bis(tricarbonyliron) dinuclear complexes have been investigated (product analysis and kinetics). In contrast with the solvolyses of the uncomplexed mesylate **17**, the solvolyses of the complexed esters can be highly chemo- and stereoselective. The nature of the products (non-rearranged bicyclo[2.2.2]oct-2-yl *vs.* rearranged bicyclo[3.2.1]oct-2-yl derivatives) depends on the relative configuration of the tricarbonyl(diene)iron moieties and on the medium. The rates of solvolyses of **17** are only slightly affected by complexation of one or both s-*cis*-butadiene units with $Fe(CO)_3$ groups, except in the cases where the diene moiety *'anti'* with respect to the mesylate is complexed onto its *'endo'* face (**20**, **23**). In these cases, significant rate-retardation effects are observed, consistent with the inductive effect of the $Fe(CO)_3$ substituent. Such retardation effects are overwhelmed by competing accelerating homoallylic participation by uncoordinated *'anti'*-diene moieties (**18**, **19**) or, as in the case of the *'anti-exo'*-$Fe(CO)_3$ complexes **21** and **22**, by possible direct metal participation to the ionization process.

Introduction. – Transition-metal π-complexes can stabilize an adjacent carbenium ion very efficiently [1] [2]. In 1959, *Hill* and *Richards* reported that ferrocenylmethyl acetate undergoes S_N1 solvolysis at a rate similar to that of triphenylmethyl acetate [3]. The same authors also found that ruthenocenyl and osmocenyl acetates undergo solvolysis very rapidly [4]. In 1960, *Fischer* [5] showed that salts of the tricarbonyl(cyclohexadienyl)iron cation can be recrystallized from H_2O. The smaller stabilizing effect of the tricarbonyl(cyclobutadienyl)iron moiety compared with that of the ferrocenyl group has been attributed to the inductive (electron-withdrawing) effect of the carbonyl groups. The high propensy of the tricarbonyl(diene)iron function to stabilize an α-carbenium[4]) has been further demonstrated for acyclic dienyl derivatives [6] [7].

The effect of a transition-metal moiety in a β-carbenium ion[4]) has also been investigated in a few isolated instances. Depending on the nature of the complex (nature of the metal and co-ligands) and on the electron demand of the reaction, the metallic substituent can either be stabilizing or destabilizing [2] [8]. Furthermore, if the geometry and flexibil-

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

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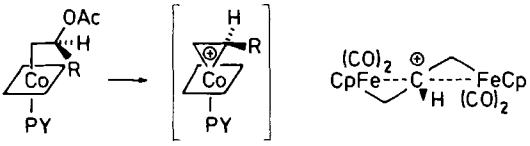
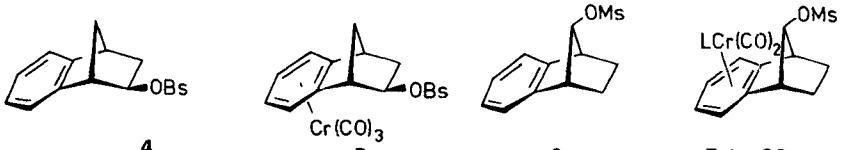
[4]) An α-carbenium ion contains an $M-C^+$ and a β-carbenium ion an $M-C-C^+$ moiety (M = metal).



1 2 3

ity of the system permit it, direct participation (non-vertical stabilization effect) of the metallic atom can occur. Such a case of participation has been evidenced in the solvolyses of 2-acetoxyalkyl(pyridine)cobaloxime **1** which were interpreted in terms of the intermediacy of metallo-bridged cations **2** [9]. Another example of direct metal participation to the stability of a β-carbenium ion was given by the X-ray crystal structure of the hexafluorophosphate **3** (Fe···C^+ distances: 2.59 and 2.72 Å) [10].

The solvolysis of $Cr(CO)_3$-complexed benzobicyclo[2.2.1]hept-5-en-2-yl and -7-yl esters have been studied [11] [12]. In this case, the hypothetical, stabilizing anchimeric effect of the Cr-atom is in competition with the destabilizing inductive effect of the carbonyl groups, as suggested by the kinetic data reported for **4–8** [12] [13].



4 **5** **6** **7** L = CO, **8** L = $P(OMe)_3$

k_{rel} (70% aq. acetone, 80°): (1.0) 0.67 k_{rel} (HCOOH, 60°): (1.0) (0.02) for **7**

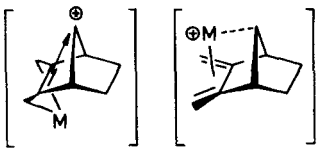
k_{rel} (AcOH, 100°): (1.0) 2.6 (3.4) for **8**

The hydrolysis of bicyclo[2.2.1]hepta-2,5-dien-7-yl *p*-toluenesulfonate was found to be strongly ($< 10^{-6}$) retarded upon complexation of the 1,4-diene by an *endo*-$Fe(CO)_3$ moiety [14]. We have reported on the acetolyses of *exo*- and *endo*-tricarbonyliron complexes of 5,6-dimethylidenebicyclo[2.2.1]hept-2-*exo*-yl (**9**, **10**) and 2,3-dimethylidenebicyclo[2.2.1]hept-7-*anti*-yl *p*-bromobenzenesulfonates (**12**, **13**) [2]. A rate-retardation effect of *ca.* $1.1 \cdot 10^5$ was measured at 65° for the acetolysis of the *exo* complex **9** compared with the acetolysis of the uncomplexed ester **11**. The retardation effect was larger ($> 5 \cdot 10^7$) with the *endo* derivative **10**. Contrastingly, the acetolysis of the 7-norbornyl derivatives **12** and **13** were not retarded compared with acetolysis of the uncomplexed diene-ester **14**. The results were interpreted in terms of competitive inductive destabilization and charge-induced dipole (polarizability) stabilizing interactions [15] by the homoconjugative tricarbonyl(diene)iron substituents on the cationic intermediates. The obser-

9 **10** **11** **12** **13** **14**

k_{rel} (AcOH, 65°): $8.7 \cdot 10^{-6}$ $2 \cdot 10^{-8}$ (1.0) k_{rel}: 0.26 38 (1.0)

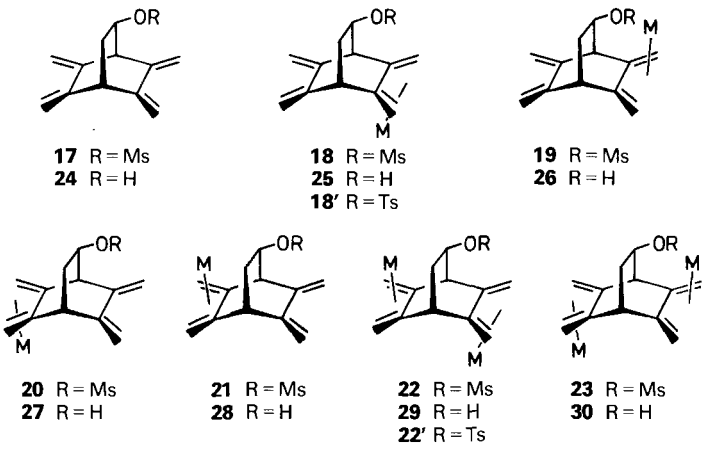
X = *p*-Bromobenzenesulfonate M = $Fe(CO)_3$



15 **16**

vation of exclusive retention of configuration at C(7) in the acetate derived from **12** and **13** suggested also the possible intervention of an anchimeric effect due to the complex moieties (*e.g.* **15**). Direct metal-atom participation (*e.g.* **16**) in the solvolysis of the *exo* complex **13** could not be excluded. A stabilizing effect due to the polarizability (vertical effect) or neighboring-group participation (non-vertical effect [16]) is possible with the 7-norbornyl isomers but not with the 2-norbornyl isomers because of the greater electronic demand in the former than in the latter systems [2] [17].

We have prepared 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl methanesulfonate (**17**) and the corresponding mono and dinuclear iron complexes **18**–**23**. We report on their buffered acetolyses and hydrolyses. We shall show that the nature of the solvolysis products depends on the configuration of the tricarbonyliron moieties and on the reaction medium. The rates of solvolyses were also dependent on the relative configuration of the metal complexes.



17 R = Ms
24 R = H

18 R = Ms
25 R = H
18' R = Ts

19 R = Ms
26 R = H

20 R = Ms
27 R = H

21 R = Ms
28 R = H

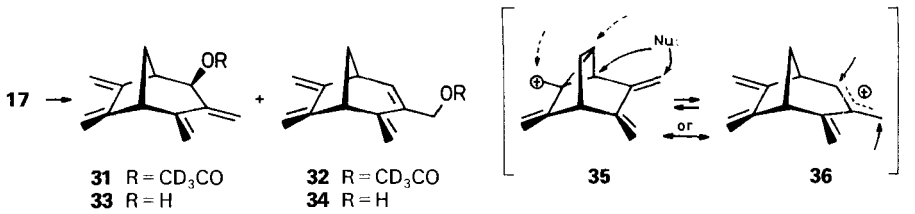
22 R = Ms
29 R = H
22' R = Ts

23 R = Ms
30 R = H

M = $Fe(CO)_3$

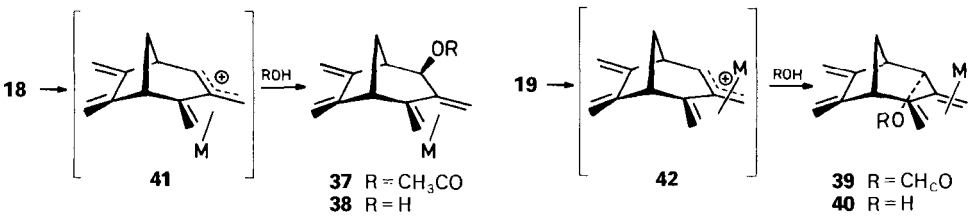
Results and Discussion. – The mesylates **17**–**23** were derived from the corresponding alcohols **24**–**30** using standard procedures (CH_3SO_2Cl/pyridine). The preparations of alcohols **24**, **25** [18], **27** [19] [20], **28** [19], **29**, and **30** [18] have already been described. Alcohol **26** was prepared by selective oxidation of the doubly complexed tetraenol **30** with Me_3NO in anhydrous acetone [21].

The buffered (AcOK) acetolysis of the uncomplexed tetraene-ester **17** (65°, 2 h) gave a mixture of unstable products from which the rearranged acetates **31** and **32** could be isolated in 53 and 13% yield, respectively. Buffered ($NaHCO_3$) hydrolysis (dioxane/H_2O 1:1, 70°, 2 h) of **17** afforded a mixture of products from which the corresponding alcohols



33 (32%) and **34** (19%) could be isolated. Hydrolysis in a more ionizing medium ($(CF_3)_2CHOH/H_2O$ 2:1, 2,6-lutidine as buffer) was a fast reaction at 20° (less than 10 min) giving alcohol **34** (18%) and a polymeric material.

These results can be interpreted in terms of the intermediacy of the cyclopropylmethyl cation **35** (or equivalent ion pairs) resulting from the homoallylic participation of the diene unit *'anti'* with respect to the mesylate. Homoconjugative participation of exocyclic s-*cis*-butadiene groups has already been evidenced in the solvolyses of 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl [22] and 2,3-dimethylidenebicyclo[2.2.1]hept-7-yl esters [23]. The cationic intermediate is attacked by the solvent (nucleophile) preferentially onto the centres shown by the heavy arrows in formula **35**. Alternatively, **35** can rearrange into the expectedly stable allylic-cation intermediate **36** which reacts with solvent to yield the observed allylic products **31**–**34**. It is also possible that **35** and **36** are *two limiting* structures for the same cationic intermediate (**35**↔**36**). The instability of the products formed and our ignorance about the other constituents of the reaction mixture does not allow one to exclude the possible quenching of **35** at the positions shown by the dotted arrows in formulae **35**.



