111. Stereoselective Control in the Base-Catalyzed H/D Exchange of 5,6-Dimethylidene-2-bicyclo[2.2.n]alkanone Tricarbonyliron Complexes. Revision of the Structures of Tricarbonyliron Complexes of 5,6-Dimethylidenebicyclo[2.2.2]oct-2-ene and 5,6-Dimethylidenebicyclo[2.2.1]hept-2-ene[1])

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(6.III.84)

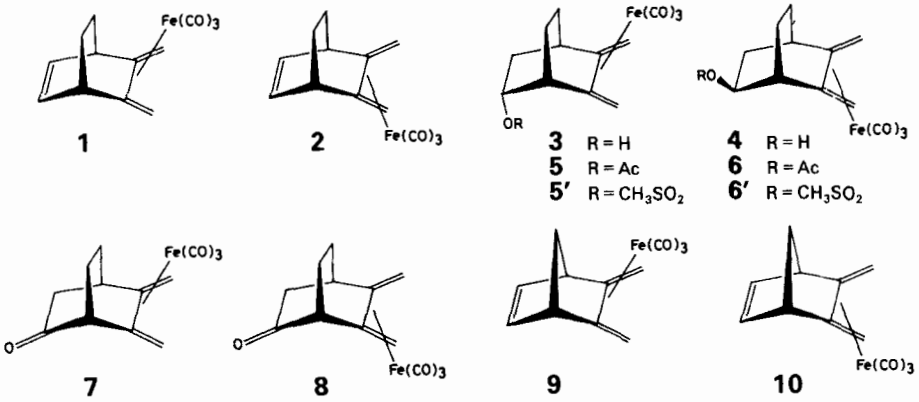
Summary

Oxidative hydroborations of *exo*- (**1**) and *endo*-$Fe(CO)_3$ (**2**) complexes of 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene are highly stereoselective and give *endo*-alcohol **3** and *exo*-alcohol **4** as major products, respectively. *Collins* oxidations of **3** and **4** furnish the corresponding *exo*- and *endo*-$Fe(CO)_3$-complexed 5,6-dimethylidene-2-bicyclo-[2.2.2]octanone **7** and **8**. $NaBH_4$ reduction of *exo*-complex **7** gives a mixture of **3** and isomeric *exo*-alcohol **18**, whereas reduction of *endo*-complex **8** gives the *endo*-alcohol, *endo*-complex **19**, as the sole product. The base-catalyzed H/D exchange of **7** and **8** afforded the dideuterated *exo*-complex **35** and the monodeuterated *endo*-complex **32**, respectively. Oxidative hydroborations of the *exo*-(**9**) and *endo*-$Fe(CO)_3$ (**10**) complexes of 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene give the corresponding *exo*-alcohols **39** and **40**. Oxidation of **39** and **40** gives the *exo*- and *endo*-complexes **41** and **42**, respectively, of 5,6-dimethylidene-2-bicyclo[2.2.1]heptanone. Only H_{exo}–C(3) can be exchanged in **42**, whereas both H-atoms at C(3) in **41** are exchangeable. The *endo*-$Fe(CO)_3$ group in **8** and **42** blocks the base-catalyzed H/D exchange of H_{endo}–C(3), thus providing a test for the configuration of the $Fe(CO)_3$ group in these systems. These studies have led to a revision of the iron configurations proposed by *Hansen et al.* [2] for **1**, **2**, **9**, and **10**.

Introduction. – During our search for optically pure 5,6-dimethylidene-2-bicyclo[2.2.2]octyl derivatives [1] we used a mixture of the tricarbonyliron complexes **1** and **2** as starting materials. These complexes were described first by *Hansen et al.* [2]. Their structural assignment (*exo*- *vs.* *endo*-$Fe(CO)_3$) was based on their mass spectra and on coordination shifts in their ^{1}H- and ^{13}C-NMR spectra. We describe here the transfor-

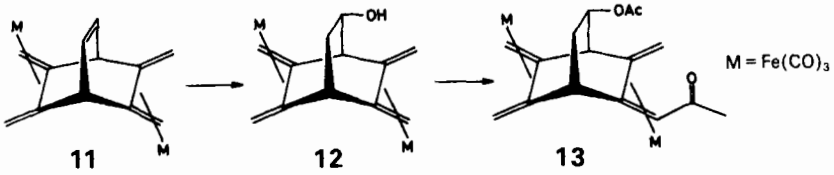
[1]) A preliminary communication was presented at the Autumn Meeting of the Swiss Chemical Society, Bern, October 14, 1983.

mation of **1** and **2** into the corresponding 2-bicyclo[2.2.2]octyl derivatives **3–8** whose properties require a revision of the structures proposed earlier [2] for **1** and **2**. Similarly, the *exo- vs. endo*-$Fe(CO)_3$ assignments in the tricarbonyl(5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)iron complexes **9** and **10** must also be revised.



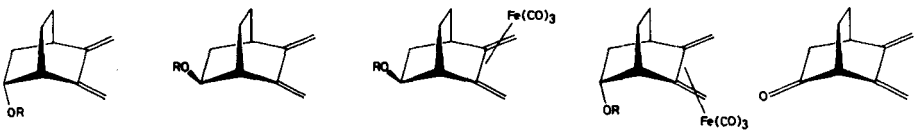
Results and Discussion. – The treatment of 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene with $Fe_2(CO)_9$ in hexane gave a 4:1 mixture of complexes **2** and **1** in 61% yield. Contrary to an earlier structural assignment [2], the major complex is the *endo*-derivative **2**, as demonstrated here-below. Hydroboration (BF_3/$NaBH_4$/THF) of the above mixture, followed by oxidative workup (H_2O_2/KOH) yielded a mixture of alcohols **3** (13%, isolated) and **4** (57%, isolated) which were readily separated by column chromatography on silica gel. When the oxidative hydroboration was repeated with a pure sample of complex **2**, only alcohol **4** was isolated, thus indicating the high stereoselectivity of the hydroboration of the uncoordinated endocyclic double bond in **2**. Under the same conditions, pure complex **1** (separated by inverse-phase HPLC) gave a 85:15 mixture of alcohols **3** and **18** (see below). In the case of reaction **2**→**4**, the selectivity can be explained by steric hindrance preventing the approach of borane onto the *endo*-face of the olefin, thus leading to the exclusive formation of **4**. Similar steric effects have already been recognized in the hydroboration of the pentaene bimetallic complex **11**. This complex was found to give exclusively alcohol **12** [3a], whose structure has been confirmed by X-ray analysis of its derivative **13** [3b].

