114. Synthesis and *Diels-Alder* Reactivity of 5,6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octanol and -octanone. Selective Oxidations of the Corresponding Bis(irontricarbonyl) Complexes[1])

by **Raphy Gabioud** and **Pierre Vogel**[2])

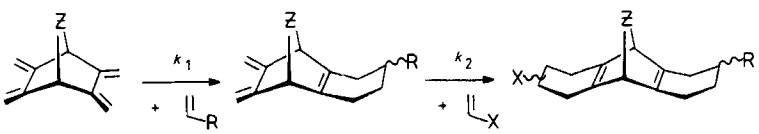
Institut de chimie organique de l'Université, 2, rue de la Barre, CH-1005 Lausanne

(24.III.83)

Summary

Hydroboration of the *syn,anti*-$[Fe(CO)_3]_2$ double complex **24** of the readily available 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octene (**22**) gave the corresponding doubly complexed 2-bicyclo[2.2.2]octanol **25**. CrO_3-oxidation furnished ketone **27**. The *syn*-$Fe(CO)_3$-groups in **25** and **27** were oxidized selectively with trimethylamine oxide and yielded the corresponding *anti*-$Fe(CO_3)$-monocomplexed tetraenes **26** and **28**. The *anti*-$Fe(CO)_3$-group in **28** could be removed, and 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone (**11**) was obtained. $NaBH_4$-reduction of **11** afforded tetraenol **10**. TCE-cycloadditions to **10** and **11** (k_1) were at least 10 times as fast as those (k_2) to the corresponding monoadducts **35/36** and **34**, respectively. This *Diels-Alder* reactivity difference vanishes ($k_1 \approx k_2$) with methyl propynoate. The latter dienophile added to the *anti*-$Fe(CO)_3$-monocomplexed tetraenone **28** with *'para'*-regioselectivity.

Introduction. – The 2,3,5,6-tetramethylidenebicyclo[2.2.n]alkanes **1** are very attractive starting materials for the preparation of polycyclic, polyfunctional systems by two successive *Diels-Alder* additions with different dienophiles [2]. The 2,3,5,6-



1 **2** **3**

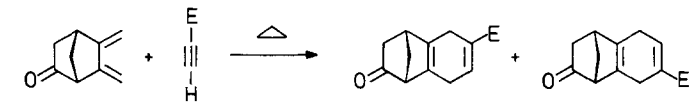
[1]) Interaction between non-conjugated chromophores, Part 20. Part 19, see [1].

[2]) Author to whom correspondence should be addressed.

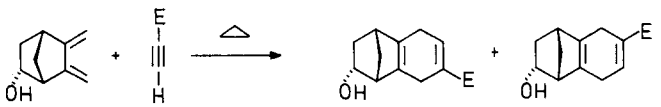
tetramethylidene-7-oxabicyclo[2.2.1]heptane (**1**, Z=O) [3] can be used to prepare various anthracycline derivatives [4]. The principle of our strategy rests upon the fact that the rates of the *Diels-Alder* additions of **1** (k_1) are significantly higher than those (k_2) of the cycloadditions of the corresponding monoadducts **2** [5].

We have shown that the rate-constant ratio k_1/k_2 depends on the nature of the dienophile and of the bridge Z in **1** [6]. The versatility of our strategy would be dramatically improved if the two cycloadditions could be stereoselective, *i.e.* if the substitution pattern of the two cyclohexene rings in the bis-adducts **3** could be controlled.

The *Diels-Alder* reactivity of an exocyclic s-*cis*-butadiene moiety grafted onto norbornane and bicyclo[2.2.2]octene systems can be affected by remote substitution of the bicyclic skeleton [7] [8][3]). For instance, the addition of the 5,6-dimethylidene-2-norbornanone (**4**) to methyl propynoate gives preferentially the *'para'*-adduct **5**, whereas 5,6-dimethylidene-2*endo*-norbornanol (**7**) yields preferentially the *'meta'*-adduct **8** [7] (minor products: **6** and **9**, resp.). These findings have encouraged us



4 **5** (major) **6** (minor)



7 **8** (major) **9** (minor)

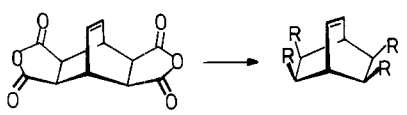
E=$COOCH_3$

to design new double exocyclic dienes **1** in which the bridge Z would be substituted in a way to control the stereo- and regioselectivity of the two successive cycloadditions with k_1 and k_2, respectively. We report here the syntheses of 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octyl derivatives **10** and **11** and of the corresponding irontricarbonyl complexes. We discuss also our preliminary results on their *Diels-Alder* reactivity.

10 **11**

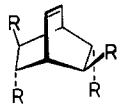
[3]) An exocyclic butadiene moiety means that each double bond is in an exocyclic position on the ring skeleton. The IUPAC name of 'norbornane' is '8,9,10-trinorbornane'.

Synthesis of the exocyclic tetraenes. – Tetraethyl bicyclo[2.2.2]oct-7-ene-2*syn*,3*syn*,5*syn*,6*syn*-tetracarboxylate (**13**) was obtained from the corresponding bis-anhydride **12**[4])[5]). Reduction of **13** with $LiAlH_4$ in THF yielded tetrol **14** (87%) which was esterified and furnished the tetrakismethanesulfonate **15** (70%). Quadruple elimination of methanesulfonic acid (*t*-BuOK/DMSO) gave the pentaene **22**

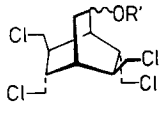


12

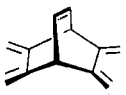
13 R = $COOC_2H_5$
14 R = CH_2OH
15 R = $CH_2OSO_2CH_3$
16 R = CH_2Cl



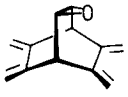
17 **18** **19**



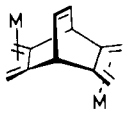
20 R′ = H
21 R′ = $CH(CH_3)OC_2H_5$



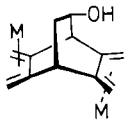
22



23



24



25
M = $Fe(CO)_3$

(67%) [9]. Difficulties encountered during the extractions made this technique impractical for the preparation of large quantities of **22**.

A better technique involved elimination of four equivalents of HCl from the tetrachloride **16**, obtained by chlorination of **14** with $SOCl_2$/pyridine. Unfortunately, the reaction **14** → **16** was low-yielded (< 40%). The most practical method was using the isomerized precursor **17** [10] which was transformed successively into **18** and **19** in high yield [11]. Quadruple elimination of HCl (*t*-BuOK/THF) from **19** gave **22** in 81% yield.

Hydroboration/oxidation [12] of **15** and **16** failed to give any trace of the corresponding alcohols, probably because of the severe steric hindrance due to the four *syn*-substituents R. Hydroboration/oxidation of the 'all-*trans*'-tetrachloride **19** gave a mixture of alcohols **20** (88%). Treatment of **20** with *t*-BuOK/THF or CsF/DMF [13] failed to yield any trace of tetraenol **10**. Similarly, the protected derivative **21** [14] led only to decomposition products when treated under the strongly basic conditions required for the quadruple elimination of HCl.

Epoxidation of **19** followed by treatment with *t*-BuOK in THF gave the epoxytetraene **23** [11]. Reduction of **23** with $LiAlH_4$, AlH_3 or lithium triethylborohydride ('superhydride' is supposed to avoid homoallylic rearrangements [15]) gave complex mixtures of products whose ^{1}H-NMR. spectra suggested partial reduction of the

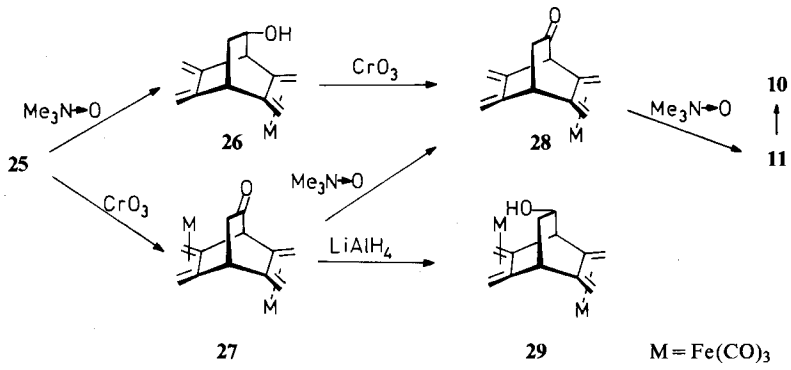
---

[4]) We wish to thank the *BASF AG*, D-6700 Ludwigshafen, for a generous gift of this compound.

[5]) The terms *syn* and *anti* indicate the relative position of a group with respect to the bridge carrying the principal group or the endocyclic double bond.

diene moieties (observation of signals typical for CH_3-groups), probably because of homoconjugative participation during reduction of the epoxide group [16]. When treated with $NaAlH_2(OCH_2CH_2OCH_3)_2$, the oxirane ring of **23** was not reduced; hydroalumination of the *syn*-diene occurred instead with the formation of a σ-allylaluminate [17]. All these unsuccessful attempts to prepare tetraenol **10** forced us to employ the bis(tricarbonyliron) complex **24** [18] of the readily available pentaene **22**.