Buffered acetolysis (AcOH/$CHCl_3$ 2:1, 0.12M, AcOK, 65°, 3 h) and hydrolysis ($(CF_3)_2CHOH/H_2O$ 2:1, 2,6-lutidine, 20°, 18 h) of the *'endo-syn'*-tricarbonylironmono-complexed mesylate **18** afforded acetate **37** and alcohol **38** in 76 and 85% isolated yield, respectively[5]). No other product of reaction could be detected by 360-MHz ^{1}H-NMR of the crude reaction mixtures, thus demonstrating the high stereoselectivity of these solvolyses. Under the same conditions, the acetolysis and hydrolysis of the *'exo-syn'* isomer **19** gave the rearranged acetate **39** and alcohol **40** in 74 and 86% isolated yield, respectively. Transesterification (abs. MeOH, anh. K_2CO_3, 20°, 2 h) of acetates **37** and **39** gave alcohols **38** and **40**, respectively. The structures of **37**–**40** were given by their elemental analysis, mode of formation, and spectral data. The relative configuration of alcohols **38** and **40** was determined by ^{1}H-NMR and with the help of lanthanide-induced shifts (see *Exper.*

[5]) The hydrolysis (dioxane/H_2O 16:9, 2,6-lutidine, saturated with $NaHCO_3$, 70°, 8 h) of the corresponding tosylate **18'** gave **38** in 60% isolated yield.

Part). In contrast with the solvolyses of the uncomplexed ester **17**, the acetolyses and hydrolyses of **18** and **19** were highly selective, giving in each case one unique product of reaction. The relative configuration of the latter depends on that of the tricarbonyliron moiety (*'endo' vs. 'exo'*) in the starting mesylate.

The results can be interpreted in terms of the formation of the expected [6] [7] stable tricarbonyl(dienyl)iron cation intermediates **41** and **42**. Their quenching by the solvent (nucleophile) occurs preferentially onto the face of the dienyl cation *'anti'* with respect to the $Fe(CO)_3$ moiety for reason of steric hindrance. This interpretation is consistent also with the kinetic data obtained for the solvolyses of **17–23** (see the *Table*). The rate constants of the buffered acetolyses and hydrolyses of **17–19** are nearly the same (the hydrolyses of **18** appeared to be 18 times slower than that of **17**). This is in sharp contrast with the kinetic data reported for the 5,6-dimethylidene-2-norbornyl derivatives **9–11** for which it has been shown that the $Fe(CO)_3$ moieties have a strong rate-retardation effect. Comparison of the rate constants measured at 65° for the buffered (0.12M AcOK) acetolyses ($CD_3COOD/CDCl_3$ 2:1) of **17** ($k = (1.4 \pm 0.3)\ 10^{-4}\ s^{-1}$, see *Table*) and of brosylate **11** ($k = 5.5 \cdot 10^{-3}\ s^{-1}$ [2]: the correction factor to apply between rate constants of brosylate *vs.* mesylate acetolysis was found to be near unity in the cases of **17** and **22**) suggests that the electronic demand in the S_N1 solvolyses of **11** and **17** are comparable. Thus, it is surprising that the tricarbonyl(diene) moieties in **18** and **19** do not retard the solvolyses of these mesylates. A possible explanation is to invoke the homoallylic participation of the *'anti'* s-*cis*-butadiene functions which is expected to disperse the positive charge in the transition states of the ionizations significantly away from the $Fe(CO)_3$ groups. Alternatively, the high stability expected for the tricarbonyl(dienyl)iron cation intermediates **41** and **42** constitutes a driving force for the ionization of the mesylate **18** and **19**, respectively, which

Table. *Rate Constants* [s^{-1}] *of the Buffered* (0.12M AcOK) *Acetolysis* ($CD_3COOD/CDCl_3$ 2:1) *and Buffered* (2,6-lutidine, 1.1 mol-equiv.) *Hydrolysis* ($(CF_3)_2CHOH/H_2O$ 2:1) *of Mesylates* **17–23**

Mesylate	Acetolysis[a])		Hydrolysis[b])	
	k	k_{rel} (65°)	Half-life	k_{rel} (25°)
17	$k_{65°} = (1.4 \pm 0.3) \cdot 10^{-4}$	(1.0)	$\tau_{1/2}(25°) = 6$ min	(1.0)
18	$k_{65°} = (2.5 \pm 0.15) \cdot 10^{-5}$	0.18	$\tau_{1/2}(25°) = 108$ min	≈ 0.06
19	$k_{65°} = (4.3 \pm 0.4) \cdot 10^{-5}$	0.3	$\tau_{1/2}(25°) = 42$ min	≈ 0.15
20	$k_{90°} = (6.7 \pm 0.7) \cdot 10^{-6}$		$\tau_{1/2}(60°) = 168$ min	
	$k_{65°} \approx 2.9 \cdot 10^{-7}$[c])	≈ 0.002	$\tau_{1/2}(25°) \approx 18650$ min[d])	≈ 0.0003
21	$k_{65°} = (3.9 \pm 0.4) \cdot 10^{-4}$	2.8	$\tau_{1/2}(25°) \approx 5$ min	≈ 1
22	$k_{65°} = (1.1 \pm 0.2) \cdot 10^{-3}$	7.9	$\tau_{1/2}(25°) \approx 6$ min	≈ 1
23	$k_{90°} = (6.9 \pm 1.2) \cdot 10^{-7}$		$\tau_{1/2}(60°) = 576$ min	
	$k_{65°} \approx 2.5 \cdot 10^{-8}$[e])	$\approx 1.8 \cdot 10^{-4}$	$\tau_{1/2}(25°) \approx 73900$ min[f])	$\approx 8 \cdot 10^{-5}$

[a]) The mesylate (0.05 mmol) was dissolved in 0.15 ml of $CDCl_3$. After addition of 0.3 ml of 0.179M AcK in CD_3COOD, the NMR tube was degassed on the vacuum line and sealed *in vacuo*. The kinetics were followed by 80-MHz ^{1}H-NMR for at least 4 half-lives.

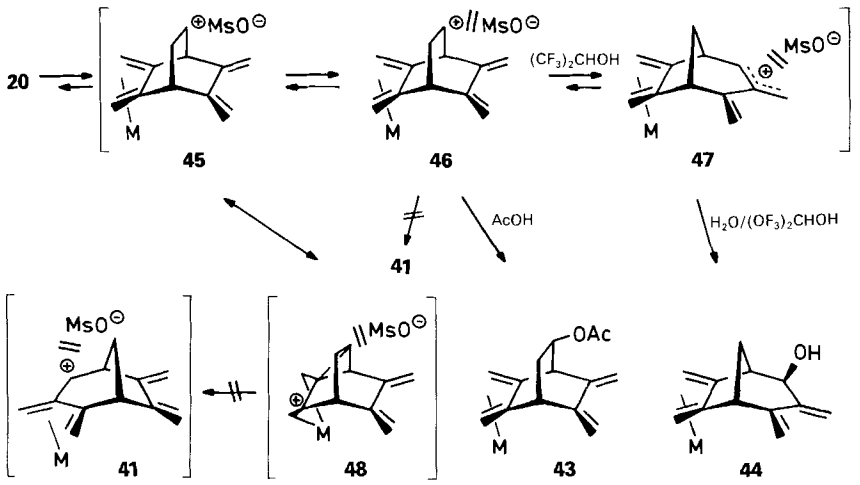
[b]) The mesylate (0.05M) was dissolved in 0.5 ml of $(CF_3)_2CHOH/H_2O$ 2:1 containing 0.055M of 2,6-lutidine. The mixture was degassed on a vacuum line, and the kinetics were followed by 80-MHz ^{1}H-NMR.

[c]) Extrapolated from the $k_{90°}$ value, with $\Delta G^{\neq} = 30.0$ kcal/mol ($k_T = T(k_B/h)e^{-\Delta G^{\neq}/RT}$).

[d]) Extrapolated from the half-life measured at 60°, with $\Delta G^{\neq} = 25.9$ kcal/mol.

[e]) Extrapolated from the $k_{90°}$ value, with $\Delta G^{\neq} = 31.6$ kcal/mol.

[f]) Extrapolated from $\tau_{1/2}$ (60°), with $\Delta G^{\neq} = 26.7$ kcal/mol.



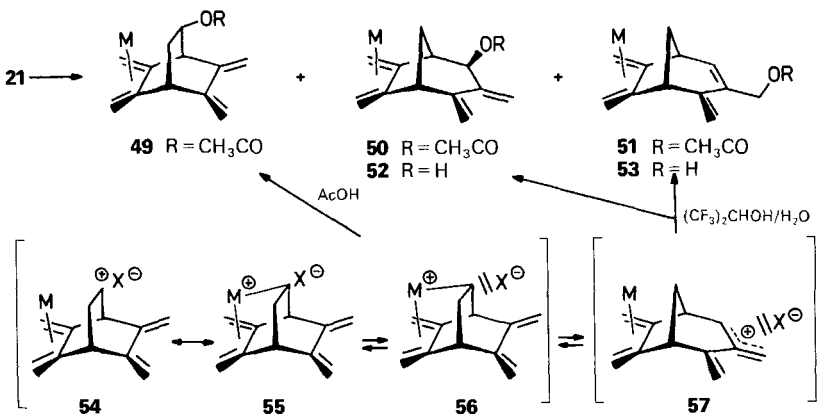
competes with the destabilizing effect, or retarding effect, due to the dipole moment of the $Fe(CO)_3$ moieties [2]. It is interesting to note that the bulk of the *'syn-exo'*-$Fe(CO)_3$ moiety in **19** does not affect significantly the rate of the solvolyses. This suggests that the transition state of these reactions corresponds to the formation of tight ion-pairs. Alternatively, homoallylic participation and skeleton rearrangement remove the possible repulsive steric hindrance between the mesylate and $Fe(CO)_3$ units.

The buffered acetolysis of the *'anti-endo'*-complexed mesylate **20** was *ca.* 500 times as slow as that of the uncomplexed ester **17**. The acetate **43** was the unique product isolated in 68% yield. Transesterification of **43** in abs. MeOH (K_2CO_3) afforded the known alcohol **27**, thus confirming the retention of configuration in this acetolysis. This demonstrated that the facile homoallylic participation by the *'anti'* s-*cis*-butadiene unit in **17** can be prohibited by complexation with $Fe(CO)_3$. This interpretation was confirmed by our kinetic data *(Table)*. It is surprising, though, that no product of inversion of configuration at C(2) could be detected. Thus, one must admit that there is an anchimeric participation of the *'anti-endo'*-tricarbonyl(diene)iron function responsible of the retention of configuration, but which is not stabilizing enough to overwhelm the destabilizing effect due to the inductive effect of the $Fe(CO)_3$ group. A similar situation has been observed for the acetolysis of **12** for which the intermediate **15** had been invoked [2].