Scheme 1



The relatively high *endo*-face selectivity of reaction **1**→**3** (major) + **18** (minor) remains unexplained at present. It may be attributed to a steric factor which would imply a larger steric hindrance to the electrophilic attack onto the *exo*- than onto the *endo*-face. However, a possible electronic effect, making the transition state of the hydroboration less destabilized by the $Fe(CO)_3$ group (inductive effect, see [4]) when the attack occurs onto the *endo*- rather than onto the *exo*-face cannot be rejected. Further experiments must be carried out in order to advance firmer hypotheses.

The complexed dienols **3** and **4** gave the corresponding acetates **5** and **6**, respectively (Ac_2O/pyridine). When treated with an excess of trimethylamine oxide in acetone [5], **5** and **6** gave the corresponding free ligands **14** and **15**. The latter were identical with the acetates derived (Ac_2O/pyridine) from the known dienols **16** and **17**, respectively [6].

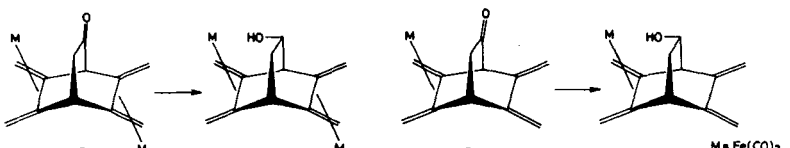


14 R = Ac **16** R = H **15** R = Ac **17** R = H **20** R = Ac **18** R = H **21** R = Ac **19** R = H **22**

Collins oxidations (CrO_3/pyridine, CH_2Cl_2) of alcohols **3** and **4** gave the corresponding complexed dienones **7** and **8**. These reactions confirmed the tricarbonyliron stereoisomerism in **3**, **5** and **4**, **6**. As in the case of the hydride reductions of the uncomplexed 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**22**) [6], the reaction of complexed dienone **7** with $NaBH_4$ in THF was not selective and afforded a 1:1 mixture of alcohols **3** and **18**. This is in agreement with the *exo*-position of the $Fe(CO)_3$ group in **7**, and consequently confirms the *exo*-configuration of the Fe-atom in **3**, **7** and **1**. The isomeric alcohols **3** and **18** were easily separated by column chromatography. Contrastingly, the $NaBH_4$ reduction of ketone **8** was highly stereoselective and gave the complexed dienol **19** in 68% yield. This result also confirmed the *endo*-position of the $Fe(CO)_3$ group in **8**, and thus in **4**, **6**, and **2**. Esterification of **18** and **19** with Ac_2O/pyridine afforded acetates **20** and **21**, respectively.

Similar stereoselectivities were observed by *Gabioud et al.* in the reduction of the diiron-complexed tetraenone **23** [7] and monocomplex **24** [8]. In both cases, only the less hindered face of the ketone was attacked by the nucleophile giving the corresponding complexes **25** and **26**.

Scheme 2



23 **25** **24** **26**

Our structural assignments of *exo- vs. endo*-$Fe(CO)_3$ configuration in complexes **1–8** were confirmed by an X-ray single crystal structure of the optically pure (+)-tricarbonyl[(1*S*,2*S*,5*S*)-*C*,5,6,*C*-η-(5,6-dimethylidene-2-*endo*-bicyclo[2.2.2]octyl *p*-bromobenzoate)]iron derived from **3** (racemate) [1]. Furthermore, when the mesylate **6'** (obtained by treatment of **4** with methanesulfonyl chloride in pyridine) was heated to 100°C with 4 mol-equiv. of CsF in anhydrous DMF, the *endo*-$Fe(CO)_3$ complex **2** was formed in low yield together with polymerized material and the formate of **4**. No trace of the *exo*-isomer **1** could be detected in the reaction mixture. Under the same conditions, the mesylate **5'** (derived from alcohol **3**) was perfectly stable (no formate and no product of elimination was formed). Control experiments also determined that the isomerization process, *exo* $\leftrightarrows$ *endo*-$Fe(CO)_3$ (**1** $\leftrightarrows$ **2**) does not occur under these conditions. However, isomerization was observed on heating **1** or **2** in DMF at 140°C (15 h). This process **1** $\leftrightarrows$ **2** was accompanied by the formation of uncomplexed triene. These experiments confirmed that stereospecific *exo* $\leftrightarrows$ *endo*-$Fe(CO)_3$ isomerizations did not occur during hydroborations of **1** and **2** and oxidations of **3** and **4**[2]).

Our results demonstrate that the mass spectra, ^1H- and ^{13}C-NMR criteria defined by *Hansen et al.* [2] lead to ambiguous structural assignments of tricarbonyl iron configuration in complexes of exocyclic s-*cis*-butadiene grafted onto bicyclic skeletons. The ^{13}C-NMR-chemical shifts (δ_C) of complexes **1–8**, **18–21** are reported in the *Table*. Comparison with the δ_C of the uncomplexed dienes shows a *deshielding* of *ca.* 3 ppm of the methylene C-atoms *syn* to the $Fe(CO)_3$ group. The methylene C-atoms *anti* to the $Fe(CO)_3$ groups are not significantly affected. A smaller deshielding of *ca.* 1 ppm is observed for the substituted atom C(2) in **3**, **4**, **18**, and **19**. Furthermore, the δ_C of C(2) in these alcohols and in the corresponding acetates **5**, **6**, **20**, and **21** do not depend upon the position (*exo vs. endo*) of the $Fe(CO)_3$ group. Comparison of the δ_C of C(2) in complexes **7** and **8** with the data reported for the uncomplexed 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**22**) [6] suggests a weak *shielding* of the ketonic C-atom upon coordination of the homoconjugated diene by a $Fe(CO)_3$ group. The effect appears to be somewhat larger (*ca.* 4 ppm) for the *endo*-complex **8** than for the *exo*-isomer **7** (*ca.* 1 ppm). $Fe(CO)_3$ complexation of the diene in 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene induces only very small deshielding effects on the C-atoms of the C(2),C(3) double bond. In contrast to the ethylene C-atoms C(7) and C(8) which are more deshielded by a *syn*- than by an *anti*-$Fe(CO)_3$ group, these olefinic C-atoms C(2) and C(3) are more deshielded by an *anti*- than by a *syn*-$Fe(CO)_3$ group.