Hydroboration/oxidation of **24** gave the corresponding alcohol **25** [18]. In the presence of a 20-fold molar excess of trimethylamine oxide [19], **25** was oxidized selectivity into the monocomplexed alcohol **26** (78%). Further oxidation of **26** into the uncomplexed tetraenol **10** was a very slow reaction, too slow to successfully compete with the decomposition of **26**. CrO_3-oxidation of **25** yielded the doubly complexed tetraenone **27** (64%), and under the same conditions, **26** furnished the monocomplexed ketone **28** (65%). When treated with a 10-molar excess of trimethylamine oxide in acetone (25°, 20 min), **27** gave a mixture of the *anti*-$Fe(CO)_3$ complexed tetraenone **28** (50%) and the uncomplexed ketone **11** (31%).



When a 30-fold molar excess of trimethylamine oxide was employed (20°, 20 h), **27** was oxidized to tetraenone **11** in good yield (85%). Reduction of **11** with $NaBH_4$ in THF furnished pure tetraenol **10** (93%). $LiAlH_4$ reduction of the doubly complexed ketone **27** gave alcohol **29** in modest yield (37%).

The selectivity of the trimethylamine oxide oxidations **25**→**26** and **27**→**28** is not yet understood. In all cases, the *syn*-$Fe(CO)_3$ group is removed more rapidly than the *anti*-$Fe(CO)_3$ group; this was also true for **24** [20].

The structures of **10**, **11**, **26–29** were given by their mode of formation, their elemental analysis and by their spectroscopic data (see *Exper. Part*). The structure of **24** was established by X-ray crystallography [18], and those of alcohols **25** [18] and **26** by ^1H- and ^{13}C-NMR. spectroscopy using $Eu(dpm)_3$ and $Yb(dpm)_3$ induced chemical shifts, respectively. NMR. signal attributions in ketones **11**, **27** and **28** were based on comparison with those reported for dienone **4** [21], 5,6-dimethylidene-2-bicyclo[2.2.2]octanone [22], and related tricarbonyl(diene)iron complexes [23].

The UV. spectrum of tetraenol **10** presents characteristics similar to those of related systems **22** [9] and **23** [11]. It shows the typical splitting of the V←N band associated with the s-*cis*-butadiene chromophores (see *Fig. 1*, compare with the UV. spectrum of 2-bicyclo[2.2.2]octanol (**30**)). This confirms the existence of a significant transannular interaction between the two homoconjugated diene functions. The UV. spectrum of tetraenone **11** displays a large band whose maximum (251 nm) coincides with the maximum of a similar band attributed to the V←N transition of the diene chromophore in the spectrum of 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**31**) [22]. It is, however, twice as intense as the V←N band in the spectrum of **31** (see *Fig. 2*). The loss of the *Franck-Condon* fine structure in the UV. spectrum of **11**, compared with that found in the spectrum of **10**, **22** and **23**, can be attributed to an increased number of transitions probably due to through-space and through-bond interactions involving the diene and carbonyl chromophores [24].

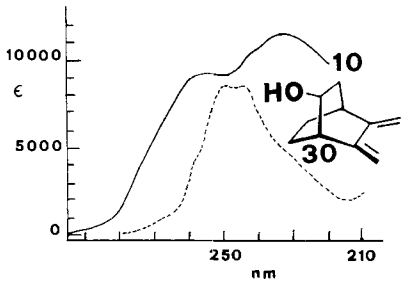


Fig. 1. *UV. spectra of tetraenol* **10** *and dienol* **30** (in dioxane)

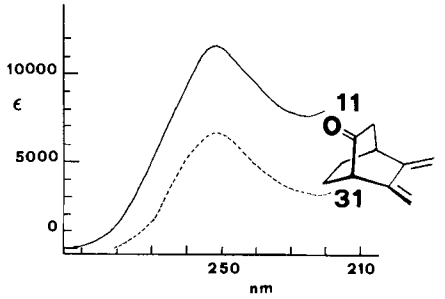
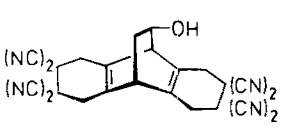
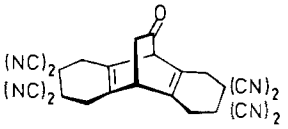


Fig. 2. *Partial UV. spectra of tetraenone* **11** *dienone* **31** (in dioxane)

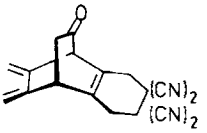
Regioselectivity of the *Diels-Alder* addition. – Tetraenes **10** and **11** added two equivalents of ethylenetetracarbonitrile (TCE, benzene, 20°) and gave the bis-adducts **32** and **33**, respectively. In the presence of one equivalent of TCE, **11** gave the monoadduct **34** in 93% isolated yield. Similarly, tetraenol **10** reacted with one equivalent of TCE yielding a 3:2 mixture of the monoadducts **35** (58%, isolated) and **36** (39%, isolated), and thus addition to the diene moiety on the same side of the hydroxy group was favoured over addition to the diene opposite to it. The



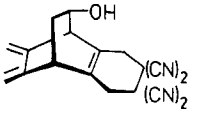
32



33

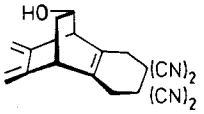


34



35

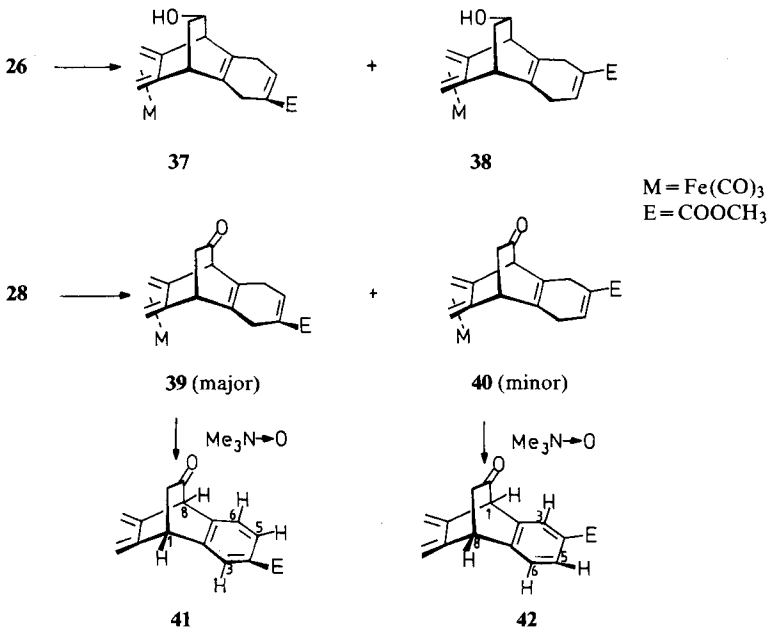
\+



36

same type of regioselectivity was observed for the TCE additions to the epoxytetraene **23** [11]. As for pentaene **22** [6] and epoxytetraene **23** [11], the additions of TCE to **10** and **11** were significantly faster than those to the corresponding monoadducts **35/36** and **34**. Such a reactivity difference ($k_1/k_2 > 10$ (estimated)) was not observed with weaker dienophiles. For instance, when **10** or **11** were allowed to react with one equivalent of methyl propynoate in benzene (60–100°), mixtures of the corresponding mono- and bis-adducts were obtained whose separation could not be achieved. For these cycloadditions the rate constants k_1 and k_2 were approximately equal. The ^{1}H- and ^{13}C-NMR. spectra f these mixtures were not sufficiently resolved for determination of regioselectivity in the methyl propynoate additions to **10** and **11**.

Methyl propynoate added to the *anti*-Fe(CO)$_3$-monocomplexed tetraenol **26** and furnished a 1:1 mixture of the adducts **37** and **38**. The absence of regioselectivity was not a surprise as the cycloadditions of methyl propynoate to 5,6-dimethylidene-2*exo*-norbornanol and dienol **30** were not found to be regioselective either [7]. More interesting, however, was the *Diels-Alder* addition of methyl propynoate to the *anti*-Fe(CO)$_3$-monocomplexed tetraenone **28** which led to a 3:1 mixture of the adducts **39** and **40**. As for the cycloadditions of dienone **4**, the *'para'*-regioisomer was the major product. This selectivity has been attributed to the electron-donating ability of the homoconjugated carbonyl group of the β,γ-enone [7] [25]. The regioselectivity was better than that for the cycloaddition of methyl propynoate to **31**, perhaps because of the *anti*-Fe(CO)$_3$ group in **28** which forces the dienophile to attack exclusively one face of the exocyclic diene (*cf.* [8]).



The structures of the bis-adducts **32** and **33** and mono-adducts **34–40** were given by their mode of formation, their elemental analysis and by their spectroscopic data (see *Exper. Part*). The relative configuration of the alcohols **35** and **36** was determined by $Yb(dpm)_3$-induced shifts in the ^{13}C-NMR. spectra. The *anti* ⇄ *syn*-$Fe(CO)_3$ isomerization has never been observed for complexes of exocyclic dienes under a large variety of conditions [26] [27]. The relative configuration of the ketones **39** and **40** was confirmed by a ^1H-NMR. analysis of the corresponding 3:1 mixture of the benzoates **41** and **42** obtained in 73% yield from **39/40** (3:1) by treatment with a large excess of trimethylamine oxide (acetone, 20°, 20 h).