The buffered hydrolysis of **20** in the strongly ionizing medium $(CF_3)_3CHOH/H_2O$ 2:1 was *ca.* 3000 times slower than that of **17**. In that case, the rearranged alcohol **44** was isolated in 77% yield (some polymeric material was also formed). The structure of **44** was given by its 360-MHz ^{1}H-NMR spectrum with the help of lanthanide-induced shifts (see *Exper. Part*). The high stereoselectivity of this hydrolysis can be attributed to the bulk of the *'anti-endo'*-$Fe(CO)_3$ group which hinders the attack of the nucleophile (H_2O) onto the *endo* face of the allylic-cation intermediate **47**. The difference in type of products (unrearranged *vs.* rearranged) observed between the acetolysis (more nucleophilic) and hydrolysis in $(CF_3)_2CHOH/H_2O$ 12:1 (less nucleophilic) can be interpreted in terms of the formation of the unrearranged tight ion-pair **45** which equilibrates with the solvent-separated ion-pair **46**. In AcOH, quenching of **46** (with retention of configuration)

competes favourably with the *Wagner-Meerwein* rearrangement **46**→**47**. In $(CF_3)_2CHOH$, **46** has the time to rearrange to the more stable allylic-cation intermediate **47**. The relatively difficult *Wagner-Meerwein* rearrangements of **45** and **46** into **47** must be attributed to the anchimeric assistance of the *'anti-endo'*-tricarbonyl(diene)iron function or/and to its inductive effect. The anchimeric assistance implies the formation of at least a partial bond between the *'endo'*-tricarbonyl(diene)iron unit and the forming carbocationic centre at C(2), as shown with the limiting structure **48**. It is rather surprising that the latter phenomenon, required to explain the retention of configuration in the acetolysis **20**→**43**, does not facilitate the *Wagner-Meerwein* rearrangement into the stable allylic-cation intermediate **47**. It is interesting to note also that the ion-pairs **45** and **46** have no time to dissociate to free ion-pairs which would allow, presumably, the rearrangement into the stable cation intermediate **41**. The non-observation of products **37** and **38** in the acetolysis and hydrolysis, respectively, of **20** is consistent with this hypothesis (see the 'memory effect' [24]).

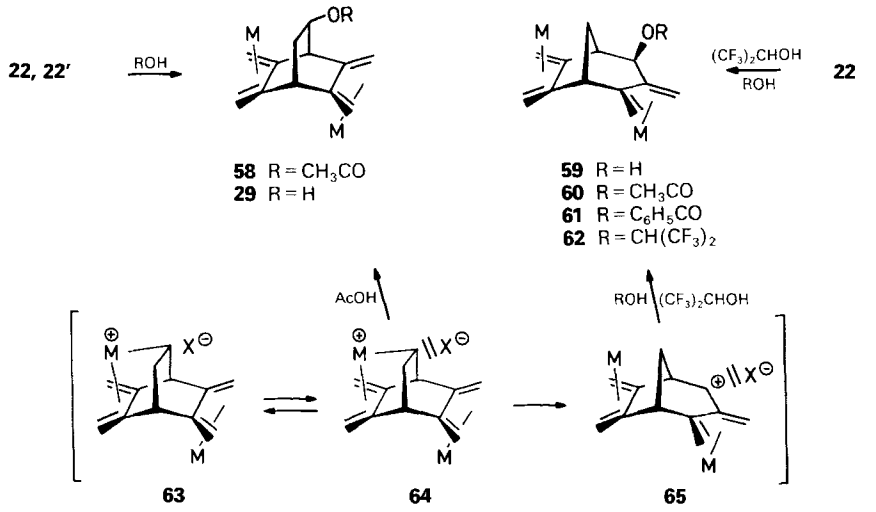
In contrast with **20**, the solvolyses of the *'anti-exo'*-complexed mesylate **21** were as fast as those of **17**–**19** and gave mixtures of products. The buffered (AcOK) acetolysis (AcOH/$CHCl_3$ 2:1, 65°, 4 h) of **21** afforded a 40:38:32 (^{1}H-NMR of the crude reaction mixture) mixture of acetates **49**/**50**/**51** in 80% isolated yield. Buffered (2,6-lutidine) hydrolysis ($(CF_3)_2CHOH/H_2O$ 2:1, 20°, 45 min) gave a 76:24 mixture of alcohols **52**/**53** in 90% isolated yield. It is interesting to note that, only in the more nucleophilic medium (AcOH), the formation of the non-rearranged product **49** was observed. This finding together with our kinetic data *(Table)* can be interpreted in terms of participation of the *'anti-exo'*-$Fe(CO)_3$ moiety to the ionization of **21**, giving the hypothetical tight ion-pair



54↔**55**. The latter has the time to equilibrate with the unrearranged solvent-separated ion-pair **56**. In the more nucleophilic medium (AcOH), **56** reacts to give the non-rearranged product **49** competitively with its rearrangement into the solvent-separated ion-pair **57**. The latter is quenched by the solvent to give the rearranged products **50**–**53**. This reaction is *exo*-face selective, probably because of a steric effect or/and a conformational effect. The same *exo* selectivity was also observed in the solvolyses of bicyclo[2.2.2]oct-2-yl [25], bicyclo[2.2.2]oct-5-en-2-yl [24] [26], and bicyclo[3.2.1]oct-2-yl derivatives [27]. In a

more ionizing medium such as $(CF_3)_2CHOH/H_2O$ 2:1, the quenching of the intermediate **56** is a too slow process compared with the exothermic rearrangement **56**→**57**, thus leading exclusively to rearranged products of solvolysis in this case. The hypothetical participation of the metal in the ionization process **21**→**55** competes with the rate-retardation effect expected for the $Fe(CO)_3$ group. The solvolytical behaviour of **21** can thus be compared with that of the *'anti-exo'*-$Fe(CO)_3$ complex of 2,3-dimethylidene-7-norbornyl ester **13** [2]. The hypothetical equilibrium **55**⇄**56** is required to explain the absence of product of inversion of configuration at C(2) in the non-rearranged acetate.

The buffered acetolysis of the *'anti-exo,syn-endo'*-doubly-complexed mesylate **22** or tosylate **22′** was slightly faster than those of **17**–**19** and **21** *(Table)*. Interestingly, the unrearranged acetate **58** was the unique product of reaction, isolated in 80% yield.



Transesterification (MeOH, K_2CO_3) of **58** gave the known alcohol **29** [18]. The buffered ($NaHCO_3$) hydrolysis of mesylate **22** and tosylate **22′** (dioxane/H_2O 2:1, 60°, 150 min) afforded the non-rearranged alcohol **29** in good yield. When using $D_2{}^{18}O$, incorporation of ^{18}O in alcohol **29** was evidenced by mass spectrometry, thus demonstrating that C–O rather than the S–O bonds were cleaved in the heterolyses of **22** and **22′** giving **29** with complete retention of configuration. In contrast, the hydrolysis ($(CF_3)_2CHOH/H_2O$ 2:1) of **22** afforded the rearranged alcohol **59** as unique product of solvolysis. Solvolyses of **22** in 100% $(CF_3)_2CHOH$ containing 3, 20, or 100 mol-equiv. of AcONa gave the rearranged acetate **60** exclusively. Similarly, when **22** was solvolyzed in 100% $(CF_3)_2CHOH$ containing sodium benzoate, the corresponding rearranged benzoate **61** was formed in good yield. When using $(CF_3)_2CHOH/H_2O$ 20:1 (= 97% $(CF_3)_2CHOH$) for the buffered (0.08M 2,6-lutidine) hydrolysis (20°, 7 min), a 4:6 mixture **59**/**62** was obtained. Ether **62** was isolated in 82% yield after solvolysis of **22** in 100% $(CF_3)_2CHOH$ (1M 2,6-lutidine). There was less than 3% of **62** in the reaction mixture of the hydrolysis of **22** in $(CF_3)_2CHOH/H_2O$ 2:1.

These results are consistent with a mechanism of solvolysis similar to that proposed for the solvolyses of the mono-complexed ester **21**. Again, assistance by the *'anti-exo'*-

$Fe(CO)_3$ group facilitates the formation of the ion-pairs **63**⇄**64**. The solvent-separated ion-pair **64** is quenched efficiently by a nucleophilic medium such as AcOH. In a more ionizing and less nucleophilic medium, **64** rearranges irreversibly to the solvent-separated ion pair **65** which is then trapped stereospecifically onto the *exo*-face of the complexed tricarbonyl(dienyl) cation giving the observed rearranged products **59–62**. It is interesting to note that the *'syn-endo'*-$Fe(CO)_3$ moiety in **22** does not lead to a retardation effect on the rates of the solvolyses of **22** compared with those of **21** (see *Table*). This observation can be interpreted in terms of a highly delocalized cationic intermediate which is generated in the rate-determining step and which is not affected in a significant fashion by the destabilizing inductive effect of the *'syn-endo'*-$Fe(CO)_3$ moiety.

Buffered acetolysis (at 90°) and hydrolysis (at 60°) of the isomeric doubly complexed ester **23** were very slow reactions (see *Table*). They led to mixtures of unidentified compounds resulting from partial decomplexation of **23** and oligomerization of the polyenes. In this case, the lack of a favourable homoallylic assistance (as for the solvolyses of **19**) and the steric hindrance to the ionization of the mesylate due to the *'syn-exo'*-$Fe(CO)_3$ moiety are probably the cause of the low S_N1 reactivity of **23**.

Conclusion. – The solvolyses of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl mesylate (**17**) give mixtures of rearranged bicyclo[3.2.1]octyl derivatives. On complexing one or both s-*cis*-butadiene units in **17** by $Fe(CO)_3$ groups, the solvolyses of the corresponding complexed mesylates may be highly steroselective, thus demonstrating the synthetic potential of these iron complexes. In the cases of the *'syn-endo'*- and *'syn-exo'*-$Fe(CO)_3$ complexes **18** and **19**, respectively, the solvolyses give exclusively the 3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-*exo*-yl (**37**, **38**) and 3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-*endo*-yl derivatives (**39**, **40**), respectively. The solvolyses of the readily available *'anti-exo,syn-endo'* doubly complexed mesylate **22** were most interesting because different products could be obtained with high stereoselectivity depending on the medium. With AcOH, the corresponding unrearranged bicyclo[2.2.2]oct-2-yl acetate **58** was obtained with complete retention of configuration. In contrast, in a less nucleophilic and more ionizing solvent such as $(CF_3)_2CHOH$, the exclusive formation of rearranged bicyclo[3.2.1]oct-2-*exo*-yl derivatives **59–62** was observed. The product selectivity was not good in the case of the solvolyses of **20**, **21**, and **23**.

The rates of solvolyses of mesylate **17** are only slightly affected by complexation of one or both s-*cis*-butadiene units with $Fe(CO)_3$ groups, except in the cases where the diene moiety *'anti'* with respect to the mesylate is complexed onto its *'endo'* face (**20**, **23**). In these latter cases, significant rate-retardation effects are observed, consistent with the inductive effect of the $Fe(CO)_3$ moiety. Such retardation effects are overwhelmed by competing accelerating homoallylic participation by uncoordinated *'anti'*-diene moieties (**18**, **19**) or, as in the case of the *'anti-exo'*-$Fe(CO)_3$ complexes **21** and **22**, by possible direct metal participation to the ionization process.

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Experimental Part

General. See [2] [18] [19]. LIS = lanthanide-induced shift.