Base-catalyzed H/D exchanges. – *Gabioud & Vogel* [7] have shown for the hexacarbonyl(tetraenone)diiron complex **23** that base-catalyzed H/D exchange occurs only with the α-H-atom *anti* to the *exo*-$Fe(CO)_3$ group, leading to the monodeuterated species **27**. No trace of the dideuterated complex **28** could be detected even under

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[2]) In our hands, the *endo* $\leftrightarrows$ *exo*-$Fe(CO)_3$ isomerization has never been observed for complexes of exocyclic dienes upon heating in the presence or the absence of ironcarbonyls [9], see, however, [2]. Neither does it occur under acidic conditions unless the bicyclic skeleton undergoes a rearrangement [10]. If an E_1-type mechanism should be operative in the elimination of *exo*-$Fe(CO)_3$-complexed 5,6-dimethylidene-2-bicyclo-[2.2.2]octyl mesylate and if skeleton rearrangement should have occurred, the reaction products should contain some 2-bicyclo[3.2.1]octyl derivatives. Even under these hypothetical conditions, the elimination of methanesulfonic acid should not affect the configuration of the iron in the bicyclo[2.2.2]oct-2-ene derivatives.

Table. *^{13}C-NMR Chemical Shifts δ_C (± 0.1 ppm; in $CDCl_3$; internal reference: δ_{CDCl_3} = 79.91 ppm) of 2-Functionalized Tricarbonyl(5,6-dimethylidenebicyclo[2.2.2]-octan)iron Complexes* **1–8, 18–21,** *and of the Corresponding Uncomplexed Ligands.* The multiplicities and ^1J(C,H) (± 1 Hz) of the signals are also given for **3–8, 18–21**

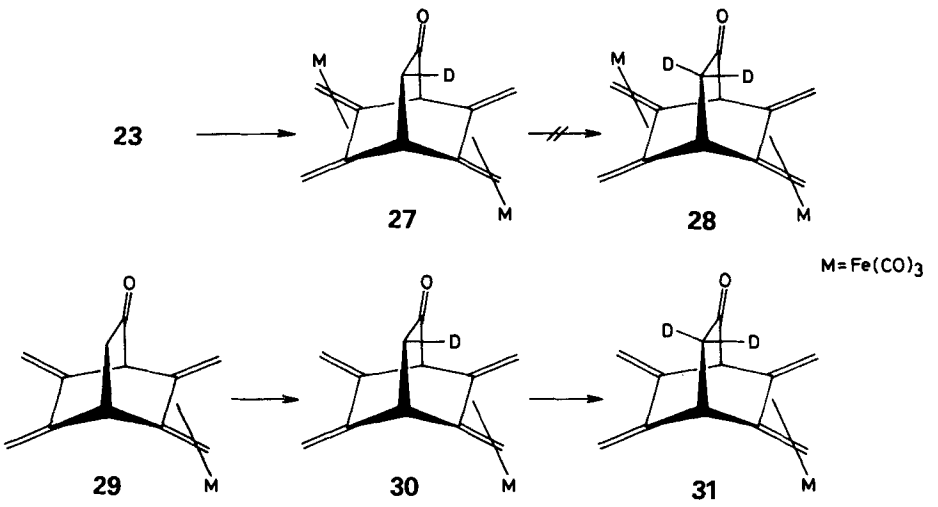
Compound	C(1)	C(2)	C(3)	C(4)	C(5)	CH_2=C(5)	C(6)	CH_2=C(6)	C(7)	C(8)	$Fe(CO)_3$	Others	
1 [2][a]	39.9	135.8	135.8	39.9	116.4	36.3	116.4	36.3	29.5	29.5	211.5	–	–
2 [2][a]	38.5	134.2	134.2	38.5	108.0	39.8	108.0	39.8	25.3	25.3	211.3	–	–
[2][b]	41.9	133.0	133.0	41.9	147.0	102.4	147.0	102.4	25.8	25.8	–	–	–
3 (*endo*-OH, *exo*-Fe)	41.6 *d*,140	70.5 *d*,150	39.7 *t*,130	33.6 *d*,140	119.9 *s*	36.9 *t*,160	107.5 *s*	38.7 *t*,160	28.0 *t*,131	26.2 *t*,131	211.7 *s*	–	–
19 (*endo*-OH, *endo*-Fe)	41.2 *d*,140	69.5 *d*,148	41.0 *t*,130	33.3 *d*,140	112.1 *s*	35.0 *t*,160	103.4 *s*	36.2 *t*,160	26.0 *t*,136	24.3 *t*,137	209.7 *s*	–	–
16 [6]	44.4	68.5	38.9	36.2	148.4	103.6	143.9	108.1	24.8	22.9	–	–	–
18 (*exo*-OH, *exo*-Fe)	41.4 *d*,139	70.0 *d*,150	36.9 *t*,132	33.7 *d*,140	113.0 *s*	36.8 *t*,160	109.7 *s*	37.0 *t*,160	29.7 *t*,132	21.4 *t*,132	211.0 *s*	–	–
4 (*endo*-OH *endo*-Fe)	40.2 *d*,140	70.1 *d*,150	39.8 *t*,130	34.6 *d*,140	110.1 *s*	37.0 *t*,160	105.9 *s*	37.3 *t*,160	26.5 *t*,133	19.0 *t*,133	211.5 *s*	–	–
17 [6]	44.2	68.6	37.2	36.8	147.9	103.4	146.5	105.3	25.8	18.2	–	–	–
5 (endo-OAc, *exo*-Fe)	37.8 *d*,142	72.8 *d*,154	36.4 *t*,130	33.2 *d*,140	111.6 *s*	36.8 *t*,160	107.4 *s*	37.9 *t*,160	27.9 *t*,132	25.9 *t*,132	211.1 *s*	170.4 *s*	21.0 *q*,130
21 (*endo*-OAc, *endo*-Fe)	38.4 *d*,142	71.9 *d*,152	38.5 *t*,130	33.0 *d*,142	111.8 *s*	36.2 *t*,160	103.8 *s*	34.6 *t*,160	26.3 *t*,135	24.1 *t*,135	210.5 *s*	171.0 *s*	21.0 *q*,130
20 (*exo*-OAc, *exo*-Fe)	38.0 *d*,140	72.1 *d*,154	34.6 *t*,132	33.5 *d*,140	113.4 *s*	37.1 *t*,160	108.8 *s*	37.0 *t*,160	28.3 *t*,130	22.4 *t*,130	211.5 *s*	170.7 *s*	21.2 *q*,130
6 (*exo*-OAc, *endo*-Fe)	36.9 *d*,142	72.5 *d*,154	37.2 *t*,130	34.1 *d*,140	110.0 *s*	37.0 *t*,160	104.9 *s*	37.3 *d*,160	26.1 *t*,132	19.8 *t*,132	209.8 *s*	170.3 *s*	21.1 *q*,129
7 (ketone, *exo*-Fe)	51.0 *d*,144	210.1 *s*	41.4 *t*,131	35.5 *d*,140	113.1 *s*	37.0 *t*,160	106.3 *s*	37.2 *t*,160	28.3 *t*,130	26.9 *t*,130	210.5 *s*	–	–
8 (ketone, *endo*-Fe)	51.3 *d*,144	206.9 *s*	45.3 *t*,130	34.2 *d*,140	109.3 *s*	37.3 *t*,160	100.4 *s*	37.5 *t*,160	25.6 *t*,135	23.1 *t*,135	210.5 *s*	–	–
22 [6]	54.8	211.3	44.2	38.2	145.9	105.2	141.4	108.1	24.9	23.9	–	–	–