When irradiating (360 MHz, ^1H-NMR.) the singlet at 4.47 ppm of **41**, attributed to the bridgehead proton H–C(8), a nuclear *Overhauser* effect (NOE) was observed for H–C(6) at 7.44 ppm (*d*, $J = 7.6$). Proton H–C(5) resonates at 7.91 ppm (*d*×*d*, $J = 7.6$ and 1.6) and H–C(3) at 7.99 ppm (*d*, $J = 1.6$, W-long-range coupling with H–C(5)). Irradiation of the triplet at 4.28 ppm ($J = 3$), attributed to H–C(1), gave a NOE at the resonance of H–C(3). Similar experiments were performed on the signals of the minor compound **42**. Irradiation of the singlet at 4.48 ppm (H–C(1) of **42**) led to a NOE at 7.93 ppm (*d*, $J = 1.6$, H–C(3)). Irradiation of the triplet at 4.25 ppm ($J = 3$, H–C(8)) gave a NOE at 7.49 ppm (*d*, 7.6, H–C(6)). The proton H–C(5) resonates at 7.94 ppm (*d*×*d*, $J = 7.6$ and 1.6)[6]).

Conclusion. – The 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanol (**10**) is the first example of a double exocyclic diene grafted onto a bicyclic skeleton in which the bridge is unsymmetrical. Contrary to that found for 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane systems [5] and 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]-octene (**22**) [6], the *Diels-Alder* reactivity of tetraenol **10** and tetraenone **11** (as for 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane [6] [9]) is not significantly larger than that of the corresponding monoadduct for cycloadditions of methyl propynoate. Consequently, **10** and **11** have limited potential as synthetic intermediates. This disavantage, nevertheless, can be overcome as the corresponding mono *anti*-$Fe(CO)_3$ complexes **26** and **28** can be prepared readily. The carbonyl group in tetraenone **28** induced regioselective cycloadditions to the homoconjugated diene thus making this system a more versatile synthetic intermediate for the preparation of polyfunctional, polycyclic systems by two successive *Diels-Alder* additions with two different dienophiles.

We thank *Hoffmann-La Roche & Co. AG*, Basel, the *Fonds National Suisse de la Recherche Scientifique*, and the *Fonds Herbette*, Lausanne, for generous support.

Experimental Part

General remarks. See [4b].

*Bicyclo[2.2.2]oct-7-ene-2*syn,*3*syn,*5*syn,*6*syn-*tetramethanol* (**14**). A solution of tetraethyl bicyclo-[2.2.2]oct-7-ene-2*syn*,3*syn*,5*syn*,6*syn*-tetracarboxylate [11] (**13**, 50 g, 0.13 mol) in anh. THF (400 ml) was added dropwise to a vigourously stirred suspension of $LiAlH_4$ (16 g, 0.42 mol) in anh. THF (350 ml). After the addition, the mixture was stirred and heated under reflux for 12 h. After cooling to 0°, H_2O (35 ml) was added dropwise and the mixture heated under reflux for 1 h. The mixture was filtered through silica gel (50 g). The precipitate and the silica gel were stirred in boiling EtOH

[6]) For details, see [28].

(400 ml) for 2 h and then filtered through more silica gel (50 g). The extraction of silica gel with boiling EtOH was repeated twice. The filtrates were united, and concentrated i.V. The residue was recrystallized from EtOH (−15°) yielding 25 g (87%) of white crystals, m.p. 180–181°. – ^{1}H-NMR. (CD_3SOCD_3): 6.09 (*m*, 2 H, H–C(7), H–C(8)); 3.6–2.9 (*m*, 8 H, 4 CH_2OH); 2.73 (*m*, 2 H, H–C(1), H–C(4)); 2.0 (*m*, 4 H, H–C(2), H–C(3), H–C(5), H–C(6)).

*5*syn,*6*syn,*7*syn,*8*syn-*Tetrakis(chloromethyl)bicyclo[2.2.2]oct-2-ene* (**16**). Anh. pyridine (1.67 g, 21 mmol) was mixed with freshly distilled $SOCl_2$ (3 g, 25 mmol). Tetrol **14** (1.14 g, 5 mmol) was added portionwise to this mixture under vigourous stirring. The temp. was maintained below 40°. After the addition, the mixture was heated to 40° for 30 min and then stirred at 20° for 2 days. The mixture was extracted with Et_2O (80 ml, 3 times). The Et_2O extract was washed with H_2O (10 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the residue recrystallized from $CHCl_3$/pentane yielding 0.6 g (40%), colourless crystals, m.p. 97–97.5°. – UV. (95% EtOH): final absorption, $\varepsilon_{210} < 100$. – IR. (KBr): 2990, 2980, 2940, 1450, 1380, 1305, 1265, 1025, 780, 740, 715, 705. – ^{1}H-NMR. ($CDCl_3$): 6.4 (*m*, 2 H); 3.8–3.2 (*m*, 8 H); 3.2 (*m*, 2 H); 2.4 (*m*, 4 H). – ^{13}C-NMR. ($CDCl_3$): 132.8 (*d*, $^1J_{C,H}$ = 167, C(2), C(3)); 44.6 (*t*, $^1J_{C,H}$ = 150, *C*H_2Cl); 44.5 (*d*, $^1J_{C,H}$ = 138, C(5), C(6), C(7), C(8)); 37.6 (*d*, $^1J_{C,H}$ = 138, C(1), C(4)). – MS. (70 eV): 306 (0.2), 304 (0.7), 302 (1.3), 300 (1.2), 219 (7), 180 (12), 178 (8), 149 (9), 129 (8), 127 (18), 105 (8), 91 (100).

5,6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octene (**22**). – *Method A.* *t*-BuOK (0.9 g, 8 mmol) was added to a stirred solution of **16** (0.302 g, 1 mmol) in anh. THF (4 ml). After stirring at 20° for 4 days, ice (5 g) was added and the mixture extracted with pentane (10 ml, 4 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the residue recrystallized from pentane at −20°, yielding 105 mg (67%) of colourless crystals.

Method B. *t*-BuOK (16.2 g, 144 mmol) was added portionwise to a stirred solution of *5syn,6anti,-7syn,8anti*-tetrakis(chloromethyl)bicyclo[2.2.2]oct-2-ene (**19**) [11] (5 g, 16.5 mmol) in anh. THF (50 ml). The mixture was stirred at 60° for 3 days and then poured onto ice (20 g) and extracted with pentane (80 ml, 3 times). The org. extract was washed with H_2O (100 ml, 5 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the residue recrystallized from pentane at −20° yielding 2.1 g (81%) of colourless crystals, m.p. 97–98°. – UV. (isooctane): 221 (9400), 227.5 (10150), 236 (9650), 252 (9030), 260 (8850), 269 *S* (5320). – IR. (CCl_4): 3060, 2980, 2860, 1780, 1620, 890. – ^{1}H-NMR. (CCl_4): 6.32 (*d*×*d*, 2 H); 5.14 (br. *s*, 4 H); 4.85 (br. *s*, 4 H); 3.78 (*d*×*d*, 2 H). – ^{13}C-NMR. ($CDCl_3/CCl_4$ 1:1): 144.3 (*s*), 132.2 (*d*, $^1J_{C,H}$ = 170); 103.9 (*t*, $^1J_{C,H}$ = 159); 53.2 (*d*, $^1J_{C,H}$ = 144 ± 3). – MS. (70 eV): 156 (75), 155 (33), 141 (65), 128 (31), 115 (27), 104 (100), 103 (31), 78 (36), 77 (24).

$C_{12}H_{12}$ (156.23) Calc. C 92.26 H 7.74% Found C 91.98 H 7.89%

*5*syn,*6*anti,*7*syn,*8*anti-*Tetrakis(chloromethyl)-2-bicyclo[2.2.2]octanols* (**20**). $NaBH_4$ (0.1 g, 2.6 mmol) and then $BF_3 \cdot Et_2O$ (0.48 g, 3.4 mmol) were added to a stirred solution of **19** (0.3 g, 1 mmol) in anh. THF (3 ml) at 0° and under N_2. After stirring at 20° for 10 h, the mixture was cooled to 0° and H_2O (0.2 g), and then aq. 3N KOH (0.3 g) and 30% H_2O_2 solution (0.3 g) were added dropwise. After stirring at 20° for 30 h, the mixture was extracted with Et_2O (10 ml, 3 times). The org. extract was washed with H_2O (20 ml, 3 times) and dried ($MgSO_4$). After solvent evaporation i.V., the oily residue was dried over paraffine and P_4O_{10} yielding 0.28 g (88%) of colourless oil. – IR. (film): 3590, 3400, 2960, 2900, 1445, 1305, 1290, 1070, 1035, 1010, 905, 750, 725, 705. – ^{1}H-NMR. ($CDCl_3$): 4.3–3.2 (*m*, 10 H); 2.4–1.0 (*m*, 8 H).

trans-*μ*-*[(2*R*,*5*S*,*7*R*)-C,*5,6*,C-*η*:C,*7,8*,C-*η-5,6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octanol)]-bis(tricarbonyliron)* (**25**). *Method A.* See [18].

Method B. $Et_2O \cdot BF_3$ (2 g, 14 mmol) was added dropwise to a vigourously stirred suspension of a 4:1 mixture of *anti,syn-* and *syn,syn*-$[Fe(CO)_3]_2$ complexes of **22** [23] (3 g) and $NaBH_4$ (0.8 g, 21 mmol) in anh. THF (30 ml) at 0°. The mixture was stirred at 20° for 3 h. After cooling to 0°, H_2O (1.6 g, 89 mmol), then aq. 3N KOH (1.6 g) and 30% H_2O_2 solution (3 g, 89 mmol) were added dropwise. The mixture was stirred at 20° for 16 h and then extracted with CH_2Cl_2 (20 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the residue purified by column chromatography (90 g SiO_2, CH_2Cl_2). The first fraction contained the unreacted *syn,syn*-$[Fe(CO)_3]_2$ complex of **22** [23] (0.5 g, 17%), and the second fraction, after recrystallization from CH_2Cl_2, yielded 2.2 g (70%) of **25** [18].