Tricarbonyl[(1RS,2SR,4RS,5SR,6RS)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-ol)]iron (**26**). A mixture of **29** [18] (280 mg, 0.62 mmol), anh. acetone (30 ml), and Et_3NO (1 g, 15.3 mmol; freshly sublimed) was stirred at 20° for 3 h (TLC (silica gel, CH_2Cl_2) control). After filtration through silica gel (100 g, CH_2Cl_2), H_2O (20 ml) was added, the aq. layer extracted with CH_2Cl_2 (100 ml, 3 times), the combined org. phase washed with H_2O (50 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was purified by medium-pressure column chromatography (*Lobar*, SiO_2, col. *B*, 5 ml/min, CH_2Cl_2/hexane 1:1). The major fraction was crystallized from CH_2Cl_2/hexane at −25°, giving 86 mg (45%) of yellow crystals. M.p. 117–118°. UV (95% EtOH): 204 (30300), 223 (sh, 25000), 255 (sh, 12870), 319 (3340). IR (KBr): 3300, 3100, 3060, 3000, 2960, 2940, 2860, 2040, 1990, 1955, 1930, 1060. ^{1}H-NMR (360 MHz, $CDCl_3$, [rel. LIS, Eu(thd)$_3$]): 5.51 (*s*, [4.3], 1 H, H–CH=C(8) *cis* to C(7)); 5.47 (*s*, [6.7], 1 H, H–CH=C(7) *cis* to C(8)); 5.14 (*s*, [1.7], 1 H, H–CH=C(8) *trans* to C(7)); 5.10 (*s*, [9.5], 1 H, H–CH=C(7) *trans* to C(8)); 4.27 (*m*, ^3J(H–C(2),H$_{anti}$–C(3)) = 9.5, ^3J(H–C(2),OH) = 5.5, ^3J(H–C(2),H$_{syn}$–C(3) = 4.0, ^3J(H–C(1),H–C(2)) = 2.5, [100], H–C(2)); 3.30 (*d*, *J* = 2.5, [54.2], H–C(1)); 3.17 (*dd*, ^3J(H$_{anti}$–C(3), H–C(4)) = 3.0, ^3J(H$_{syn}$–C(3), H–C(4)) = 2.5, [22.6], H–C(4)); 2.44 (*ddd*, *J* = 13.5, 9.5, 3.0, [32.8], H–C(3) *'anti'* to OH); 1.85 (*d*, *J* = 5.5, OH); 1.83 (*d*, *J* = 2.5, [17.7], 1 H, H–CH=C(5) *trans* to C(6)); 1.66 (*d*, *J* = 2.5, [27.7], 1 H, H–CH=C(6) *trans* to C(5)); 1.6 (*ddd*, *J* = 13.5, 4.0, 2.5, [42.7], H–C(3) *'syn'* to OH); 0.23 (*d*, *J* = 2.5, [16.9], 1 H, H–CH=C(5) *cis* to C(6)); 0.19 (*d*, *J* = 2.5, [19.1], 1 H, H–CH=C(6) *cis* to C(5)). MS (70 eV): 314 (0.9, $M^{+\cdot}$), 286 (16), 258 (88), 230 (100), 212 (75), 156 (51), 141 (20), 129 (17), 128 (20), 115 (19). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.224): C 57.36, H 4.49; found: C 57.28, H 4.53.

(±)-5,6,7,8-Tetramethylidenebicyclo[2.2.2]oct-2-yl Methanesulfonate (**17**). To a soln. of **24** [18] (87 mg, 0.5 mmol) in anh. pyridine (1 ml) at 0°, methanesulfonyl chloride (MsCl; 74 mg, 0.6 mmol) was added. The mixture was stirred at 20° for 30 min under N_2. CH_2Cl_2 (15 ml) was added, the soln. washed with 1N HCl (10 ml, 4 times) and H_2O (10 ml, 3 times), dried ($MgSO_4$), and evaporated: 105 mg (83%), colourless oil. UV (95% EtOH): 251 (sh, 9300), 237 (10400). UV (dioxane): 254 (11600), 246 (11600). IR (CH_2Cl_2): 3090, 2970, 2950, 1715, 1360, 1330, 1220, 1180, 1155, 1025, 1000, 970, 950. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.5, 5.4, 5.3, 5.3, 5.1, 5.0, 4.9, 4.9 (8*s*, 8 H); 3.5 (*d*, *J* = 3.0, H–C(1)); 3.1 (*t*, *J* = 3.0, H–C(4)); 3.0 (*s*, CH_3SO_3); 2.3, 1.8 (2*m*, CH_2(3)).

Tricarbonyl[(1RS,2SR,4RS,5RS,6SR)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl methanesulfonate)]iron (**18**). Same procedure as for the preparation of **17** using 100 mg (0.5 mmol) of **25** [18]. Crystallization from CH_2Cl_2/hexane gave 160 mg (82%), yellow crystals. M.p. 108–109°. IR (KBr): 3040, 2970, 2940, 2040, 1980, 1960, 1385, 1360, 1330, 1185, 1175, 1020, 970, 945, 910, 890, 850, 840. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.39, 5.12, 5.03, 4.83 (4*s*, 4 H); 5.33 (*m*, H–C(2)); 3.72 (*d*, *J* = 3.0, H–C(1)); 3.3 (*t*, *J* = 3.0, H–C(4)); 3.05 (*s*, CH_3SO_3); 2.63 (*ddd*, *J* = 13.0, 9.0, 3.0, H–C(3) *'anti'* to MsO); 2.05 (*m*, H–C(3) *'syn'* to MsO); 1.90, 1.89, 0.34, 0.33 (4*d*, *J* = 3.0, 4 H). MS (70 eV): 364 (14, $M^{+\cdot}$ − 28), 336 (50), 308 (100), 286 (11), 241 (9), 229 (8), 212 (29). Anal. calc. for $C_{16}H_{16}FeO_6S$ (392.21): C 49.00, H 4.11; found: C 49.16, H 4.21.

Tricarbonyl[(1RS,2SR,4RS,5RS,6SR)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl p-toluenesulfonate)]iron (**18'**). *p*-Toluenesulfonyl chloride (TsCl; 250 mg, 1.32 mmol) was added to **25** (290 mg, 0.92 mmol) in anh. pyridine (4 ml) at 0°. After stirring at 20° for 2 days, CH_2Cl_2 (50 ml) was added. The soln. was washed successively with cold H_2O (50 ml), 1N HCl (50 ml), H_2O (50 ml), sat. aq. $NaHCO_3$ soln. (50 ml), and H_2O (50 ml, twice), dried ($MgSO_4$), and evaporated. The residue was purified by filtration on a short column of *Florisil* (10 g, CH_2Cl_2). Crystallization from CH_2Cl_2/hexane at −25° gave 320 mg (75%) of yellowish crystals. M.p. 111.5–112°. IR (KBr): 3090, 3060, 3000, 2980, 2940, 2040, 1975, 1950, 1350, 1190, 1175, 1155, 1100, 1020, 940, 920, 895, 860, 820, 670. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.82 (*dt*, *J* = 8.0, 1.5, 2 H); 7.37 (*dt*, *J* = 8.0, 1.5, 2 H); 5.32, 5.17 (2*s*, 2 H); 5.14 (*ddd*, *J* = 9.0, 3.5, 3.0, H–C(2)); 4.91, 4.77 (2*s*, 2 H); 3.50 (*d*, *J* = 3.5, H–C(1)); 3.22 (*t*, *J* = 3.0, H–C(4)); 2.48 (*s*, CH_3); 2.43 (*ddd*, *J* = 14.5, 9.0, 3.0, H–C(3) *'anti'* to TsO); 1.92 (*dt*, *J* = 14.5, 3.0, H–C(3) *'syn'* to TsO); 1.84, 1.74, 0.30, 0.29 (4*d*, *J* = 2.5, 4 H). MS (70 eV): 440 (3, $M^{+\cdot}$ − 28), 412 (17), 384 (90), 252 (6), 229 (8), 212 (22), 156 (55), 141 (36), 128 (24), 115 (20), 105 (18), 91 (50), 58 (100). Anal. calc. for $C_{22}H_{20}FeO_6S$ (468.31): C 56.43, H 4.30; found: C 56.36, H 4.27.

Tricarbonyl[(1RS,2SR,4RS,5SR,6RS)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl methanesulfonate)]iron (**19**). A mixture of **26** (55 mg, 0.175 mmol), anh. pyridine (1 ml) and MsCl (50 µl, 74 mg, 0.65 mmol) was stirred at 20° for 2 h. After addition of CH_2Cl_2 (50 ml), the soln. was washed successively with H_2O (50 ml), 1N HCl (50 ml, 3 times), H_2O (50 ml), sat. aq. $NaHCO_3$ soln. (50 ml), and H_2O (50 ml, twice), dried ($MgSO_4$), and evaporated. The residue was purified by filtration through a short column of silica gel (5 g, CH_2Cl_2). Crystallization from hexane/CH_2Cl_2 gave 45 mg (66%) of yellowish crystals. M.p. 118–119°. IR (KBr): 3060, 3000, 2960, 2000, 1970, 1945, 1340, 1175, 940, 920. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.58, 5.51, 5.25, 5.16, (4*s*, 4 H); 5.15 (*ddd*, *J* = 10.0,

4.5, 2.5, H–C(2)); 3.62 (*d*, *J* = 2.5, H–C(1)); 3.22 (*dd*, *J* = 3.0, 2.5, H–C(4)); 3.02 (*s*, CH_3SO_3); 2.57 (*ddd*, *J* = 14.0, 10.0, 3.0, H–C(3) *'anti'* to MsO); 1.94 (*ddd*, *J* = 14.0, 4.5, 2.5, H–C(3) *'syn'* to MsO); 1.85, 0.24 (2*d*, *J* = 2.5, 2 H); 1.72, 0.18 (2*d*, *J* = 3.0, 2 H). MS (70 eV): 364 (11, $M^{+\cdot} - 28$), 336 (29), 308 (99), 212 (93), 156 (100), 141 (86), 128 (55), 115 (57), 104 (29). Anal. calc. for $C_{16}H_{16}FeO_6S$ (392.21): C 49.00, H 4.11; found: C 49.17, H 4.16.

Tricarbonyl[(1RS,2RS,4RS,5RS,6SR)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl methanesulfonate)]iron (**20**). Same procedure as for **19** using 92 mg (0.293 mmol) of **27** [19], 0.9 ml of pyridine and 40 µl of MsCl: 109 mg (95%), yellowish crystals. M.p. 153.5–154°. UV (95% EtOH): 204 (23300), 222 (sh, 19900), 280 (2600). IR (KBr): 3090, 3050, 2990, 2960, 2040, 1985, 1970, 1950, 1345, 1330, 1180. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.48, 5.31, 4.97, 4.86 (4*s*, 4 H); 5.25 (*ddd*, *J* = 9.5, 3.0, 2.5, H–C(2)); 3.58 (*d*, *J* = 3.0, H–C(1)); 3.23 (*dd*, *J* = 3.0, 2.5, H–C(4)); 3.08 (*s*, CH_3SO_3); 2.60 (*ddd*, *J* = 14.0, 9.5, 3.0, H–C(3) *'anti'* to MsO); 2.08 (*dt*, *J* = 14.0, 2.5, H–C(3) *'syn'* to MsO); 1.85 (*d*, *J* = 2.5, 2 H); 0.27, 0.20 (2*d*, *J* = 2.5, 2 H). MS (70 eV): 392 (1, $M^{+\cdot}$), 364 (16), 336 (37), 308 (100), 229 (6), 212 (19), 156 (23), 141 (23). Anal. calc. for $C_{16}H_{16}FeO_6S$ (392.211): C 49.00, H 4.11; found: C 49.05, H 4.15.