[a]) With corrected $Fe(CO)_3$ configurations.

[b]) 5,6-Dimethylidenebicyclo[2.2.2]oct-2-ene.

forcing conditions [7]. With the monocomplex **29**, however, dideuteration could be achieved, although the first step **29**→**30** was about 100 times faster than the exchange **30**→**31**.

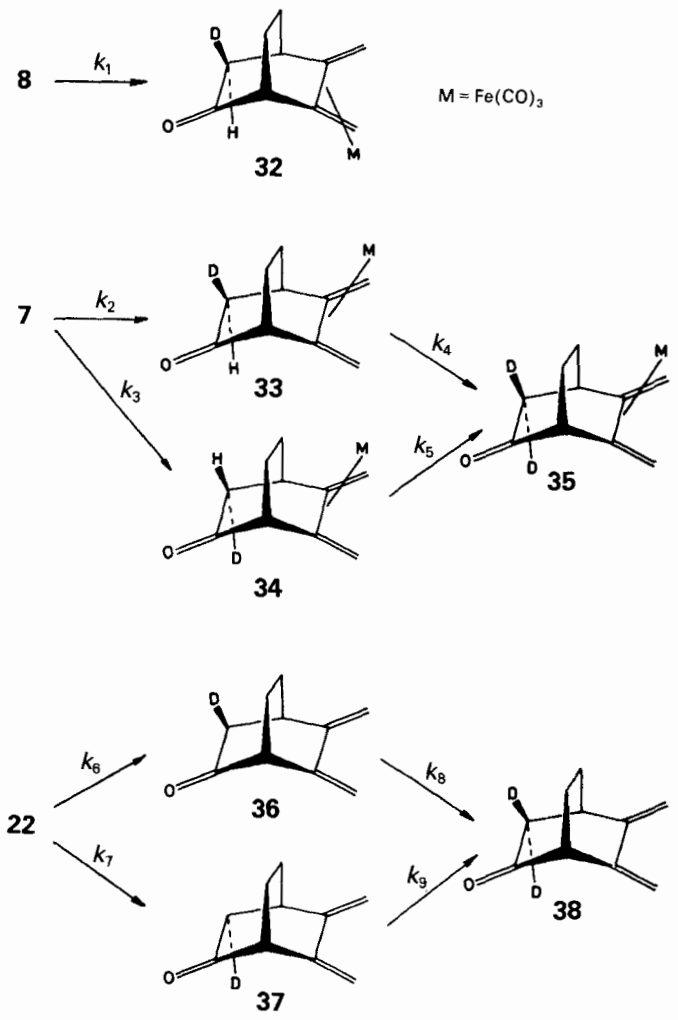
Scheme 3



Under similar conditions we observed the *endo*-complex **8** to exchange H_{exo}–C(3), giving exclusively the monodeuterated complex **32**. No exchange at the *endo*-C(3) position could be detected after several days at 30°C (CH_3ONa in CD_3OD/CD_2Cl_2 1:1). Contrastingly, both H-atoms at C(3) in the *exo*-isomer **7** were exchanged at −10°C giving the dideuterated complex **35**. By following the disappearance of the H_{exo}–C(3) signals at δ_H 2.16, 2.39, and 2.01 ppm in **7**, **8**, and **22**, respectively (360-MHz-1H-NMR), the rate constants $k_1 \approx 1.6 \cdot 10^{-3}$ (for **8**→**32**), $k_2 \approx 1.53 \cdot 10^{-3}$ (**7**→**33**), and $k_6 \approx 1.5 \cdot 10^{-3}$ $dm^3mol^{-1}s^{-1}$ (**22**→**36**) were evaluated at −10°C in CD_3OD/CD_2Cl_2 1:1 containing 0.25M CH_3ONa. The other rate constants k_3 (**7**→**34**) and k_7 (**22**→**37**) for the H_{endo}–C(3)/D exchange, as well as k_4 (**33**→**35**), k_5 (**34**→**35**), k_8 (**36**→**38**), and k_9 (**37**→**38**) for the dideuteration steps could not be determined as easily. Nevertheless, the ^{1}H-NMR kinetic data allowed to estimate the following rate constant ratios: for **7**, $k_2/k_3 \approx k_2/k_4 = 5 \pm 3$ and for **22**, $k_6/k_7 \approx k_6/k_8 = 7 \pm 3$. It is interesting to note that diene complexation of dienone **22** with an *endo*- or *exo*-$Fe(CO)_3$ group does not affect significantly the rate of the base-catalyzed H/D exchange of the ketone at H_{exo}-C(3). However, when the $Fe(CO)_3$ group is in the *endo*-position, the H_{endo}–C(3) exchange is completely blocked. This property can thus be used to assign the configuration of the iron in complexes **7** and **8**.

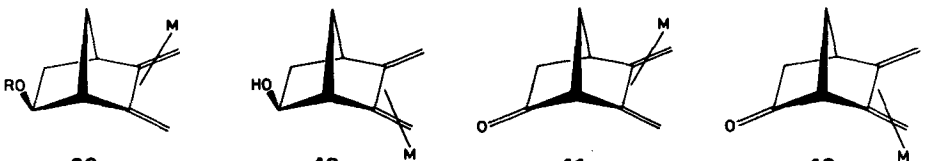
We now show that this property can also be used in the bicyclo[2.2.1]heptyl derivatives **41** and **42**. The results reported below militate against the iron-configuration assignments proposed by *Hansen et al.* [2] for irontricarbonyl complexes of 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene (see **9** and **10**) and of 5,6-dimethylidenebicyclo[2.2.1]-heptane, the latter being correlated with the former by catalytic hydrogenations [2].