*Tricarbonyl[(1*R*,*2*S*,*5*R*)-C,*5,6*,C-*η-(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanol)]iron* (**26**). Freshly sublimed trimethylamine oxide (2.7 g, 36 mmol) was added portionwise to a stirred solution

of **25** (0.8 g, 1.76 mmol) in anh. acetone (100 ml). The mixture was stirred at 25° for 50 min and then filtered. CH_2Cl_2 (300 ml) and H_2O (100 ml) were added. The org. phase was washed with H_2O (100 ml, 3 times). The aq. layers were united and extracted with CH_2Cl_2 (50 ml). The org. extracts were united and dried ($MgSO_4$). After solvent evaporation i.V., the residue was purified by column chromatography on silica gel (25 g, AcOEt/hexane 1:1) and recrystallized from CH_2Cl_2: 0.43 g (78%), yellow crystals, m.p. 91–92°. – UV. (95% EtOH): 285 *S* (2800). – IR. (KBr): 3580, 3400, 3100, 3060, 3000, 2960, 2920, 2880, 2050, 2040, 1970, 1615, 1460, 1400, 1340, 1330, 1220, 1170, 1150, 1125, 1050, 1030, 985, 970, 950, 890. – ^{1}H-NMR. ($CDCl_3$): 5.22 (*s*, 1 H, *H*CH=C(8) *cis* to C(7)); 5.13 (*s*, 1 H, *H*CH=C(7) *cis* to C(8)); 4.85 (*s*, 1 H, HC*H*=C(8) *trans* to C(7)); 4.73 (*s*, 1 H, HC*H*=C(7) *trans* to C(8)); 4.45 (*m*, 1 H, H–C(2)); 3.32 (*d*, *J* = 3, 1 H, H–C(1)); 3.20 (*t*, *J* = 3, 1 H, H–C(4)); 2.50 (*d* × *d* × *d*, *J* = 13, 9, 3, 1 H, H–C(3) *trans* to OH); 1.85 (*d*, *J* = 3, 2 H, HC*H*=C(5) and HC*H*=C(6) *trans* to C(5), C(6)); 1.8–1.5 (*m*, 2 H, H–C(3) *cis* to OH and HO); 0.34 (*d*, *J* = 3, 1 H, *H*CH=C(6) *cis* to C(5)); 0.30 (*d*, *J* = 3, 1 H, *H*CH=C(5) *cis* to C(6)). – ^{13}C-NMR. ($CDCl_3$): 210.9 (*s*, Fe(*C*O)$_3$, [8.2][7]); 145.2 (*s*, C(8), [17.0]); 143.3 (*s*, C(7), [20.5]); 108.0 (*s*, C(5), [27.1]); 105.8 (*t*, $^1J_{C,H}$ = 159, H_2C=C(7), [11.1]); 104.0 (*s*, C(6), [36.1]); 103.5 (*t*, $^1J_{C,H}$ = 159, H_2C=C(8), [9.1]); 70.4 (*d*, $^1J_{C,H}$ = 150, C(2), [100]); 53.3 (*d*, $^1J_{C,H}$ = 135, C(1), [45.4]); 44.9 (*d*, $^1J_{C,H}$ = 135, C(4), [29.4]); 39.2 (*t*, $^1J_{C,H}$ = 138, C(3), [41.6]); 37.9 (*t*, $^1J_{C,H}$ = 160, H_2C=C(6), [22.1]); 36.1 (*t*, $^1J_{C,H}$ = 160, H_2C=C(5), [15.0]). – MS. (70 eV): 314 (2), 286 (16), 258 (48), 230 (100), 212 (19), 184 (15), 162 (19), 160 (19), 157 (21), 156 (88), 155 (19), 142 (22), 141 (66), 132 (23), 130 (20), 129 (44), 128 (54), 127 (28), 115 (77), 105 (27), 95 (21).

$C_{15}H_{14}FeO_4$ (314.12) Calc. C 57.36 H 4.49% Found C 57.38 H 4.59%

trans-*μ*-*[(5R*, 7S*)*-C, 5, 6, C-*η*: C, 7, 8, C-*η*-*(5, 6, 7, 8-Tetramethylidene-2-bicyclo[2.2.2]octanone)]bis-(tricarbonyliron)* (**27**). CrO_3 (5.15 g, 51 mmol) was added portionwise and under N_2 to a mixture of anh. pyridine (8.1 g, 104 mmol) and CH_2Cl_2 (90 ml) cooled to 0°. After stirring at 20° for 10 min, a solution of **25** (2.5 g, 5.5 mmol) in anh. CH_2Cl_2 (15 ml) was added at once and the mixture stirred at 20° for 6–8 min until disappearance of **25** (control by TLC.; overexposure to these conditions can oxidize the tricarbonyliron groups!). The mixture was filtered through silica gel (5 g), and the precipitate was washed with CH_2Cl_2 (100 ml). After solvent evaporation i.V., the oily residue was purified by column chromatography on silica gel (60 g, hexane/CH_2Cl_2 3:2). The main fraction was crystallized from CH_2Cl_2/hexane yielding 1.6 g (64%), yellow crystals, m.p. 146–147°. – UV. (95% EtOH): 265 *S* (2600). – IR. ($CHCl_3$): 2990, 2910, 2050, 1990, 1970, 1735, 1465, 1445, 1410, 1310, 1260, 1145, 1100. – ^{1}H-NMR. ($CDCl_3$): 3.89 (*s*, 1 H, H–C(1)); 3.62 (*t*, *J* = 2.6, 1 H, H–C(4)); 2.83–2.69 (*d* × *d*, *J* = 18, 2.6, 2 H, 2 H–C(3)); 2.15, 2.14, 2.05, 1.86 (4 *d*, *J* = 3, 4 H, HC*H*=C(5), HC*H*=C(6), HC*H*=C(7) and HC*H*=C(8) *trans* to C(5), C(6) and to C(7), C(8), respectively); 0.68, 0.60, 0.50, 0.40 (4 *d*, *J* = 3, 4 H, *H*CH=C(5), *H*CH=C(6), *H*CH=C(7) and *H*CH=C(8) *cis* to C(5), C(6) and C(7), C(8), respectively). – ^{13}C-NMR. ($CDCl_3$): 209.2 (*s*, $Fe_2(CO)_6$); 200.3 (*s*, C(2)); 110.5, 109.9, 103.4, 101.6 (4 *s*, C(5), C(6), C(7), C(8)); 59.3 (*d*, $^1J_{C,H}$ = 150, C(1)); 42.3 (*t*, $^1J_{C,H}$ = 134, C(3)); 40.8 (*d*, $^1J_{C,H}$ = 150, C(4)); 39.3, 38.6, 37.4, 36.0 (4 *t*, $^1J_{C,H}$ = 160, H_2C=C(5), H_2C=C(6), H_2C=C(7), H_2C=C(8)). – MS. (70 eV): 452 (0.5), 424 (9), 396 (24), 368 (18), 340 (14), 312 (25), 284 (88), 282 (16), 258 (25), 256 (13), 229 (17), 198 (15), 176 (24), 148 (30), 115 (30), 112 (100).

$C_{18}H_{12}Fe_2O_7$ (451.99) Calc. C 47.83 H 2.68% Found C 47.77 H 2.62%

Tricarbonyl[(1R, 5R*)*-C, 5, 6, C-*η*-*(5, 6, 7, 8-tetramethylidene-2-bicyclo[2.2.2]octanone)]iron* (**28**) *Method A.* Freshly sublimed trimethylamine oxide (1 g, 13.3 mmol) was added to a stirred solution of **27** (0.5 g, 1.1 mmol) in anh. acetone (100 ml). After stirring at 25° for 20 min, the mixture was filtered and H_2O (100 ml) added. The reaction time varied from one batch to another due to the purity of the trimethylamine oxide; the reaction was followed by TLC. The mixture was extracted with CH_2Cl_2 (50 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the oily residue purified by column chromatography on silica gel (25 g, CH_2Cl_2/hexane 1:1). The first fraction contained 0.170 g (50%) of **28**, yellow crystals, m.p. 109–110°; the second fraction yielded 0.060 g (31%)

---

[7]) In brackets the relative induced shifts upon addition of Yb(dpm)$_3$. Linear induced shifts were observed for concentration ratios $0.03 < [Yb(dpm)_3]/[\text{analyzed compounds}] < 0.3$; correlation coefficient > 0.999 (4 successive additions of lanthanide complex).

of **11**. *Data of* **28**: UV. (95% EtOH): 315 *S* (1900), 285 *S* (2900). – IR. (CH_2Cl_2): 2990, 2060, 1990, 1740, 1620, 1410, 1315, 1100, 900. – ^{1}H-NMR. ($CDCl_3$): 5.45, 5.35 (2 *s*, 2 H, *H*CH=C(7) and *H*CH=C(8) *cis* to C(7), C(8)); 5.01, 4.95 (2 *s*, HC*H*=C(7) and HC*H*=C(8) *trans* to C(7), C(8)); 3.72 (*s*, 1 H, H–C(1)); 3.45 (*t*, *J* = 3, 1 H, H–C(4)); 2.58 (*d*, *J* = 3, 2 H, H_2C(3)); 1.91, 1.80 (2 *d*, *J* = 3, 2 H, HC*H*=C(5) and HC*H*=C(6) *trans* to C(5), C(6)); 0.39, 0.23 (2 *d*, *J* = 3, 2 H, *H*CH=C(5) and *H*CH=C(6) *cis* to C(5), C(6)). – ^{13}C-NMR. ($CDCl_3$): 210.0 (*s*, $Fe(CO)_3$); 204.8 (*s*, C(2)); 144.0 (*s*, C(8)); 139.7 (*s*, C(7)); 109.6 (*s*, C(5)); 108.4 (*t*, $^1J_{C,H}$ = 160, H_2C=C(7)); 105.3 (*t*, $^1J_{C,H}$ = 160, H_2C=C(8)); 102.9 (*s*, C(6)); 62.4 (*d*, $^1J_{C,H}$ = 150, C(1)); 44.8 (*d*, $^1J_{C,H}$ = 150, C(4)); 40.3 (*t*, $^1J_{C,H}$ = 133, C(3)); 36.1, 36.0 (2 *t*, $^1J_{C,H}$ = 158, H_2C=C(5), H_2C=C(6)). – MS. (70 eV): 284 (19), 256 (66), 228 (100), 198 (42), 149 (36), 148 (78), 129 (42), 128 (41), 115 (42), 97 (36), 95 (44), 91 (33), 84 (55), 81 (75), 71 (58), 69 (97).