Tricarbonyl[(1RS,2RS,4RS,5SR,6RS)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl methanesulfonate)]iron (**21**). Same procedure as for the preparation of **19**, using 43 mg (0.137 mmol) of **28** [19], 1 ml of anh. pyridine, and 40 µl of MsCl. Column chromatography on *Florisil* (5 g, CH_2Cl_2) and crystallization from hexane/CH_2Cl_2 yielded 45 mg (84%), yellow crystals. M.p. 148–149°. UV (95% EtOH): 203 (23400), 216 (22800), 252 (sh, 2700), 310 (2300). IR (KBr): 3100, 3060, 3010, 2990, 2960, 2040, 1980, 1950, 1925, 1355, 1175, 930, 865. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.75, 5.57, 5.30, 5.16 (4*s*, 4 H); 4.94 (*ddd*, *J* = 10.0, 3.5, 3.5, H–C(2)); 3.63 (*d*, *J* = 3.5, H–C(1)); 3.29 (*t*, *J* = 3.0, H–C(4)); 3.05 (*s*, CH_3SO_3); 2.34 (*ddd*, *J* = 14.5, 10.0, 3.0, H–C(3) *'anti'* to MsO); 1.97 (*ddd*, *J* = 14.5, 3.5, 3.0, H–C(3) *'syn'* to MsO); 1.91, 1.85, 0.36, 0.32 (4*d*, *J* = 2.5, 4 H). MS (70 eV): 392 (2, $M^{+\cdot}$), 364 (13), 338 (8), 308 (100), 229 (8), 212 (32), 157 (43), 141 (32), 129 (34). Anal. calc. for $C_{16}H_{16}FeO_6S$ (392.211): C 49.00, H 4.11; found: C 48.84, H 3.95.

trans-*μ*-*[(1RS,2RS,4SR,5SR,6RS,7RS,8SR)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-Tetramethylidenebicyclo-[2.2.2]oct-2-yl methanesulfonate)]bis(tricarbonyliron)* (**22**). See [27].

trans-*μ*-*[(1RS,2RS,4SR,5SR,6RS,7RS,8SR)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-Tetramethylidenebicyclo-[2.2.2]oct-2-yl* p*-toluenesulfonate)]bis(tricarbonyliron)* (**22'**). To a soln. of **29** (227 mg, 0.5 mmol) in anh. pyridine (1 ml) at 0°, TsCl (114 mg, 0.6 mmol) was added, and the mixture was stirred at 20° for 1 h under N_2. After addition of CH_2Cl_2 (15 ml), the soln. was washed with 1N HCl (10 ml, 4 times) and H_2O (10 ml, 3 times), dried ($MgSO_4$), and evaporated. Crystallization from CH_2Cl_2/hexane gave 275 mg (90%), yellow crystals. M.p. 119–121°. UV (95% EtOH): 285 (sh, 3100), 225 (sh, 30500). IR (KBr): 3000, 2980, 2960, 2045, 1990, 1965, 1595, 1440, 1400, 1375, 1360, 1290, 1260, 1230, 1190, 1175, 1140, 1090. ^{1}H-NMR ($CDCl_3$, 80 MHz): 7.9–7.2 (*m*, 4 H); 5.15 (*m*, H–C(2)); 3.63 (*d*, *J* = 3, H–C(1)); 3.43 (*t*, *J* = 3, H–C(4)); 2.49 (*m*, 1 H); 2.46 (*s*, CH_3); 2.06, 2.05 (2*d*, *J* = 3, 2 H); 1.95 (*m*, 1 H); 1.88, 1.75, 0.65, 0.60, 0.36, 0.28 (6*d*, *J* = 3, 6 H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 144.8, 133.2 (2*s*); 129.7 (*d*, ^1J(C,H) = 164); 127.6 (*d*, ^1J(C,H) = 170); 111.8, 106.8, 105.0, 102.0 (4*s*, C(5), C(6), C(7), C(8)); 79.4 (*d*, ^1J(C,H) = 161, C(2)); 46.6 (*d*, ^1J(C,H) = 148, C(1)); 42.1 (*d*, ^1J(C,H) = 146, C(4)); 39.3 (*t*, ^1J(C,H) = 138, C(3)); 40.1, 38.1, 37.3, 36.2 (4*t*, ^1J(C,H) = 164); 21.3 (*q*, ^1J(C,H) = 130, CH_3). MS (70 eV): 609 (13), 607 (13), 581 (17), 553 (60), 552 (57), 525 (26), 497 (21), 473 (18), 441 (34), 381 (100). Anal. calc. for $C_{25}H_{20}Fe_2O_9S$ (608.19): C 49.37, H 3.31; found: C 49.39, H 3.36.

trans-*μ*-*[(1RS,2SR,4SR,5SR,6RS,7RS,8SR)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-Tetramethylidenebicyclo-[2.2.2]oct-2-yl methanesulfonate)]bis(tricarbonyliron)* (**23**). Same procedure as for the preparation of **19**, using 145 mg (0.32 mmol) of **30** [18], 1.5 ml of pyridine, and 200 µl of MsCl: 110 mg (65%), yellowish crystals. M.p. 136–137°. UV (95% EtOH): 206 (21800), 222 (sh, 17600), 308 (1900). IR (KBr): 3060, 3000, 2980, 2960, 2040, 2000, 1980, 1965, 1930, 1355, 1335, 1185, 1175, 945. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.45 (*ddd*, *J* = 9.5, 4.0, 2.5, H–C(2)); 3.75 (*d*, *J* = 2.5, H–C(1)); 3.38 (*dd*, *J* = 3.0, 2.5, H–C(4)); 3.10 (*s*, CH_3SO_3); 2.83 (*ddd*, *J* = 14.0, 9.5, 3.0), 2.27 (*ddd*, *J* = 14.0, 4.0, 2.0, CH_2(3)); 2.11, 2.07, 1.93, 1.78, 0.58, 0.49, 0.34, 0.27 (8*d*, *J* = 2.5–3.0, 8 H). MS (70 eV): 532 (1, $M^{+\cdot}$), 504 (1), 476 (14), 448 (3), 420 (1), 392 (1), 364 (100). Anal. calc. for $C_{19}H_{16}Fe_2O_9S$ (532.09): C 42.89, H 3.03; found: C 42.92, H 3.16.

Acetolysis of **17**. A mixture of **17** (60 mg, 0.24 mmol), $CDCl_3$ (0.8 ml), CD_3COOD (1.6 ml), AcOK (25 mg), and Ac_2O (50 mg) was heated to 65° for 2 h. After cooling to 20°, CH_2Cl_2 (5 ml) was added, the mixture washed with H_2O (2 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (CH_2Cl_2). The 1st fraction contained a mixture of unidentified compounds. The 2nd gave 28 mg (53%) of **31** and the 3rd 7 mg (13%) of **32**. *(±)-3,4,6,7-Tetramethylidenebicyclo[3.2.1]oct-2-*exo*-yl (D$_3$)Acetate* (**31**): Colourless oil. UV (95% EtOH): 260 (sh, 4600), 233 (10100). IR ($CHCl_3$): 3090, 3030, 3010, 2980, 2960, 2880, 2400, 1985, 1730, 1640, 1620, 1420, 1320. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.47, 5.41, 5.33, 5.14, 5.11, 4.97, 4.96, 4.72 (8*d*, *J* = 1.5, 8 H); 5.31 (*dd*, *J* = 4.0, 1.5, H–C(2)); 3.34 (*d*, *J* = 4.0, H–C(5)); 3.04 (*t*, *J* = 4.0, H–C(1)); 2.11 (*d*, *J* = 11.0,

H–C(8)); 1.77 (*dtd*, J = 11.0, 4.0, 1.5, H–C(8)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 170.4 (*s*, CO), 149.6, 149.55, 146.1, 141.6 (4*s*, C(3), C(4), C(6), C(7)); 119.5 (*td*, ^1J(C,H) = 163, ^3J(C,H) = 3, *C*=C(3)); 106.7, 106.65, 104,4 (3*t*, ^1J(C,H) = 160, *C*=C(4), *C*=C(6), *C*=C(7)); 76.8 (*d*, ^1J(C,H) = 154, C(2)); 51.6 (*d*, ^1J(C,H) = 146, C(1)); 46.5 (*d*, ^1J(C,H) = 146, C(5)); 31.9 (*t*, ^1J(C,H) = 138, C(8)).

(±)-(4,6,7-Trimethylidenebicyclo[3.2.1]oct-2-en-3-yl)methyl (D$_3$)Acetate (**32**): Colourless oil, polymerized quickly. MS (70 eV): 219 (38), 177 (25), 175 (23), 160 (10), 155 (32), 141 (67), 129 (25), 128 (51), 46 (100).

Hydrolysis of **17** *in H$_2$O/Dioxane.* A mixture of **17** (45 mg, 0.18 mmol), dioxane (4 ml), H_2O (2 ml), and sat. aq. $NaHCO_3$ soln. (2 ml) was heated to 70° for 2 h. After addition of H_2O (25 ml), the mixture was extracted with CH_2Cl_2 (50 ml, 3 times), the combined org. extract washed with H_2O (30 ml, twice), dried ($MgSO_4$), and evaporated. The residue was purified by medium-pressure chromatography on silica gel (*Lobar*, col. *A*, 3.5 ml/min, CH_2Cl_2/pentane 4:1) giving 2 fractions. The 1st yielded 10 mg (32%) of **33** after crystallization from pentane at −25° and the 2nd 6 mg (19%) of **34**. *(1*RS,*2*RS,*5*SR*)-3,4,6,7-Tetramethylidenebicyclo[3.2.1]octan-2-*exo*-ol* (**33**): Colourless powder, polymerized quickly. M.p. 55–56°. IR ($CHCl_3$): 3600, 3090, 3020, 2990, 2960, 2880, 1425, 1010, 975, 920, 900. ^{1}H-NMR (360 MHz, $CDCl_3$, [rel. LIS, Eu(thd)$_3$]): 5.43 (*s*, [8.4], 1 H, H–CH=C(7) *cis* to C(6)); 5.333 (*s*, [10.0], 1 H, H–CH=C(6) *cis* to C(7)); 5.329 (*d*, J = 1.5, [24.2], 1 H, H–CH=C(3) *cis* to C(4)); 5.04 (*s*, [7.5], 1 H, H–CH=C(7) *trans* to C(6)); 5.02 (*d*, J = 1.5, [34.4], 1 H, H–CH=C(3) *trans* to C(4)); 4.98 (*d*, J = 1.5, [21.7], 1 H, H–CH=C(4) *cis* to C(3)); 4.96 (*s*, [11.3], 1 H, H–CH=C(6) *trans*, to C(7)); 4.80 (*d*, J = 1.5, [17.0], 1 H, H–CH=C(4) *trans* to C(3)); 4.25 (*m*, ^3J(H–C(1),H–C(2)) = 4.0, ^4J(H–C(2),H$_{anti}$–C(8)) = 1.5, [100], H–C(2)); 3.33 (*d*, J = 5.0, [21.4], H–C(5)); 2.99 (*dd*, ^3J(H–C(1), H$_{anti}$–C(8)) = 5.0, ^3J(H–C(1),H–C(2)) = 4.0, [58.7], H–C(1)); 2.19 (*d*, J = 12.0, [68.7], H–C(8) *syn* to OH); 1.76 (*dtd*, ^2J(H$_{anti}$–C(8),H–C(8)) = 12.0, ^3J(H$_{anti}$–C(8),H–C(1)) = ^3J(H$_{anti}$–C(8),H–C(5)) = 5.0, ^4J(H–C(2),H$_{anti}$–C(8)) = 1.5, [25.3], H–C(8) *anti* to OH); 1.64 (br. *s*, OH). MS (70 eV): 174 (100, $M^{+\cdot}$), 155 (55), 141 (75), 128 (72), 115 (62), 105 (25), 91 (88).