Scheme 4



Recently, we reported on the oxidative hydroboration of a 1:1 mixture of **9** and **10** that gave complexed dienols **39** and **40** in modest yield [4c]. The structures of **39** and **40** were determined unambiguously by chemical correlation with the (+)-(1*S*,2*R*)-5,6-dimethylidene-2-*exo*-bicyclo[2.2.1]heptyl-*exo*-irontricarbonyl *p*-bromobenzoate[3]) for which an X-ray single crystal structure had been obtained [11]. Hydroboration (BF_3/$NaBH_4$/THF) followed by oxidative workup (H_2O_2/KOH) of pure (HPLC) **9** (the ma-

[3]) The correct name and stereochemical prefixes of this complex are: (+)-tricarbonyl[(1*R*,2*R*,5*R*)-*C*,5,6,*C*-η-(5,6-dimethylidene-2-*exo*-bicyclo[2.2.1]heptyl *p*-bromobenzoate)]iron. The stereochemical prefixes given in [11] refer to the free ligand and should not be used for the complex.



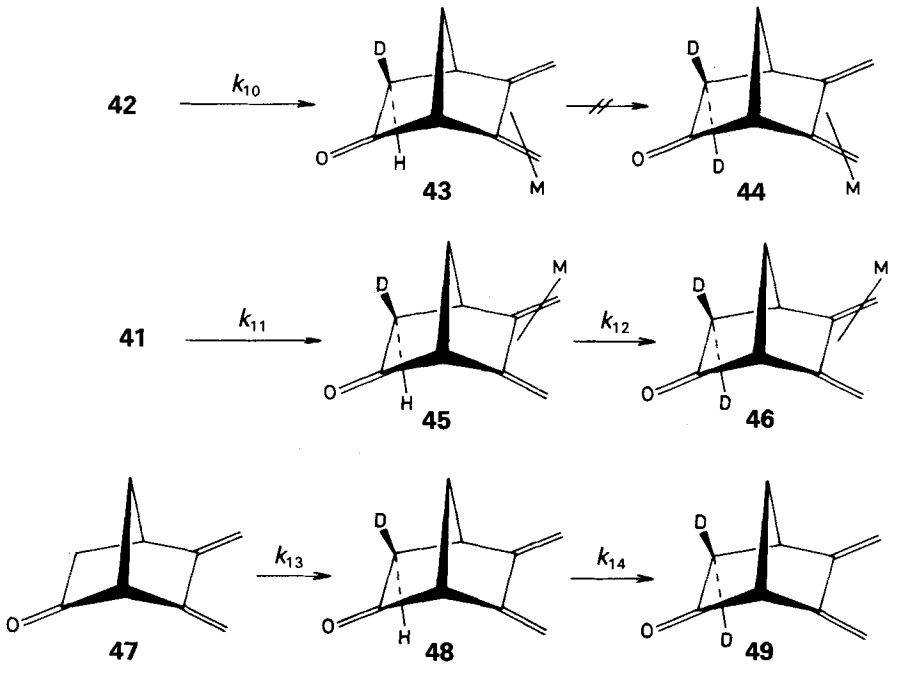
39 R = H
50 R = CH_3SO_2

40 **41** **42**

M = $Fe(CO)_3$

jor product obtained by treatment of 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene with $Fe_2(CO)_9$ in hexane at 69°C, attributed to the *endo*-complex **10** by *Hansen et al.* [2]) afforded alcohol **39** as sole product. *Collins* oxidation of **39** and **40** gave the corresponding ketones **41** and **42**. As observed for **8**, the base-catalyzed exchange (K_2CO_3 or NaOD in CD_3OD/CD_2Cl_2) of the *endo*-complex **42** furnished exclusively the monodeuterated product **43**. No trace of the dideuterated analog **44** could be detected, even after prolonged exposure to the basic conditions (2 weeks, 30°C; heating at higher temperature led to decomposition of the complexes). As expected, the *exo*-isomer **41** exchanged the two H-atoms at C(3) under the above conditions giving successively **45** and **46**. By following the base-catalyzed H/D exchanges (360-MHz-^{1}H-NMR; K_2CO_3 in $CD_3OD/CDCl_3$ 1:1; 25°C), the following rate constants were evaluated $k_{10} \approx 3.1 \cdot 10^{-4}$ (**42**→**43**), $k_{11} \approx 2.7 \cdot 10^{-4}$ (**41**→**45**), and $k_{12} \approx 0.9 \cdot 10^{-6}$ (**45**→**46**) $dm^3mol^{-1}s^{-1}$.