$C_{15}H_{12}FeO_4$ (312.11) Calc. C 57.73 H 3.88% Found C 57.85 H 4.09%

Method B. CrO_3 (515 mg, 5.1 mmol) was added portionwise and under N_2 to a stirred solution of anh. pyridine (810 mg, 10.3 mmol) in anh. CH_2Cl_2 (10 ml) cooled to 0°. After stirring at 20° for 10 min, a solution of **26** (170 mg, 0.54 mmol) in anh. CH_2Cl_2 (2 ml) was added. The mixture was stirred at 20° for 6–8 min (control by TLC.) and then filtered through silica gel (1 g). The precipitate was washed with CH_2Cl_2 (10 ml). After evaporation of the solvent i.V., the oily residue was purified by column chromatography on silica gel (8 g, CH_2Cl_2/hexane 1:1) and recrystallization from hexane: 110 mg (65%), m.p. 109–110°.

trans-*μ*-*[(2R*,5R*,7S*)*-C,*5,6*,C-*η*:C,*7,8*,C-*η*-*(5,6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octanol)]-bis(tricarbonyliron)* (**29**). Ketone **27** (80 mg, 0.18 mmol) was added to a stirred solution of $LiAlH_4$ (5 mg, 0.13 mmol) in anh. THF (0.5 ml). After stirring at 20° for 15 min, the mixture was cooled to 0° and H_2O (20 mg) added. The mixture was filtered through silica gel and the precipitate washed with CH_2Cl_2 (5 ml). After evaporation of the solvent i.V., the residue was purified by column chromatography on silica gel (3 g, CH_2Cl_2) and recrystallized from CH_2Cl_2 yielding 30 mg (37%), yellow crystals, m.p. 183–184°. – UV. (95% EtOH): 287 *S* (2500). – IR. (KBr): 3600, 3270, 3000, 2960, 2900, 2050, 1980, 1475, 1460, 1450, 1440, 1325, 1265, 1230, 1165, 1135, 1060, 1040, 1005, 960. – ^{1}H-NMR. (CD_2Cl_2): 4.60 (*d*×*d*×*d*×*d*, *J* = 9, 5, 3, 2, 1 H, H–C(2)); 3.36 (*d*, *J* = 3, 1 H, H–C(1)); 3.28 (*t*, *J* = 3, 1 H, H–C(4)); 2.62 (*d*×*d*×*d*, *J* = 13, 9, 3, H–C(3) *trans* to OH); 2.19 (*d*, *J* = 5, 1 H, HO); 2.06, 2.03 (2 *d*, *J* = 3, 2 H, HC*H*=C(7) and HC*H*=C(8) *trans* to C(7), C(8)); 1.86 (*d*×*d*×*d*, *J* = 13, 3, 2, 1 H, H–C(3) *cis* to OH); 1.85, 1.67 (2 *d*, 2 H, HC*H*=C(5) and HC*H*=C(6) *trans* to C(5), C(6)); 0,54, 0.48 (2 *d*, 2 H, *H*CH=C(7) and *H*CH=C(8) *cis* to C(7), C(8)); 0.29 and 0.24 (2 *d*, 2 H, *H*CH=C(5) and *H*CH–C(6) *cis* to C(5), C(6)). – MS. (70 eV): 426 (4), 398 (38), 370 (36), 342 (15), 314 (58), 286 (100), 284 (16), 258 (16), 230 (29), 212 (25).

$C_{18}H_{14}Fe_2O_7$ (454.0) Calc. C 47.62 H 3.11% Found C 47.71 H 3.14%

5,6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octanone (**11**). *Method A.* Freshly sublimed trimethylamine oxide (4 g, 53 mmol) was added to a stirred solution of **27** (0.8 g, 1.77 mmol) in anh. acetone (400 ml). After stirring at 20° for 20 h, the mixture was concentrated i.V. to 100 ml. After addition of H_2O (100 ml), the mixture was extracted with hexane (100 ml, 3 times). The org. extract was dried ($MgSO_4$) and the solvent evaporated i.V. The residue was purified by column chromatography on silica gel (20 g, CH_2Cl_2/hexane 1:1) and recrystallized from hexane at −20° yielding 260 mg (85%), white solid (which was rapidly polymerized by standing at 20°), m.p. 55–56°. – UV. (95% EtOH): 251 (11500), 302 (450). UV. (dioxane): 251 (11600), 305 (440), see *Figure 2.* – IR. ($CHCl_3$): 2960, 2930, 2870, 2040, 1990, 1735, 1610, 1460, 1380, 1125, 900. – ^{1}H-NMR. ($CDCl_3$): 5.38 (*s*, 2 H, *H*CH=C(6) and *H*CH=C(7) *cis* to C(5) and C(8), resp.); 5.32 (*s*, 2 H, *H*CH=C(5) and *H*CH=C(8) *cis* to C(6) and C(7), resp.); 4.98 (*s*, 4 H, HC*H*=C(5), HC*H*–C(6), HC*H*=C(7) and HC*H*=C(8) *trans* to C(6), C(5), C(8) and C(7), resp.); 3.75 (*s*, 1 H, H–C(1)); 3.40 (*t*, *J* = 3, 1 H, H–C(4)); 2.4 (*d*, *J* = 3, 2 H, H_2C(3)). – ^{13}C-NMR. ($CDCl_3$): 205.8 (*s*, C(2)); 143.8 (*s*, C(5), C(8)); 139.3 (*s*, C(6), C(7)); 108.9 (*t*, $^1J_{C,H}$ = 160, H_2C=C(6), H_2C=C(7)); 106.2 (*t*, $^1J_{C,H}$ = 159, H_2C=C(5), H_2C=C(8)); 67.1 (*d*, $^1J_{C,H}$ = 144, C(1)); 48.4 (*d*, $^1J_{C,H}$ = 144, C(4)); 44.1 (*t*, $^1J_{C,H}$ = 132, C(3)); attributions based on comparison with related systems, see [21] [22]. – MS. (70 eV): 172 (23), 144 (22), 130 (54), 129 (86), 128 (64), 127 (27), 115 (100), 91 (25), 89 (20), 77 (32).

$C_{12}H_{12}O$ (172.23) Calc. C 83.69 H 7.02% Found C 83.46 H 7.03%

Method B. Freshly sublimed trimethylamine oxide (400 mg; 5.3 mmol) was added to a stirred solution of **28** (60 mg, 0.2 mmol) in anh. acetone (40 ml). After stirring at 20° for 15 h, H_2O (20 ml) was added and the mixture extracted with hexane (30 ml, 3 times). The org. extract was dried ($MgSO_4$) and evaporated i.V. The residue was purified by column chromatography on silica gel (3 g, CH_2Cl_2/hexane 1:1) and recrystallized from hexane at −20° yielding 30 mg (91%) of pure **11**.