*(1*RS,*5*RS*)-(4,6,7-Trimethylidenebicyclo[3.2.1]oct-2-en-3-yl)methanol* (**34**): Colourless oil, polymerized quickly. IR ($CHCl_3$): 3600, 3090, 3020, 2990, 2960, 2880, 1630, 1600, 1425, 1010, 975, 920, 900. ^{1}H-NMR (360 MHz, $CDCl_3$ [rel. LIS, Eu(thd)$_3$]): 6.26 (*dd*, J = 7.0, 1.0, [43.2], H–C(2)); 5.43 (*s*, [7.2], 1 H, H–CH=C(6) *cis* to C(7)); 5.21 (*s*, [6.4], 1 H, H–CH=C(7) *cis* to C(6)); 5.16 (*s*, [8.4], 1 H, H–CH=C(6) *trans* to C(7)); 4.95 (*d*, ^5J(H–C(2),H–C(4)) = 1.0, [15.8], 1 H, H–CH=C(4) *trans* to C(3)); 4.89 (*s*, [6.7], 1 H, H–CH=C(7) *trans* to C(6)); 4.83 (*s*, [38.3], 1 H, H–CH=C(4) *cis* to C(3)); 4.26 (*m*, *AB*, $\nu_0\delta$ = 9.33, J = 13.0, [100], CH_2–C(3)); 3.48 (*d*, J = 4.0, [12.7], H–C(5)); 3.21 (*m*, J = 7.0, 3.5, [11.9], H–C(1)); 1.89 (*d*, J = 11.0, [15.4], H–C(8) *syn* to OH); 1.85 (*m*, J = 11.0, 4.0, 3.5, 1.0, [9.3], H–C(8) *anti* to OH). MS (70 eV): 174 (25, $M^{+\cdot}$), 156 (5), 141 (12), 128 (25), 115 (16), 105 (9), 91 (25), 77 (16), 58 (100).

Hydrolysis of **17** *in (CF$_3$)$_2$CHOH/H$_2$O 2:1.* A mixture of **17** (128 mg, 0.5 mmol), 2,6-lutidine (= 2,6-dimethylpyridine; 30 µl), $(CF_3)_2CHOH$ (4 ml), and H_2O (2 ml) was stirred at 20° for 10 min. CH_2Cl_2 (30 ml) and H_2O (10 ml) were added to the dark-brown soln. The aq. layer was extracted with CH_2Cl_2 (20 ml, 3 times), the combined org. phase washed with H_2O (30 ml), 1N HCl (30 ml), sat. aq. $NaHCO_3$ soln. (30 ml, twice), and H_2O (30 ml, twice), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (10 g, CH_2Cl_2/pentane 4:1) yielding 16 mg (18%) of **34** which crystallized from pentane at −25°.

Acetolysis of **18**. To a soln. of **18** (25.6 mg, 0.065 mmol) in $CHCl_3$ (0.2 ml), 0.179M AcONa in abs. AcOH (0.4 ml) was added. The mixture was degassed on the vacuum line (freeze/thaw cycles) and sealed in a *Pyrex* tube *in vacuo*. After heating to 65° for 3 h, the tube was cooled in liq. N_2 and opened. CH_2Cl_2 (20 ml) was added the soln. washed with ice-cold H_2O (30 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was purified by filtration through a short column of silica gel (5 g, CH_2Cl_2) yielding 18 mg (76%) of **37** (see below) after crystallization from CH_2Cl_2/hexane at −65°.

*Tricarbonyl[(1*RS,*2*RS,*3*RS,*4*SR,*5*SR*)-C,*3,4*,C-η-*(3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-*exo*-yl acetate)]iron* (**37**). To a soln. of AcONa (55 mg, 0.67 mmol) in anh. $(CF_3)_2CHOH$ (2 ml), **18** (36 mg, 0.092 mmol) was added and the mixture stirred at 20° for 90 min. CH_2Cl_2 (50 ml) and H_2O (50 ml) were added. The aq. layer was extracted with CH_2Cl_2 (30 ml, twice), the combined org. phase washed with ice-cold H_2O (30 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was purified by filtration on a short column of silica gel (5 g, CH_2Cl_2). Crystallization from CH_2Cl_2/hexane at −25° gave 29 mg (85%) of yellowish crystals. M.p. 127–128°. UV (isooctane): 205 (22800), 310 (1600). IR (KBr): 3080, 3060, 2960, 2940, 2870, 2030, 1970, 1955, 1925, 1725, 1365, 1220. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.53, 5.35, 5.13, 4.84 (4*s*, 4 H); 5.45 (*d*, J = 2.5, H–C(2)); 3.29 (*d*, J = 3.5, H–C(5)); 3.23 (*m*, J = 4.5, 2.5, H–C(1)); 2.32 (*d*, J = 11.5, H–C(8) *syn* to AcO); 2.15 (*s*, CH_3COO); 1.95 (*ddd*, J = 11.5, 4.5, 3.5, H–C(8) *anti* to AcO); 1.81, 1.52, 0.37, −0.19 (4*d*, J = 3.0, 4 H). MS (70 eV): 356 (2, $M^{+\cdot}$), 328 (9), 300 (42), 272 (100), 212 (44), 156 (31), 141 (44), 128 (35), 115 (42). Anal. calc. for $C_{17}H_{16}FeO_5$ (356.165): C 57.33, H 4.53; found: C 57.46, H 4.53.

Hydrolysis of **18'** *in Dioxane/H$_2$O 16:9.* A mixture of **18'** (300 mg, 0.64 mmol), dioxane (8 ml), H_2O (3 ml), and

sat. aq. $NaHCO_3$ soln. (1.5 ml) was heated to 70° for 8 h. After cooling to 0°, the mixture was extracted with CH_2Cl_2 (30 ml, twice), the combined extract washed with H_2O (10 ml, twice), dried ($MgSO_4$), and evaporated. The residue was purified by filtration through a short column of silica gel (10 g, CH_2Cl_2). After crystallization from CH_2Cl_2/hexane at −25°, 120 mg (60%) of *tricarbonyl[(1RS,2RS,3RS,4SR,5SR)-C,3,4,C-η-(3,4,6,7-tetramethylidenebicyclo[3.2.1]octan-2-exo-ol)]iron* (**38**) were obtained, yellowish crystals. M.p. 115.5–116° (dec.). UV (95% EtOH): 204 (21900), 223 (sh, 17300), 310 (1420). IR (KBr): 3340, 2995, 2960, 2945, 2045, 1995, 1970, 1950. ^{1}H-NMR (80 MHz, $CDCl_3$, [rel. LIS, $Eu(thd)_3$]): 5.48 (*s*, [9.1], 1 H); 5.2 (*s*, [8.2], 1 H); 5.1 (*s*, [9.3], 1 H); 4.8 (*s*, [10.6], 1 H); 4.3 (*m*, [100], H–C(2)); 3.23 (*m*, J = 4.5, [64.5], [20.8], H–C(1) and H–C(5), resp.); 2.35 (*m*, OH); 2.34 (*d*, J = 11.0, [64.1], H–C(8) *syn* to OH); 1.9 (*dt*, J = 11.0, 4.5, [24.8], H–C(8) *anti* to OH); 1.78 (*d*, J = 2.5, [15.6], 1 H, H–CH=C(4) *trans* to C(3)); 1.53 (*d*, J = 2.5, [45.3], 1 H, H–CH=C(3) *trans* to C(4)); 0.35 (*d*, J = 2.5, [19.2], 1 H, H–CH=C(4) *cis* to C(3)); −0.18 (*d*, J = 2.5, [30.2], 1 H, H–CH=C(3) *cis* to C(4)). MS (70 eV): 314 (5, $M^{+\cdot}$), 286 (16), 258 (43), 230 (100), 212 (5), 158 (21). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.39, H 4.44.

Hydrolysis of **18** *in* $(CF_3)_2CHOH/H_2O$ *2:1.* A soln. of **18** (35 mg, 0.089 mmol) in $(CF_3)_2CHOH$ (4 ml), H_2O (2 ml), and 2,6-lutidine (30 µl) was stirred at 20° for 18 h. After addition of CH_2Cl_2 (50 ml) and H_2O (50 ml), the aq. layer was extracted with CH_2Cl_2 (30 ml, twice), the combined org. phase washed with H_2O (20 ml), 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml, twice), and H_2O (20 ml), dried ($MgSO_4$), and evaporated. The residue was filtered on silica gel (5 g, CH_2Cl_2). Crystallization from CH_2Cl_2/hexane at −25° gave 24 mg (85%) of pure **38**.

Acetolysis of **19**. Same procedure as for the acetolysis of **18**, using 19.2 mg (0.049 mmol) of **19**: 17 mg (74%) of **39** as a yellowish oil. It was transformed into **40** (see below) on treatment with abs. MeOH (10 ml) containing anh. K_2CO_3 (100 mg) at 20° for 1 h.

Hydrolysis of **19** *in* $(CF_3)_2CHOH/H_2O$ *2:1.* A mixture of **19** (32 mg, 0.082 mmol), $(CF_3)_2CHOH$ (2 ml), H_2O (1 ml), and 2,6-lutidine (30 µl) was stirred at 20° for 7 h. CH_2Cl_2 (30 ml) and H_2O (30 ml) were added. The aq. layer was extracted with CH_2Cl_2 (30 ml, twice), the combined org. washed successively with 1N HCl (20 ml, twice), sat. aq. $NaHCO_3$ soln. (20 ml, twice), and H_2O (20 ml), dried ($MgSO_4$), and evaporated. The residue was filtered through a short column of silica gel (5 g, CH_2Cl_2). After crystallization from CH_2Cl_2/hexane at −25°, 22 mg (86%) of *tricarbonyl[(1RS,2SR,3SR,4RS,5SR)-C,3,4,C-η-(3,4,6,7-tetramethylidenebicyclo[3.2.1]octan-2-endo-ol)]-iron* (**40**) were obtained, yellowish crystals. M.p. 74–76°. UV (95% EtOH): 205 (24800), 218 (sh, 22900), 306 (2180). IR (KBr): 3300, 2960, 2050, 1975, 1955, 1050, 1040, 900, 890. ^{1}H-NMR (360 MHz, $CDCl_3$, [rel. LIS, $Eu(thd)_3$]): 5.80 (*s*, [20.3], 1 H); 5.48 (*s*, [15.4], 1 H); 5.32 (*s*, [34.2], 1 H); 5.16 (*s*, [14.9], 1 H); 4.68 (br. *dd*, ^3J(H–C(2),OH) = 11.5, ^3J(H–C(1),H–C(2)) = 5.5, ^4J(H–C(2),H_{cis}–CH=C(3)) = 0.75, [100], H–C(2)); 3.26 (*t*, J = 5.5, [50.2], H–C(1)); 2.98 (*d*, J = 4.5, [20.3], H–C(5)); 2.39 (*d*, J = 11.5, OH); 2.24 (*d*, J = 11.5, [24.4], H–C(8) *syn* to C(2)); 2.12 (*ddd*, J = 11.5, 5.5, 4.5, [17.8], H–C(8) *anti* to C(2)); 2.03 (*d*, J = 3.0, [56.4], 1 H, H–CH=C(3) *trans* to C(4)); 1.73 (*d*, J = 2.0, [16.4], 1 H, H–CH=C(4) *trans* to C(3)); 0.22 (*dd*, J = 3.0, 0.75, [35.2], 1 H, H–CH=C(3) *cis* to C(4)); 0.10 (*d*, J = 2.0, [21.9], 1 H, H–CH=C(4) *cis* to C(3)). MS (70 eV): 314 (10, $M^{+\cdot}$), 286 (18), 258 (17), 230 (100), 212 (48), 156 (33), 141 (39), 128 (38), 115 (48), 105 (14), 91 (61). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.26, H 4.58.

Acetolysis of **20**. Same procedure as for the acetolysis of **18**, using 19.2 mg (0.049 mmol) of **20**: 16 mg (68%) of **43** as a yellow oil. Its transesterification (abs. MeOH, K_2CO_3, 20°, 1 h) gave pure **44**.