Scheme 5



M = $Fe(CO)_3$

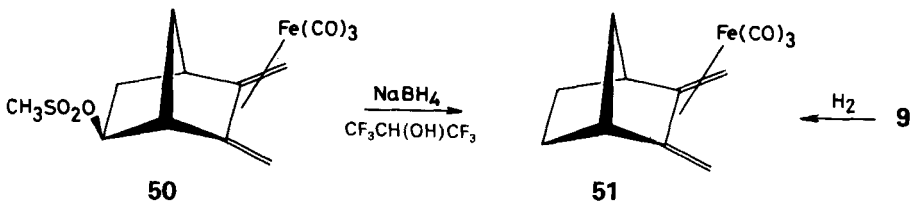
The rate constants for base-catalyzed H/D exchange of the uncomplexed dienone **47** have also been determined. Under the same conditions, exchange of H_{exo}–C(3) (giving **48**) was definitively faster ($k_{13} \approx 3.5 \cdot 10^{-4}$ dm^{3}mol^{-1}s^{-1}, 25°C) than the exchange of H_{endo}–C(3) in **48** (and **47**) ($k_{14} < 10^{-6}$ dm^{3}mol^{-1}s^{-1}). The relatively large rate constant ratio $k_{13}/k_{14} > 350$ is typical of 2-bicyclo[2.2.1]heptanone derivatives [13-15]. As in the bicyclo[2.2.2]octane analogs **7**, **8**, and **22**, the $Fe(CO)_3$ coordination of dienone **47** does not affect significantly the rate of H/D exchanges, except for H_{endo}–C(3) in the *endo*-complexes **42** and **43**.

The structures of **43**, **45**, and **46** were deduced from their ^{1}H- and ^{13}C-NMR spectra.

The signals at δ_H 2.41 and 2.26 ppm of H_{exo}–C(3) and H_{endo}–C(3), respectively, in **41** disappeared completely in **46** (> 95% dideuteration). The corresponding ^{13}C-NMR signal (δ_C 38.6 ppm), which was a *t* with $^1J_{C,H}$ = 135 Hz in **41**, was replaced by a *tt* in **46** with $^1J_{C,D}$ = 20 Hz. The signal at δ_H 2.59 ppm of the *endo*-complex **42** attributed to H_{exo}–C(3) and H–C(7) *syn* to the $Fe(CO)_3$ group was replaced by a smaller signal in **43**. Furthermore, the signal of H_{endo}–C(3) at δ_H 2.26 ppm which displayed a typical geminal coupling constant $^2J_{H,H}$ = 17 Hz (coupling with H_{exo}–C(3)) *in* **42** was replaced by a narrower *m* in the ^{1}H-NMR spectrum of **43**. The ^{13}C-NMR spectrum of **43** displayed a *dt* for H(D)–C(3) with $^1J_{C,H}$ = 141 Hz and $^1J_{C,D}$ = 20 Hz.

Reduction ($NaBH_4$, $CF_3CH(OH)CF_3$, 80°C, 4 h) of the methanesulfonate **50** (derived from pure alcohol **39**) gave the *exo*-$Fe(CO)_3$ complex **51** which was identical with the complex obtained by catalytical hydrogenation of **9** and incorrectly reported as having the *endo*-$Fe(CO)_3$ configuration [2]. The latter experiment demonstrates also that stereospecific *endo* ⇆ *endo*-$Fe(CO)_3$ isomerizations did not occur during the oxidative hydroborations of complexes **9** and **10**.

Scheme 6



Conclusion. – The oxidative hydroboration of tricarbonyliron complexes of 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene and 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene were highly stereoselective and gave alcohols whose structures necessitated a revision of the iron-configuration assignments proposed earlier by *Hansen et al.* An $Fe(CO)_3$ group blocks the H/D exchange at H_{endo}–C(3) in tricarbonyliron complexes of 5,6-dimethylidene-2-bicyclo[2.2.2]octanone and 5,6-dimethylidene-2-bicyclo[2.2.1]heptanone, thus defining an analytical test for the configuration (*exo vs. endo*) at the Fe-atom in these systems. $NaBH_4$ reduction of these ketones were stereoselective in the case of *endo*-$Fe(CO)_3$ complexes.

We thank *Hoffmann-La Roche and Co.*, Basel, the *Swiss National Science Foundation* and the *Fonds Herbette*, Lausanne, for financial support. We are grateful to Prof. *H.-J. Hansen* for helpful discussions and communication of unpublished results.

Experimental Part

General Remarks. – Melting points (m.p.; not corrected): *Tottoli* apparatus. IR spectra ($\tilde{\nu}$[cm^{-1}]): *Beckmann IR-20A* and *Perkin-Elmer 577* spectrophotometers. UV spectra: *Philips Pye-Unicam SP 8/100* (λ_{max} [nm],ε[$dm^3mol^{-1}cm^{-1}$]). ^{1}H-NMR spectra: *Bruker WP-80CW* (80 MHz) or *Bruker WH-360FT* (360 MHz) spectrometers, the latter equipped with an *Aspect 2000* computer, 32 K memory space; deuterium signal of solvent as lock signal, TMS as internal reference $\delta_H = 0.0$ ppm; δ_H[ppm] (apparent multiplicity, apparent coupling constants J(H,H) in Hz, number of protons, attribution). ^{13}C-NMR spectra: *Bruker WP-60FT* (15.08 MHz; spectral width 3750 Hz, 4096 points), deuterium signal of $CDCl_3$ as lock signal; δ_C[ppm] (apparent multiplicity, apparent coupling constants J(C,H) in Hz); *s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *m* = multiplet, br. = broad. Mass spectra (MS): in electron ionization mode, *Hewlett-Packard HP5980A*. Elemental analyses: *Ilse Beetz* in Kronach (Germany) and Mikrolabor of the ETH, Zürich (*E. Manser*). Prep. HPLC separations: *Dupont 830003-904*, UV detector (254 nm), silica gel (*Zorbax Sil*, 7 μm; 21.2 mm × 25 cm). None of the procedures reported here have been optimized.