(±)-5,6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octanol (**10**). $NaBH_4$ (15 mg, 0.4 mmol) was added under N_2 to a stirred solution of **11** (20 mg, 0.11 mmol) in anh. THF (1 ml). After stirring at 20° for 16 h, H_2O (5 ml) was added and the mixture extracted with CH_2Cl_2 (4 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the residue recrystallized from pentane at −20°: 19 mg (93%), colourless crystals, m.p. 97–98°. – UV. (95% EtOH): 254 (8600), 239 (9850), 233 (10000). UV. (dioxane): 256 (9100), 233 (11600); *cf. Figure 1.* – IR. ($CHCl_3$): 3610, 3570, 3450, 3095, 3000, 2960, 1800, 1615, 1440, 1390, 1140, 1045, 980, 895. – ^{1}H-NMR. ($CDCl_3$): 5.43 (*s*, 1 H, *H*CH=C(6) *cis* to C(5), [20.2][8])); 5.29 (*s*, 1 H, *H*CH=C(7) *cis* to C(8), [11.8]); 5.23 (*s*, 1 H, *H*CH=C(5) *cis* to C(6), [14.2]); 5.18 (*s*, 1 H, HC*H*=C(8) *cis* to C(7), [10.4]); 4.88 (*s*, 1 H, HC*H*=C(6) *trans* to C(5), [24.6]); 4.86 (*s*, 1 H, HC*H*=C(8) *trans* to C(7), [10.0]); 4.80 (*s*, 1 H, HC*H*=C(5) *trans* to C(6), [13.9]); 4.75 (*s*, 1 H, HC*H*=C(7) *trans* to C(8), [12.2]); 3.98 (*t*×*t*, *J* = 9, 3, 1 H, H–C(2), [100]); 3.12 (*d*, *J* = 3, 1 H, H–C(1), [55.5]); 3.05 (*t*, *J* = 3, 1 H, H–C(4), [25.0]); 2.23 (*d*×*d*×*d*, *J* = 14, 9, 3, 1 H, H–C(3) *trans* to HO, [32.5]); 1.69 (*d*, *J* = 9, HO); 1.50 (*d*×*t*, *J* = 14, 3, 1 H, H–C(3) *cis* to HO, [59.3]). – ^{13}C-NMR. ($CDCl_3$): 145.9 (*s*, C(5), [24.9][7])); 145.4 (*s*, C(8), [17.0]); 143.3 (*s*, C(7), [20.3]); 141.3 (*s*, C(6), [34.1]); 109.1 (*t*, $^1J_{C,H}$ = 158, H_2C=C(6), [22.8]); 107.1 (*t*, $^1J_{C,H}$ = 158, H_2C=C(7), [10.6]); 104.8 (*t*, $^1J_{C,H}$ = 157, H_2C=C(5), [14.4]); 104.6 (*t*, $^1J_{C,H}$ = 157, H_2C=C(8), [8.7]); 68.5 (*d*, $^1J_{C,H}$ = 149, C(2), [100]); 56.5 (*d*, $^1J_{C,H}$ = 132, C(1), [44.4]); 48.1 (*d*, $^1J_{C,H}$ = 132, C(4), [24.3]); 39.5 (*t*, $^1J_{C,H}$ = 132, C(3), [44.9]). – MS. (70 eV): 174 (21), 156 (11), 155 (11), 146 (13), 145 (13), 141 (13), 133 (13), 132 (68), 131 (32), 130 (64), 129 (77), 128 (59), 127 (23), 117 (19), 116 (19), 155 (100), 105 (10), 103 (13), 102 (11), 91 (41).

$C_{12}H_{14}O$ (174.24) Calc. C 82.72 H 8.10% Found C 82.84 H 7.99%

15-Hydroxytetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (**32**; *bis-adduct of TCE to* **10**). A mixture of **10** (174 mg, 1 mmol) and freshly sublimed TCE (256 mg, 2 mmol) in anh. benzene (10 ml) was stirred at 20° for 16 h. The solvent was evaporated i.V. and the residue washed with toluene (10 ml). Recrystallization from acetone/CH_2Cl_2 yielded 0.4 g (93%), white solid, m.p. > 230° (dec.). – UV. (95% EtOH): final absorption, ε_{210} = 6600. – IR. (KBr): 3600, 3500, 2980, 2950, 2910, 2260, 1700, 1440, 1370, 1310, 1270, 1230, 1180, 1145, 1130, 1090, 1045, 1030, 980. – ^{1}H-NMR. (CD_3COCD_3): 4.2 (*m*, 1 H, H–C(15)); 3.4–3.9 (*m*, 10 H); 3.0 (HO); 2.0 (*m*, 1 H, H–C(16) *trans* to OH); 1.2 (*m*, 1 H, H–C(16) *cis* to OH). – MS. (70 eV): non volatile substance.

(1R,11R*)- and (1R*,11S*)-11-Hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**35**/**36**; *monoadducts of TCE to* **10**). A mixture of freshly sublimed TCE (128 mg, 1 mmol) and **10** (174 mg, 1 mmol) in anh. benzene (6 ml) was stirred at 20° for 3 h. The solvent was evaporated i.V. and the residue purified by column chromatography on silica gel (10 g, AcOEt/hexane 1:1). The first fraction contained **35**, the second **36**. Recrystallization from CH_2Cl_2 yielded 175 mg (58%) of **35**, colourless crystals, m.p. > 230° (dec.) and 120 mg (39%) of **36**, colourless crystals, m.p. > 230° (dec.). *Spectroscopic data of* **35**: UV. (95% EtOH); 243 (7900). UV. (dioxane): 244 (8400). – IR. (KBr): 3600, 3450, 3090, 2990, 2960, 2930, 2860, 2260, 1625, 1440, 1270, 1240, 1225, 1170, 1080, 1050, 1040, 980, 965, 910, 890. – ^{1}H-NMR. (CD_3COCD_3): 5.34, 5.22 (2 *s*, 2 H, *H*CH=C(9) and *H*CH=C(10) *cis* to C(9), C(10)); 4.98, 4.89 (2 *s*, 2 H, HC*H*=C(9) and HC*H*=C(10) *trans* to C(9), C(10)); 4.18 (*m*, 1 H, H–C(11)); 3.52 (*m*, 4 H, H_2C(3), H_2C(6)); 3.38 (*m*, 1 H, H–C(1)); 3.24 (*m*, 1 H, H–C(8)); 2.78 (*s*, 1 H, HO); 2.05 (*m*, 1 H, H–C(12) *trans* to HO); 1.41 (*m*, 1 H, H–C(12) *cis* to HO). – ^{13}C-NMR. (CD_2Cl_2): 143.2 (*s*, C(9), [15.6][7])); 140.9 (*s*, C(10), [18.1]); 130.2 (*s*, C(7), [26.6]); 128.8 (*s*, C(2), [35.0]); 111.5 (*s*, C(4), [9.0]); 111.3 (*s*, C(5), [6.1]); 108.0 (*t*, $^1J_{C,H}$ = 160, H_2C=C(9), [8.2]); 105.1 (*t*, $^1J_{C,H}$ = 160, H_2C=C(10), [9.0]); 71.0 (*d*, $^1J_{C,H}$ = 151, C(11), [100]); 54.3 (*d*, $^1J_{C,H}$ = 137, C(1), [44.5]); 45.9 (*d*, $^1J_{C,H}$ = 139, C(8), [24.2]); 38.7 (*s*, *C*N, [11.1]); 38.5 (*t*, $^1J_{C,H}$ = 132, C(12), [45.1]); 36.1 (*t*, $^1J_{C,H}$ = 139, C(3), [19.2]); 34.4 (*t*, $^1J_{C,H}$ = 139, C(6), [14.7]). – MS. (70 eV): 284 (13), 259 (23), 258 (100), 230 (6), 192 (10), 166 (18), 140 (13), 131 (12), 130 (54), 129 (27), 128 (24), 127 (12), 115 (31), 91 (17).

$C_{18}H_{14}N_4O$ (302.34) Calc. C 71.51 H 4.67% Found C 71.56 H 4.73%

---

[8]) In brackets the relative induced shifts upon addition of Eu(dpm)$_3$.

Spectroscopic data of **36**: UV. (95% EtOH): 243 (8000). UV. (dioxane): 244 (8450). – IR. (KBr): 3590, 3450, 3090, 2950, 2920, 2260, 1710, 1625, 1435, 1400, 1370, 1340, 1260, 1235, 1180, 1160, 1140, 1090, 1040, 990, 975, 910, 890. – ^{1}H-NMR. (CD_3COCD_3): 5.43, 5.25 (2 *s*, 2 H, *H*CH=C(9) and *H*CH=C(10) *cis* to C(9), C(10)); 4.92, 4.88 (2 *s*, 2 H, HC*H*=C(9) and HC*H*=C(10) *trans* to C(9), C(10)); 4.00 (*m*, 1 H, H–C(11)); 3.53 (*m*, 4 H, $H_2C(3)$, $H_2C(6)$); 3.23 (*m*, 1 H, H–C(1)); 3.16 (*m*, 1 H, H–C(8)); 2.73 (*s*, 1 H, HO); 2.08 (*m*, 1 H, H–C(12) *trans* to HO); 1.35 (*m*, 1 H, H–C(12) *cis* to HO). – ^{13}C-NMR. (CD_2Cl_2): 143.9 (*s*, C(9), [23.8]); 139.1 (*s*, C(10), [34.5]); 132.6 (*s*, C(7), [17.6]); 128.7 (*s*, C(2), [20.3]); 111.2 (*s*, C(5), [3.9]); 111.0 (*s*, C(4), [4.5]); 110.2 (*t*, $^1J_{C,H}$ = 159, H_2C=C(10), [24.3]); 105.5 (*t*, $^1J_{C,H}$ = 159, H_2C=C(9), [14.7]); 68.2 (*d*, $^1J_{C,H}$ = 149, C(11), [100]); 54.1 (*d*, $^1J_{C,H}$ = 141, C(1), [44.8]); 45.8 (*d*, $^1J_{C,H}$ = 141, C(8), [23.2]); 38.6 (*s*, CN, [5.9]); 37.1 (*t*, $^1J_{C,H}$ = 132, C(12), [44.1]); 34.5 (*t*, $^1J_{C,H}$ = 139, C(3), [10.3]); 34.5 (*t*, $^1J_{C,H}$ = 139, C(6), [9.2]). – MS. (70 eV): 284 (15), 259 (29), 258 (100), 166 (22), 130 (58), 129 (26), 128 (23), 127 (19), 115 (33), 111 (18), 97 (21), 85 (25).