Hydrolysis of **20** *in* $(CF_3)_2CHOH/H_2O$ *2:1.* A mixture of **20** (21 mg, 0.054 mmol), $(CF_3)_2CHOH$ (2 ml), H_2O (1 ml), and 2,6-lutidine (30 µl) was heated to 60° for 28 h. After cooling to 20°, CH_2Cl_2 (50 ml) and H_2O (50 ml) were added. The aq. layer was extracted with CH_2Cl_2 (30 ml, twice), the combined org. phase washed with 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml, twice), and H_2O (20 ml), dried ($MgSO_4$), and evaporated. The residue was filtered through a short column of silica gel (5 g, CH_2Cl_2). After crystallization from CH_2Cl_2/hexane at −25°, 13 mg (77%) of pure *tricarbonyl[(1RS,2SR,5SR,6SR,7RS)-C,6,7,C-η-(3,4,6,7-tetramethylidenebicyclo[3.2.1]octan-2-exo-ol)]iron* (**44**) were obtained, yellowish crystals. M.p. 134–135° (dec.). IR (KBr): 3280, 2940, 2050, 1985, 1970, 1955, 1010, 915, 900, 885. ^{1}H-NMR (360 MHz, $CDCl_3$, [rel. LIS, $Eu(thd)_3$]): 5.79 (*s*, [27.2], 1 H, H–CH=C(3) *cis* to C(4)); 5.37 (*s*, [42.3], 1 H, H–CH=C(3) *trans* to C(4)); 5.23 (*s*, [20.7], 1 H, H–CH=C(4) *cis* to C(3)); 4.82 (*s*, [16.8], 1 H, H–CH=C(4) *trans* to C(3)); 4.47 (*m*, [100], H–C(2)); 3.35 (*d*, J = 5.0, [21.4], H–C(5)); 3.0 (*dd*, J = 5.0, 3.0, [64.4], H–C(1)); 2.82 (*m*, J = 11.5, 5.0, 5.0, 1.5, [23.9], H–C(8) *anti* to OH); 2.66 (*d*, J = 11.5, [69.9], H–C(8) *syn* to OH); 1.95 (*d*, J = 3.0, OH); 1.89 (*d*, J = 3.0, [11.4], 1 H); 1.77 (*d*, J = 3.0, [8.3], 1 H); 0.36 (*d*, J = 3.0, [9.5], 1 H); 0.23 (*d*, J = 3.0, [7.8], 1 H). MS (70 eV): 286 (11, $M^{+\cdot}$ − 28), 258 (39), 230 (100), 212 (5), 200 (9). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.48, H 4.49.

Acetolysis of **21**. Same procedure as for the acetolysis of **18** using 19.2 mg (0.049 mmol) of **21** (heating to 65° for 4 h). Column chromatography on silica gel (5 g, CH_2Cl_2) followed by medium-pressure chromatography (*Lobar, Merck*, SiO_2 *LiChroprep Si 60*, 40–63 µm, CH_2Cl_2/hexane 1:2, 4 ml/min) gave 6 mg (34%) of **50**, 4 mg (23%) of **49**, and 4 mg (23%) of **51**.

Tricarbonyl[(1RS,2RS,4RS,5SR,6RS)-C,5,6,C-η-(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl acetate)]-iron (**49**). Ac_2O (300 mg) was added to a soln. of **28** [19] (19 mg, 0.06 mmol) in pyridine (0.5 ml) maintained at 0° under Ar. The mixture was stirred at 20° for 7 h. CH_2Cl_2 (50 ml) was added, the soln. washed successively with H_2O (20 ml), 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml), and H_2O (20 ml, twice); dried ($MgSO_4$), and evaporated. The residue was filtered through a column of silica gel (5 g, CH_2Cl_2/hexane 1:1). Crystallization from CH_2Cl_2/hexane at −25° yielded 18 mg (84%) of yellowish crystals. M.p. 106.5–107°. UV (isooctane): 208 (24300), 219 (23000), 252 (sh, 12100), 308 (2920). UV (95% EtOH): 204 (24900), 220 (sh, 22900), 253 (sh, 11400), 309 (2890). IR (KBr): 3080, 3040, 2980, 2960, 2040, 1985, 1960, 1730, 1430, 1370, 1230, 1210, 1180, 1135, 1030, 890. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.63, 5.51, 5.11, 5.11 (4*s*, 4 H); 4.92 (*m*, ^3J(H–C(2),H_{anti}–C(3)) = 9.3, ^3J(H–C(1),H–C(2)) = 3.3, ^3J(H–C(2),H_{syn}–C(3)) = 3.0, H–C(2)); 3.46 (*d*, *J* = 3.3, H–C(1)); 3.23 (*dd*, ^3J(H_{anti}–C(3),H–C(4)) = 3.0, ^3J(H_{syn}–C(3)),H–C(4)) = 2.5, H–C(4)); 2.25 (*ddd*, *J* = 13.5, 9.3, 3.0, H–C(3) *'anti'* to OAc); 2.05 (*s*, CH_3COO); 1.86, 1.82, 0.32, 0.28 (4*d*, *J* = 2.5, 4H); 1.76 (*ddd*, *J* = 13.5, 3.0, 2.5, H–C(3) *'syn'* to OAc). MS (70 eV): 356 (7, $M^{+\cdot}$), 328 (20), 300 (20), 272 (100), 212 (81), 174 (41), 156 (45), 141 (59), 128 (69), 115 (79), 91 (45). Anal. calc. for $C_{17}H_{16}FeO_5$ (356.187): C 57.33, H 4.33; found: C 57.23, H 4.62.

*Tricarbonyl[(1RS,2SR,5SR,6RS,7SR)-C,6,7,C-η-(3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-*exo*-yl acetate)]iron* (**50**): Yellowish oil. IR ($CHCl_3$): 3020, 3000, 2960, 2050, 1980, 1735, 1605, 1440, 1375, 1240, 1040, 1010, 900. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.65 (*dd*, *J* = 3.5, 1.5, H–C(2)); 5.60, 5.31, 5.23, 4.96 (4*d*, *J* = 1.5, 4H); 3.11 (*d*, *J* = 4.5, H–C(5)); 2.80 (*dd*, *J* = 4.5, 3.5, H–C(1)); 2.34 (*d*, *J* = 11.5, H–C(8) *syn* to AcO); 2.27 (*m*, *J* = 11.5, 4.5, 4.5, 1.5, H–C(8) *anti* to AcO); 2.12 (*s*, CH_3COO); 1.97, 1.83, 0.44, 0.35 (4*d*, *J* = 2.5, 4H). MS (70 eV): 356 (10, $M^{+\cdot}$), 328 (28), 300 (11), 272 (100), 212 (70), 156 (26), 141 (32), 128 (23), 115 (33).

Tricarbonyl[(1RS,5SR,6RS,7SR)-C,6,7,C-η-(4,6,7-trimethylidenebicyclo[3.2.1]oct-2-en-3-yl)methyl acetate]iron (**51**): Yellowish oil. IR ($CHCl_3$): 3040, 2970, 2060, 1980, 1740, 1605, 1450, 1375, 1060, 1035, 960, 910. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.51 (br. *d*, *J* = 6.5, H–C(2)); 5.15 (*d*, ^5J(H–C(2),H–CH=C(4)) = 1.5, 1 H, H–CH=C(4) *trans* to C(3)); 5.00 (*s*, 1 H, H–CH=C(4) *cis* to C(3)); 4.72 (*AB*, *J* = 1.0, J_{AB} = 13.0, $\nu_o\delta$ = 26.3, CH_2–C(3)); 3.21 (*d*, *J* = 4.5, H–C(5)); 2.97 (*dd*, *J* = 6.5, 4.5, H–C(1)); 2.42 (*m*, *J* = 10.0, 4.5, 4.5, 1.0, H–C(8) *anti* to AcO); 2.15 (*d*, *J* = 10.0, H–C(8) *syn* to AcO); 2.10 (*s*, CH_3COO); 1.96, 1.90, 0.45, 0.38 (4*d*, *J* = 2.5, 4 H). MS (70 eV): 356 (19, $M^{+\cdot}$), 328 (50), 300 (100), 272 (62), 212 (47), 156 (27), 141 (32), 128 (26), 115 (36), 104 (11), 91 (24).

Hydrolysis of **21** *in* $(CF_3)_2CHOH/H_2O$ *2:1*. Same procedure as for the hydrolysis of **19**, using 19 mg (0.048 mmol) of **21**. The crude reaction mixture was separated by medium-pressure chromatography (*Lobar, Merck*, SiO_2 *LiChroprep Si 60*, 40–63 μm, CH_2Cl_2/petroleum ether 4:1,5–6 ml/min) giving first 11 mg (72%) of **52** (after crystallization from CH_2Cl_2/hexane at −25°) and then 3.5 mg (23%) of **53** (after crystallization from CH_2Cl_2/hexane at −25°). *Tricarbonyl[(1RS,2SR,5SR,6RS,7SR)-C,6,7,C-η-(3,4,6,7-tetramethylidenebicyclo[3.2.1]octan-2-*exo*-ol)]iron* (**52**): Yellowish crystals. M.p. 121–122°. IR (KBr): 3610, 3800, 3020, 2990, 2960, 2880, 2050, 1980, 1420, 1010, 975, 920, 900. ^{1}H-NMR (360 MHz, $CDCl_3$, [rel. LIS, Eu(thd)$_3$]): 5.53 (*d*, *J* = 1.5, [24.5], 1 H, H–CH=C(3) *cis* to C(4)); 5.26 (*d*, *J* = 1.5, [21.7], 1 H, H–CH=C(4) *cis* to C(3)); 5.18 (*d*, *J* = 1.5, [35.7], 1 H, H–CH=C(3) *trans* to C(4)); 4.98 (*d*, *J* = 1.5, [17.7], 1 H, H–CH=C(4) *trans* to C(3)); 4.56 (*d*, *J* = 3.0, [100], H–C(2)); 3.12 (*d*, *J* = 5.0, [21.8], H–C(5)); 2.76 (*dd*, *J* = 4.5, 3.0, [54.9], H–C(1)); 2.42 (*d*, *J* = 11.5, [65.7], H–C(8) *syn* to OH); 2.27 (*m*, *J* = 11.5, 5.0, 4.5, 1.5, [25.7], H–C(8) *anti* to OH); 1.94 (*dd*, ^2J = 2.5, ^4J = 0.7, [7.3], 1 H); 1.83 (*dd*, ^2J = 2.5, ^4J = 0.7, [11.4], 1 H); 0.42 (*d*, *J* = 2.5, [10.7], 1 H); 0.33 (*d*, *J* = 2.5, [11.5], 1 H). MS (70 eV): 314 (16, $M^{+\cdot}$), 286 (66), 258 (63), 230 (100), 212 (24), 200 (5). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.28, H 4.54.

Tricarbonyl[(1RS,5SR,6RS,7SR)-C,6,7,C-η-(4,6,7-trimethylidenebicyclo[3.2.1]oct-2-ene-3-methanol)]-iron (**53**). Yellowish crystals. M.p. 118–120°. IR ($CHCl_3$): 3620, 3020, 2960, 2050, 1975, 1450, 1270. ^{1}H-NMR (360 MHz, $CDCl_3$ [rel. LIS, Eu(thd)$_3$]): 6.51 (*m*, ^3J = 6.5, ^5J = 1.5, [52.6], H–C(2)); 5.16 (*d*, *J* = 1.5, [17.7], 1 H, H–CH=C(4) *trans* to C(3)); 5.09 (*s*, [43.5], 1 H, H–CH=C(4) *cis* to C(3)); 4.35 (*m*, [100], CH_2–C; 3.23 (*m*, ^3J = 4.0, ^4J = 0.7, [15.3], H–C(5)); 3.0 (br. *dd*, ^3J = 6.5, ^3J = 4.0, ^4J = 0.7, [14.5], H–C(1)); 2.45 (*td*, *J* = 10.0, 4.0, 1.0, [11.8], H–C(8) *anti* to OH); 2.16 (*d*, *J* = 10.0, [10.1], H–C(8) *syn* to OH); 1.98 (*dd*, *J* = 2.5, 0.7, [8.9], 1H); 1.92 (*dd*, *J* = 2.5, 0.7, [7.7], 1H); 0.47 (*d*, *J* = 2.5, [8.9], 1H); 0.39 (*d*, *J* = 2.5, [9.5], 1H). MS (70 eV): 314 (23, $M^{+\cdot}$), 286 (65), 258 (100), 230 (79), 212 (36), 174 (23), 156 (35), 141 (48), 128 (71), 115 (61), 105 (25), 91 (90). Anal. calc. for $C_{15}H_{14}FeO_4$ (314.127): C 57.36, H 4.49; found: C 57.20, H 4.45.