*Tricarbonyl[(1*RS,*2*SR,*5*RS*)*-*C,*5,6,*C*-η-(5,6-dimethylidene-2-*endo*-*bicyclo[2.2.2]octanol)]iron* (**3**) *and Tricarbonyl[(1*RS,*2*RS,*5*SR*)*-*C,*5,6,*C*-η-(5,6-dimethylidene-2-*exo*-*bicyclo[2.2.2]octanol)]iron* (**4**). A mixture of 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene [16] (28 g, 0.212 mol) and $Fe_2(CO)_9$ (84 g, 0.23 mol) in hexane (1600 ml) was heated under reflux for 3 h. After cooling to r.t., the mixture was filtered through silica gel (200 g) and the residue washed with hexane (500 ml). Alumina (400 g) was added and the mixture stirred for 24 h at r.t. (until disappearance of the green colour). After solvent evaporation *i.v.* 35.2 g (61%) of a 4:1 mixture of *endo*-$Fe(CO)_3$ complex **2** [^{1}H-NMR ($CDCl_3$): 6.25 (*m*, 2H); 3.35 (*m*, 2H); 2.0 (*d*, 2H); 1.75 (*m*, 4H); 0.38 (*d*, 2H)] and *exo*-$Fe(CO)_3$ complex **1** [^{1}H-NMR ($CDCl_3$): 6.60 (*m*, 2H); 3.35 (*m*, 2H); 1.80 (*d*) and 1.75 (*m*) (6H); 0.10 (*d*, 2H)] was obtained as a yellow solid (see also ^{13}C-NMR in the *Table*). Freshly distilled $BF_3 \cdot Et_2O$ (37.2 g, 0.26 mol) was added dropwise and under N_2 to a vigourously stirred suspension of the above mixture **1/2** (35.2 g, 0.13 mol) and of $NaBH_4$ (14 g) in anh. THF (560 ml) cooled to 0°. After stirring at r.t. for 3 h, the mixture was cooled again to 0°. H_2O (29.8 ml, 1.65 mol), 3N aq. KOH (29.8 ml) and 30% aq. H_2O_2 (55.7 ml, 1.65 mol) were added dropwise and successively. After stirring at r.t. for 24 h, the mixture was extracted with CH_2Cl_2 (100 ml, 3×). The extract was dried ($MgSO_4$) and evaporated *i.v.* to dryness. The crude mixture **3/4** was purified and separated by column chromatography on silica gel (250 g, AcOEt/hexane 1:3). The first fraction contained **3** which was recrystallized from Et_2O/hexane 1:1 yielding 5 g (13%) of **3**, yellow crystals, m.p. 131–2°. The second fraction contained **4** which was recrystallized from Et_2O/hexane 1:1 yielding 21.5 g (57%) of **4**, yellow crystals, m.p. 115–7°.

The same procedure repeated with pure **1** and **2** (separated by HPLC (*Dupont Zorbax ODS*, MeCN/THF/H_2O 4:1:1, 10 ml/min)) gave a 85:15 mixture of **3/18** (54%), and pure **4** (47%), respectively.

Data of **3**. UV (isooctane): 220 (23500), 290 (2150). IR (KBr): 3420, 2960, 2920, 2880, 2050, 1995, 1980, 1960, 1080, 1030, 1005, 940. ^{1}H-NMR ($CDCl_3$): 4.1 (*m*, 1H, H–C(2)); 2.66 (*m*, 1H, H–C(1)); 2.6 (*m*, 1H, H–C(4)); 2.47 (*m*, 1H); 1.82 (*d*, J = 2.5, 1H); 1.80 (*d*, J = 2.5, 1H); 1.7–1.4 (*m*, 5H); 0.35 (*d*, J = 2.5, 1H); 0.33 (*d*, J = 2.5, 1H). ^{13}C-NMR ($CDCl_3$): see *Table*. MS (70 eV): 290 (3.5), 262 (54.7), 234 (83.7), 206 (96.5), 188 (81.4), 178 (59.3), 160 (100). Anal. calc. for $C_{13}H_{14}FeO_4$ (290.10): C 53.82, H 4.86; found: C 53.83 H 4.78.

Data of **4**. UV (isooctane): 210 (21500), 249 (2090). IR (KBr): 3360, 2960, 2920, 2880, 2040, 1980, 1950, 1045, 1000. ^{1}H-NMR ($CDCl_3$): 3.93 (*dm*, J = 10, 1H, H–C(2)); 2.52 (*m*, 1H, H–C(1)); 2.47 (*m*, 1H); 2.0 (*m*, 3H); 1.79 (*d*, J = 2.5, 1H); 1.73 (*d*, J = 2.5, 1H); 1.7–1.45 (*m*, 3H); 0.28 (*d*, J = 2.5, 1H); 0.26 (*d*, J = 2.5, 1H). ^{13}C-NMR: see *Table*. MS (70 eV): 290 (2.4), 262 (45.5), 234 (99), 206 (100), 188 (10), 186 (11), 184 (11), 178 (45), 176 (14), 162 (27), 160 (22). Anal. calc. for $C_{13}H_{14}FeO_4$ (290.10): C 53.82, H 4.86; found: C 54.02, H 4.83.