$C_{18}H_{14}N_4O$ (302.34) Calc. C 71.51 H 4.67% Found C 71.32 H 4.72%

15-Oxotetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (**33**; *bis-adduct of TCE to* **11**). A mixture of TCE (128 mg, 1 mmol) and **11** (86 mg, 0.5 mmol) in anh. benzene (8 ml) was stirred at 20° for 16 h. The solvent was evaporated and the residue recrystallized from acetone yielding 200 mg (93%), colourless crystals, m.p. > 280° (dec.). – UV. (95% EtOH): 293 (550). – IR. (KBr): 2990, 2970, 2940, 2260, 1730, 1625, 1440, 1420, 1360, 1305, 1270, 1240, 1225, 1155, 1085, 1070, 965, 920. – ^{1}H-NMR. (CD_3COCD_3): 4.1 (*s*, 1 H, H–C(1)); 4.0 (*t*, *J* = 3, 1 H, H–C(8)); 3.6–3.9 (*m*, 8 H); 2.1 (*m*, 2 H, $H_2C(16)$). – MS. (70 eV): non volatile compound.

$C_{24}H_{12}N_8O$ (428.42) Calc. C 67.29 H 2.82% Found C 67.44 H 2.99%

9,10-Dimethylidene-11-oxotricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (**34**; *mono-adduct of TCE to* **11**). A mixture of TCE (128 mg, 1 mmol) and **11** (172 mg, 1 mmol) in anh. benzene (5 ml) was stirred at 20° for 2 h. The solvent was evaporated and the residue recrystallized from CH_2Cl_2 yielding 280 mg (93%), white solid, m.p. > 220° (dec.). – UV. (95% EtOH): 293 (540), 249 (6600). UV. (dioxane): 297 (500), 250 (6800). – IR. (KBr): 3110, 2990, 2980, 2940, 2260, 1740, 1620, 1440, 1410, 1320, 1235, 1190, 1170, 1150, 1130, 1070, 1050, 995, 970, 940, 920, 905. – ^{1}H-NMR. (CD_2Cl_2): 5.48 (*s*, 1 H, *H*CH=C(10) *cis* to C(9)); 5.39 (*s*, 1 H, *H*CH=C(9) *cis* to C(10)); 5.09 (*s*, 1 H, HC*H*=C(10) *trans* to C(9)); 5.05 (*s*, 1 H, HC*H*=C(9) *trans* to C(10)); 3.64 (*s*, 1 H, H–C(1)); 3.34 (*t*, *J* = 3, 1 H, H–C(8)); 3.2–3.3 (*m*, 4 H, $H_2C(3)$, $H_2C(6)$); 2.22 (*m*, 2 H, $H_2C(12)$). – MS. (70 eV): 300 (4), 259 (13), 258 (52), 193 (9), 192 (8), 166 (20), 149 (13), 140 (39), 139 (13), 130 (100), 129 (35), 128 (35), 115 (50), 105 (28).

$C_{18}H_{12}N_4O$ (300.32) Calc. C 71.99 H 4.03% Found C 71.97 H 4.14%

1:1 Mixture of tricarbonyl[methyl (1R,9S*,12S*)-C,9,10,C-η-(12-hydroxy-9,10-dimethylidenetricyclo-[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate)]iron* (**37**) *and tricarbonyl[methyl (1R*,9R*,11S*)-C,9,10,C-η-(11-hydroxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate)]iron* (**38**) *(adducts of methyl propynoate to* **26**). A mixture of **26** (100 mg, 0.32 mmol), methyl propynoate (0.5 g, 5.9 mmol) and a trace of hydroquinone was heated under N_2 at 60° for 3 h. The excess of dienophile was evaporated i.V. and the residue purified by column chromatography on silica gel (5 g, CH_2Cl_2) yielding 90 mg (71%) of **37**/**38** (1:1), yellow oil. – IR. ($CHCl_3$): 3610, 3480, 3000, 2960, 2040, 1985, 1710, 1695, 1650, 1440, 1325, 1260, 1140, 1065, 1030, 980, 945, 905. – ^{1}H-NMR. ($CDCl_3$): 6.9 (*m*, 2 H); 4.4 (*m*, 2 H); 3.7 (*s*, 6 H); 3.3 (*d*, *J* = 3, 2 H); 3.1 (*t*, *J* = 3, 2 H); 3.0 (*m*, 8 H); 2.4 (*m*, 2 H); 2.1–1.9 (*m*, 6 H); 1.5 (*m*, 2 H); 0.5 (*d*, *J* = 3, 4 H). – ^{13}C-NMR. ($CDCl_3$): 211.0 (*s*, $Fe(CO)_3$); 167.1 (*s*, *C*OO); 137.3, 135.3, 133.8, 131.8, 128.1, 109.3, 105.1 (7 *s*); 136.3 (*d*, $^1J_{C,H}$ = 163, C(5)); 70.7 (*d*, $^1J_{C,H}$ = 153, C(12) of **37** and C(11) of **38**); 51.6 (*qa*, $^1J_{C,H}$ = 147); 51.5, 51.1 (2 *d*, $^1J_{C,H}$ = 139, C(8) of **37** and C(1) of **38**); 42.8, 42.4 (2 *d*, $^1J_{C,H}$ = 139, C(1) of **37** and C(8) of **38**); 41.5, 41.4, 39.0, 38.9 (4 *t*, $^1J_{C,H}$ = 160); 37.6 (*t*, $^1J_{C,H}$ = 132); 29.1, 29.0, 27.4, 27.2 (4 *t*, $^1J_{C,H}$ = 128, C(3), C(6)). – MS. (70 eV): 370 (9), 342 (7), 314 (87), 312 (12), 255 (8), 254 (23), 242 (10), 240 (17), 238 (6), 236 (8), 234 (5), 213 (20), 212 (100), 210 (20).

$C_{19}H_{18}FeO_6$ (398.20) Calc. C 57.31 H 4.56% Found C 57.28 H 4.63%

3:1 Mixture of [methyl (1R,9S*)-C,9,10,C-η-9,10-dimethylidene-12-oxotricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate)]tricarbonyliron* (**39**) *and [methyl (1R*,9R*)-C,9,10,C-η-9,10-dimethylidene-11-oxotricyclo[6.2.2.0^{2,7}]dodeca-2(7),4-diene-4-carboxylate)tricarbonyliron* (**40**). A mixture of **28** (0.1 g, 0.32 mmol), methyl propynoate (1 g, 11.9 mmol) and a trace of hydroquinone was heated under N_2 to 60° for 2 h. The excess of dienophile was evaporated i.V. and the oily residue purified by column chromatography on silica gel (5 g, AcOEt/hexane 1:3): 100 mg (79%) **39/40** (3:1), yellow oil. – IR. ($CHCl_3$): 3000, 2960, 2050, 1995, 1980, 1730, 1690, 1650, 1440, 1330, 1300, 1285, 1260, 1140, 1110, 1080, 1050, 950. – ^{1}H-NMR. ($CDCl_3$): 7.0 (*m*, 2 H, H–C(5)); 3.8 (*s*, 6 H); 3.61 (*s*, H–C(1) of **40**); 3.56 (*s*, H–C(8) of **39**); 3.38 (*t*, *J* = 3, H–C(1) of **39**); 3.32 (*t*, *J* = 3, H–C(8) of **40**); 3.1 (*m*, 8 H); 2.4 (*m*, 4 H); 2.1 (*d*, 4 H); 0.6, 0.5 (*d*, *J* = 3, 4 H). – ^{13}C-NMR. ($CDCl_3$) of **39**: 210.2 (*s*, Fe(*C*O)$_3$); 204.9 (*s*, *C*O); 166.7 (*s*, *C*OO); 139.2 (*s*, C(2)); 135.6 (*d*, $^1J_{C,H}$ = 159, C(5)); 130.5 (*s*, C(7)); 127.8 (*s*, C(4)); 110.2 (*s*, C(10)); 103.9 (*s*, C(9)); 60.3 (*d*, $^1J_{C,H}$ = 144, C(8)); 51.7 (*qa*, $^1J_{C,H}$ = 147, *C*H$_3$O); 42.9 (*d*, $^1J_{C,H}$ = 142, C(1)); 40.2 (*t*, $^1J_{C,H}$ = 160, H$_2$*C*=C(10)); 39.3 (*t*, $^1J_{C,H}$ = 160, H$_2$*C*=C(9)); 35.2 (*t*, $^1J_{C,H}$ = 136, C(11)); 29.1 (*t*, $^1J_{C,H}$ = 133, C(6)); 27.8 (*t*, $^1J_{C,H}$ = 133, C(3)). – ^{13}C-NMR. ($CDCl_3$) of **40**: 210.2 (*s*, Fe(*C*O)$_3$); 204.8 (*s*, C(11)); 166.7 (*s*, *C*OO); 137.2 (*s*, C(7)); 135.5 (*d*, $^1J_{C,H}$ = 159, C(5)); 132.6 (*s*, C(2)); 127.9 (*s*, C(4)); 110.2 (*s*, C(9)); 103.9 (*s*, C(10)); 60.7 (*d*, $^1J_{C,H}$ = 144, C(1)); 51.7 (*qa*, $^1J_{C,H}$ = 147, *C*H$_3$O); 42.5 (*d*, $^1J_{C,H}$ = 142, C(8)); 40.4 (*t*, $^1J_{C,H}$ = 160, H$_2$*C*=C(10)); 39.1 (*t*, $^1J_{C,H}$ = 160, H$_2$*C*=C(9)); 35.2 (*t*, $^1J_{C,H}$ = 136, C(12)); 29.4 (*t*, $^1J_{C,H}$ = 133, C(6)); 27.5 (*t*, $^1J_{C,H}$ = 133, C(3)). – MS. (70 eV): 396 (1), 368 (12), 340 (16), 312 (100), 252 (19), 242 (15), 240 (15), 226 (16), 224 (20), 222 (14), 214 (20), 212 (48), 210 (9).