Acetolysis of **22**. Same procedure as for the acetolysis of **18**, using 26 mg (0.049 mmol) of **22**: 19 mg (80%) of **58**, described in [28].

Buffered Hydrolysis of **22** *in Dioxane/*$D_2{}^{18}O$. A mixture of anh. dioxane (140 μl), $D_2{}^{18}O$ (70 μl), $NaHCO_3$ (0.5 mg), and **22** (3.5 mg, 0.007 mmol) in a flame-dried flask was heated to 60° for 150 min under Ar. After cooling to 20°, dioxane (1 ml) was added. The soln. was analyzed by MS, and the signals were compared with those obtained for a reaction mixture using H_2O instead of $D_2{}^{18}O$, demonstrating incorporation of ^{18}O in **29**.

Hydrolysis of **22** *in* $(CF_3)_2CHOH/H_2O$ *2:1.* A mixture of **22** (78 mg, 0.147 mmol), $(CF_3)_2CHOH$ (8 ml), H_2O (4 ml), and 2,6-lutidine (30 µl) was stirred at 20° for 75 min. CH_2Cl_2 (30 ml) and H_2O (30 ml) were added. The aq. layer was extracted with CH_2Cl_2 (30 ml, 3 times), the combined extract washed with H_2O (30 ml), 1N HCl (30 ml), sat. aq. $NaHCO_3$ soln. (30 ml, twice), and H_2O (30 ml), dried ($MgSO_4$), and evaporated. The residue was filtered through a short column of silica gel (5 g, CH_2Cl_2). Crystallization from CH_2Cl_2/hexane gave 55 mg (83%) of trans-*µ-[(1*RS,*2*SR,*3*SR,*4*RS,*5*RS,*6*RS,*7*SR*)*-C,3,4,C-η:C,6,7,C-η-(3,4,6,7-tetramethylidenebicyclo[3.2.1]-octan-2-*exo-ol)]bis(tricarbonyliron)* (**59**) as yellow crystals. M.p. 143.5–144°. IR (KBr): 3600, 3060, 3000, 2980, 2960, 2910, 2040, 1980, 1450, 1245, 1125, 1010, 960. ^{1}H-NMR (360 MHz, $CDCl_3$, [rel. LIS, $Eu(thd)_3$]): 4.65 (*m*, [100], H–C(2)); 3.13 (*d*, *J* = 4.0, [21.4], H–C(5)); 2.98 (br. *d*, *J* = 3.5, [67.4], H–C(1)); 2.73 (*d*, *J* = 11.5, [62.5], H–C(8) *syn* to OH); 2.65 (*m*, *J* = 11.5, 4.0, 3.5, [27.1]. H–C(8) *anti* to OH); 2.4 (*d*, *J* = 4.0, OH); 2.13 (*d*, *J* = 2.5, [9.0], 1 H); 1.95 (*d*, *J* = 3.0, [15.7], 1 H); 1.88 (*d*, *J* = 3.5, [12.1], 1 H'); 1.73 (*d*, *J* = 3.0, [46.3], 1 H); 0.58 (3*d*, *J* = 3.0, 2.5, 3.5, resp., [21.5], [12.1], [11.1], resp., 3 H); 0.1 (*d*, *J* = 3.0, [30.1], 1 H). MS (70 eV): 454 (5, $M^{+\cdot}$), 426 (36), 398 (84), 370 (83), 342 (8), 314 (94), 286 (100), 258 (25), 230 (61). Anal. calc. for $C_{18}H_{14}Fe_2O_7$ (454.01): C 47.62, H 3.11; found: C 47.72, H 3.17.

trans-*µ-[(1*RS,*2*SR,*3*SR,*4*RS,*5*RS,*6*RS,*7*SR*)*-C,3,4,C-η:C,6,7,C-η-(3,4,6,7-Tetramethylidenebicyclo-[3.2.1]oct-2-exo-*yl acetate)]bis(tricarbonyliron)* (**60**). A mixture of **22** (23 mg, 0.043 mmol), AcONa (29 mg, 0.35 mmol), and anh. $(CF_3)_2CHOH$ (3 ml) was stirred at 20° for 1 h. CH_2Cl_2 (30 ml) and H_2O (30 ml) were added. The aq. layer was extracted with CH_2Cl_2 (30 ml, twice), the combined org. extracts washed with H_2O (30 ml), sat. aq. $NaHCO_3$ soln. (30 ml), and H_2O (30 ml, twice), dried ($MgSO_4$), and evaporated. The residue was filtered through silica gel (10 g, CH_2Cl_2/hexane 1:1). Crystallization from pentane at –20° gave 15 mg (70%) of yellowish crystals. M.p. 120.5–121°. UV (isooctane): 227 (19800), 258 (6500), 305 (2800). UV (95% EtOH): 206 (23500), 283 (3800), 305 (3200). IR (KBr): 3070, 3000, 2980, 2960, 2950, 2045, 2030, 1995, 1990, 1980, 1975, 1960, 1945, 1920, 1740, 1450, 1440, 1370, 1235, 1215, 1015. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.79 (br. *d*, *J* = 1.0, H–C(2)); 3.17 (br. *d*, *J* = 3.0, H–C(5)); 2.92 (br. *s*, H–C(1)); 2.69 (*m*, CH_2(8)); 2.18 (*s*, CH_3COO); 2.19, 0.63 (2*d*, *J* = 2.7, 2 H); 1.95, 1.68, 0.57, 0.03 (4*d*, *J* = 3.0, 4 H); 1.90, 0.60 (2*d*, *J* = 3.5, 2 H). MS (70 eV): 496 (4, $M^{+\cdot}$), 468 (20), 440 (24), 412 (32), 384 (12), 356 (22), 328 (100), 241 (57), 213 (81), 196 (22), 172 (34), 156 (18), 141 (21). Anal. calc. for $C_{20}H_{16}Fe_2O_8$ (495.84): C 48.43, H 3.25; found: C 48.48, H 3.46.

trans-*µ-[(1*RS,*2*SR,*3*SR,*4*RS,*5*RS,*6*RS,*7*SR*)*-C,3,4,C-η:C,6,7,C-η-(3,4,6,7-Tetramethylidenebicyclo-[3.2.1]oct-2-exo-*yl benzoate)]bis(tricarbonyliron)* (**61**). A mixture of **22** (62 mg, 0.16 mmol), potassium benzoate (150 mg, 0.94 mmol), and anh. $(CF_3)_2CHOH$ (7 ml) was stirred at 20° for 90 min. CH_2Cl_2 (50 ml) and H_2O (50 ml) were added. The aq. layer was extracted with CH_2Cl_2 (50 ml, twice), the combined org. phase washed with H_2O (30 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was filtered through silica gel (5 g, CH_2Cl_2). Crystallization from hexane at –20° gave 55 mg (83%), yellow crystals. M.p. 167–168°. UV (isooctane): 209 (44100), 224 (45000), 280 (6100). UV (95% EtOH): 208 (46000), 224 (44100), 280 (6000). IR (KBr): 3080, 3000, 2970, 2045, 2035, 2000, 1990, 1985, 1980, 1935, 1715, 1270, 1250, 710. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.16 (*dd*, *J* = 7.5, 1.5, 2 H); 7.67 (*tt*, *J* = 7.5, 1.5, 1 H); 7.53 (*t*, *J* = 7.5, 2 H); 6.06 (*d*, *J* = 1.5, H–C(2)); 3.24 (*d*, *J* = 4.0, H–C(5)); 3.08 (*dd*, *J* = 4.5, 1.5, H–C(1)); 2.84 (*d*, *J* = 11.5, 1 H), 2.75 (*m*, *J* = 11.5, 4.5, 4.0, 1 H, CH_2(8)); 2.27, 0.69 (2*d*, *J* = 2.7, 2 H); 2.0, 1.79, 0.62, 0.09 (4*d*, *J* = 3.0, 4 H); 1.94, 0.64 (2*d*, *J* = 3.5, 2 H). MS (70 eV): 558 (1, $M^{+\cdot}$), 530 (11), 502 (32), 474 (49), 446 (4), 418 (9), 390 (100). Anal. calc. for $C_{25}H_{18}Fe_2O_8$ (558.12): C 53.80, H 3.25; found: C 53.67, H 3.34.

trans-*µ-[(1*RS,*2*SR,*3*SR,*4*RS,*5*RS,*6*RS,*7*SR*)*-C,3,4,C-η:C,6,7,C-η-(3,4,6,7-tetramethylidene-2-(2,2,2-tri-fluoro-1-(trifluoromethyl)ethoxy)bicyclo[3.2.1]octane)]bis(tricarbonyliron)* (**62**). A mixture of **22** (28 mg, 0.053 mmol), 2,6-lutidine (0.25 ml), and anh. $(CF_3)_2CHOH$ (2.25 ml) was stirred at 20° for 7 min, CH_2Cl_2 (30 ml) and H_2O (20 ml) were added. The aq. layer was extracted with CH_2Cl_2 (30 ml, twice), the combined org. phase washed with 1N HCl (20 ml, twice), sat. aq. $NaHCO_3$ soln. (20 ml, twice), and H_2O (20 ml), dried ($MgSO_4$), and evaporated. The residue was filtered through silica gel (5 g, CH_2Cl_2). Crystallization from CH_2Cl_2/hexane at –25° yielded 26 mg (82%), yellow crystals. M.p. 145.5–146°. UV (95% EtOH): 206 (45600), 222 (sh, 35200), 308 (4050). IR (KBr): 3080, 3020, 2990, 2980, 2960, 2050, 2040, 2000, 1990, 1970, 1935, 1370, 1290, 1215, 1195, 1190, 1135, 1120, 1105. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.58 (*m*, ^3J = 1.5, ^4J = 1.0, H–C(2)); 4.41 (*sept.*, *J* = 5.7, $(CF_3)_2CH$); 3.18 (*d*, *J* = 4.0, H–C(5)); 2.97 (*dd*, *J* = 4.5, 1.5, H–C(1)); 2.78 (*d*, *J* = 11.5, 1 H), 2.69 (*m*, ^2J = 11.5, ^3J = 4.5, 4.0, ^4J = 1.0, 1 H, CH_2(8)); 2.09 (*dd*, ^2J = 2.7, ^4J = 0.7, 1 H, H–CH=C(6) *trans* to C(7)); 1.98, 0.65 (2*d*, *J* = 3.0, CH_2=C(4)); 1.91 (*dd*, ^2J = 3.5, ^4J = 0.5, 1 H, H–CH=C(7) *trans* to C(6)); 1.79, 0.60, 0.17 (3*d*, *J* = 3.5, 3 H); 0.59 (*d*, *J* = 2.7, 1 H). MS (70 eV): 604 (0.4, $M^{+\cdot}$), 576 (2), 548 (8), 520 (13), 492 (1), 464 (26), 436 (41), 380 (25), 285 (11), 269 (8), 241 (11), 232 (22), 212 (41), 57 (100). Anal. calc. for $C_{21}H_{14}F_6Fe_2O_7$ (604.043): C 41.76, H 2.34; found: C 41.80, H 2.35.

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