$C_{19}H_{16}FeO_6$ (396.18) Calc. C 57.60 H 4.07% Found C 57.42 H 4.23%

3:1 Mixture of (±)-methyl 9,10-dimethylidene-12-oxotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene-4-carboxylate (**41**) *and (±)-methyl 9,10-dimethylidene-11-oxotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene-4-carboxylate* (**42**). Freshly sublimed trimethylamine oxide (4 g, 53 mmol) was added to a stirred solution of the 3:1 mixture of **39/40** obtained above (0.6 g, 1.5 mmol) in anh. acetone (400 ml). After stirring at 20° for 20 h, the mixture was concentrated by evaporation i.V. to 100 ml. The mixture was filtered, and then H_2O (100 ml) was added, followed by extraction with CH_2Cl_2 (80 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated i.V. and the residue purified by column chromatography on silica gel (30 g, AcOEt/hexane 1:1): 0.28 g (73%) **41/42** (3:1), colourless oil. – IR. (CH_2Cl_2): 3100, 3000, 2960, 1735, 1725, 1620, 1585, 1440, 1335, 1310, 1290, 1280, 1195, 1160, 1115, 985, 970, 900. – ^{1}H-NMR. (CD_3COCD_3): 7.4–8.0 (*m*, 6 H); 5.58, 5.52, 5.25, 5.23 (4 *s*, 8 H); 4.48 (*s*, 1 H, H–C(1) of **42**); 4.47 (*s*, 1 H, H–C(8) of **41**); 4.28 (*t*, *J* = 3, 1 H, H–C(1) of **41**); 4.25 (*t*, *J* = 3, 1 H, H–C(8) of **42**); 3.86 (*s*, 6 H); 2.3–2.5 (*m*, 4 H). – ^{13}C-NMR. ($CDCl_3$) of **41**: 205.2 (*s*, C(12)); 166.7 (*s*, *C*OO); 142.9 (*s*, C(2)); 141.1 (*s*, C(9)); 138.3 (*s*, C(7)); 134.6 (*s*, C(10)); 129.9 (*s*, C(4)); 129.1 (*d*, $^1J_{C,H}$ = 164, C(5)); 125.2 (*d*, $^1J_{C,H}$ = 161, C(3)); 124.8 (*d*, $^1J_{C,H}$ = 164, C(6)); 109.9 (*t*, $^1J_{C,H}$ = 160, H$_2$*C*=C(9)); 107.1 (*t*, $^1J_{C,H}$ = 159, H$_2$*C*=C(10)); 65.1 (*d*, $^1J_{C,H}$ = 144, C(8)); 52.9 (*qa*, $^1J_{C,H}$ = 147, *C*H$_3$O); 46.4 (*d*, $^1J_{C,H}$ = 145, C(1)); 40.9 (*t*, $^1J_{C,H}$ = 133, C(11)). – ^{13}C-NMR. ($CDCl_3$) of **42**: 205.2 (*s*, C(11)); 166.6 (*s*, *C*OO); 142.7 (*s*, C(10)); 140.0 (*s*, C(2)); 138.5 (*s*, C(9)); 131.3 (*s*, C(7)); 129.9 (*s*, C(4)); 129.6 (*d*, $^1J_{C,H}$ = 164, C(5)); 126.3 (*d*, $^1J_{C,H}$ = 164, C(3)); 123.8 (*d*, $^1J_{C,H}$ = 160, C(6)); 109.9 (*t*, $^1J_{C,H}$ = 160, H$_2$*C*=C(10)); 107.2 (*t*, $^1J_{C,H}$ = 159, H$_2$*C*=C(9)); 64.6 (*d*, $^1J_{C,H}$ = 143, C(1)); 52.1 (*qa*, $^1J_{C,H}$ = 147, *C*H$_3$O); 46.6 (*d*, $^1J_{C,H}$ = 145, C(8)); 40.7 (*t*, $^1J_{C,H}$ = 133, C(12)). – MS. (70 eV): 254 (18), 221 (15), 212 (100), 181 (55), 165 (18), 153 (41), 152 (70), 151 (26), 149 (15).

$C_{16}H_{14}O_3$ (254.29) Calc. C 75.58 H 5.55% Found C 75.21 H 5.61%

REFERENCES

[1] *M. Avenati & P. Vogel,* Helv. Chim. Acta *66*, 1279 (1983).
[2] *P. Vogel,* Chimia *36*, 10, 302 (1982).
[3] *C. Mahaim, P.-A. Carrupt, J.-P. Hagenbuch, A. Florey & P. Vogel,* Helv. Chim. Acta *63*, 1149 (1980).
[4] a) *P.-A. Carrupt & P. Vogel,* Tetrahedron Lett. *1979*, 4533; b) *Y. Bessière & P. Vogel,* Helv. Chim. Acta *63*, 232 (1980); c) *J. Tamariz, L. Schwager, J.H.A. Stibbard & P. Vogel,* Tetrahedron Lett. *24*, 1497 (1983).
[5] *O. Pilet & P. Vogel,* Helv. Chim. Acta *64*, 2563 (1981); L. *de Piccioto, P.-A. Carrupt & P. Vogel,* J. Org. Chem. *47*, 3796 (1982).
[6] *O. Pilet, J.-L. Birbaum & P. Vogel,* Helv. Chim. Acta *66*, 19 (1983).
[7] *M. Avenati, P.-A. Carrupt, D. Quarroz & P. Vogel,* Helv. Chim. Acta *65*, 188 (1982).
[8] *M. Avenati & P. Vogel,* Helv. Chim. Acta *65*, 204 (1982).
[9] *A. Chollet, M. Wismer & P. Vogel,* Tetrahedron Lett. *1976*, 4271; *A. Barakat,* travail de diplôme, Université de Lausanne 1977.
[10] *F. Iordache, F. Chiraleu & M. Avram,* Rev. Roum. Chim. *20*, 233 (1975); Chem. Abstr. *83*, 57812j (1975).
[11] *R. Gabioud & P. Vogel,* Tetrahedron *36*, 149 (1980).
[12] *H.C. Brown & B.C. Subba Rao,* J. Am. Chem. Soc. *81*, 6428 (1959).
[13] *J.-P. Hagenbuch & P. Vogel,* Chimia *31*, 136 (1977); *A. Chollet, J.-P. Hagenbuch & P. Vogel,* Helv. Chim. Acta *62*, 511 (1979).
[14] *J.F.W. McOmie,* 'Protective Groups in Organic Chemistry', Plenum Press, London 1973.
[15] *S. Krishnamurthy, R.M. Schubert & H.C. Brown,* J. Am. Chem. Soc. *95*, 8486 (1973); *E.R. Walker,* Chem. Soc. Rev. *5*, 23 (1976).
[16] *A. Chollet & P. Vogel,* Helv. Chim. Acta *61*, 732 (1978).
[17] *R. Gabioud, G. Chapuis & P. Vogel,* J. Org. Chem. *47*, 3316 (1982).
[18] *Ph. Narbel, A.A. Pinkerton, E. Tagliaferri, J. Wenger, R. Roulet, R. Gabioud & D. Schwarzenbach,* J. Organomet. Chem. *208*, 335 (1981).
[19] *Y. Shvo & E. Hazum,* J. Chem. Soc., Chem. Commun. *1974*, 336; *A.P. Humphries & S.A.R. Knox,* J. Chem. Soc., Dalton *1978*, 1514.
[20] *Ph. Narbel, R. Roulet, E. Tagliaferri & P. Vogel,* J. Organomet. Chem. *194*, 103 (1980).
[21] *D. Quarroz, J.-M. Sonney, A. Chollet, A. Florey & P. Vogel,* Org. Magn. Reson. *9*, 611 (1977).
[22] *M. Avenati, O. Pilet, P.-A. Carrupt & P. Vogel,* Helv. Chim. Acta *65*, 178 (1982).
[23] *Ph. Narbel, T. Boschi, R. Roulet, P. Vogel, A.A. Pinkerton & D. Schwarzenbach,* Inorg. Chim. Acta *36*, 161 (1979); *U. Steiner, H.-J. Hansen, K. Bachmann & W.v. Philisborn,* Helv. Chim. Acta *60*, 643 (1977).
[24] *P.-A. Carrupt & P. Vogel,* Tetrahedron Lett. *22*, 4721 (1981); *J.-M. Sonney & P. Vogel,* Helv. Chim. Acta *63*, 1034 (1980); see also: *R. Grinter, S.F. Mason & G.W. Vane,* Trans. Faraday Soc. *60*, 285 (1964); *H. Labhart & G. Wagnière,* Helv. Chim. Acta *42*, 2219 (1959); *P.H. Schippers & H.P.J.M. Dekkers,* J. Am. Chem. Soc. *105*, 79 (1983).
[25] *P.-A. Carrupt & P. Vogel,* Tetrahedron Lett. *23*, 2563 (1982).
[26] *A.A. Pinkerton, G. Chapuis, P. Vogel, U. Hänisch, Ph. Narbel, T. Boschi & R. Roulet,* Inorg. Chim. Acta *35*, 197 (1979).
[27] *Ch. Barras, L.G. Bell, R. Roulet & P. Vogel,* Helv. Chim. Acta *64*, 2841 (1981).
[28] *R. Gabioud,* Doctoral dissertation, University of Lausanne, July 1982.