*Tricarbonyl[(1*RS,*2*SR,*5*RS*)*-*C,*5,6,*C*-η-(5,6-dimethylidene-2-*endo*-*bicyclo[2.2.2]octyl acetate)]iron* (**5**). Pure **3** (0.5 g, 1.72 mmol) was dissolved in Ac_2O (6 ml). After the addition of pyridine (1 ml), the mixture was stirred at r.t. for 5 h. H_2O (20 ml) and $CHCl_3$ (10 ml) were added, and the mixture was stirred vigourously for 2 min. The aq. layer was extracted with $CHCl_3$ (10 ml, 3×). The combined org. phases were washed with 2N HCl (10 ml, 2×) and H_2O (10 ml, 2×) and dried ($MgSO_4$). After evaporation *i.v.*, the crude acetate was recrystallized from pentane yielding 496 mg (87%) of yellow crystals, m.p. 102–3°. UV (isooctane): 220 (18810), 293 (2200). IR (KBr): 3060, 2960, 2920, 2870, 2020, 1980, 1955, 1730, 1460, 1440, 1380, 1370, 1320, 1250, 1230, 1140, 1070, 1060, 1020. ^{1}H-NMR ($CDCl_3$): 5.3 (*m*, 1H); 2.81 (*m*, 1H); 2.64 (*m*, 1H); 2.48 (*m*, 1H); 2.0 (*s*, 3H); 1.81 (*d*, J = 2.5, 1H); 1.76 (*d*, J = 2.5, 1H); 1.8–1.4 (*m*, 5H); 0.32 (*d*, J = 2.5, 1H); 0.28 (*d*, J = 2.5, 1H). ^{13}C-NMR: see *Table*. MS (70 eV): 332 (5), 304 (26), 276 (41), 249 (12), 248 (76), 221 (16), 220 (100), 205 (9), 189 (12), 188 (76), 186 (37), 184 (13), 174 (19), 162 (14), 160 (29), 148 (7), 134 (36), 132 (19), 117 (12), 115 (24), 105 (44). Anal. calc. for $C_{15}H_{16}FeO_5$ (332.137): C 54.24, H 4.85; found: C 54.31, H 4.95.

*Tricarbonyl[(1RS,2RS,5SR)-C,5,6,C-η-(5,6-dimethylidene-2-*exo*-bicyclo[2.2.2]octyl acetate)]iron* (**6**). From **4**, as above for **5** from **3**: 495 mg (87%) of **6**, yellow crystals, m.p. 77–8°. UV (isooctane): 219 (19970), 293 (2330). IR (KBr): 2980, 2960, 2940, 2040, 1990, 1955, 1740, 1435, 1380, 1360, 1250, 1040, 1010. ^{1}H-NMR ($CDCl_3$): 4.8 (*m*, 1H); 2.86 (*m*, 1H); 2.59 (*m*, 1H); 2.32 (*m*, 1H); 2.07 (*s*, 3H); 2.0 (*m*, 2H); 1.86 (*d*, J = 2.5, 1H); 1.76 (*d*, J = 2.5, 1H); 1.8–1.5 (*m*, 3H); 0.28 (*d*, J = 2.5, 1H); 0.26 (*d*, J = 2.5, 1H). ^{13}C-NMR: see *Table*. MS (70 eV): 332 (4.5), 304 (23), 276 (51), 249 (17), 248 (100), 246 (24), 220 (29), 188 (33), 186 (19), 184 (5), 174 (5), 162 (7), 161 (8), 134 (20), 133 (31), 132 (7), 115 (19), 105 (62), 104 (9), 91 (59). Anal. calc. for $C_{15}H_{16}FeO_5$ (332.137): C 54.24, H 4.85; found: C 54.20, H 4.87.

Tricarbonyl[(1RS,5RS)-C,5,6,C-η-(5,6-dimethylidene-2-bicyclo[2.2.2]octanone)]iron (**7**). CrO_3 (6 g, 59.5 mmol) was added portionwise to a vigourously stirred solution of anh. pyridine (9.44 g, 118.9 mmol) in CH_2Cl_2 (105 ml) cooled to 0° under N_2. After stirring at r.t. for 10 min, a solution of **3** (2.5 g, 8.6 mmol) in anh. CH_2Cl_2 (15 ml) was added and the mixture stirred at 20° for 5–8 min (control of the disappearance of **3** by TLC). The mixture was filtered through silica gel (100 g) and the residue washed with CH_2Cl_2. After evaporation *i.v.*, the crude oil was purified by column chromatography (100 g SiO_2, AcOEt/hexane 1:3) and recrystallized from Et_2O/hexane 1:4 yielding 1.76 g (71%) of yellow crystals, m.p. 97–8°. UV (isooctane): 209 (13000), 294 (2550), 302 (2680), 314 (2740), 324 (2420). IR (KBr): 2980, 2960, 2920, 2880, 2040, 1980, 1960, 1730, 1465, 1440, 1310, 1140, 1080. ^{1}H-NMR ($CDCl_3$): 3.08 (*m*, 1H, H–C(1)); 2.93 (*m*, 1H, H–C(4)); 2.5 (*m*, 2H); 2.2–1.7 (*m*, 4H); 1.86 (*d*, J = 2.5, 1H); 1.79 (*d*, J = 2.5, 1H); 0.38 (*d*, J = 2.5, 1H); 0.25 (*d*, J = 2.5, 1H). ^{13}C-NMR: see *Table*. MS (70 eV): 288 (36), 260 (44), 232 (75), 204 (100), 174 (61), 160 (19), 148 (28). Anal. calc. for $C_{13}H_{12}FeO_4$ (288.084): C 54.20, H 4.20; found: C 54.20, H 4.26.

Tricarbonyl[(1RS,5SR)-C,5,6,C-η-(5,6-dimethylidene-2-bicyclo[2.2.2]octanone)]iron (**8**). From **4** (2.5 g, 8.6 mmol), as above for **7** from **3**: 1.7 g (69%) of **8**, yellow crystals, m.p. 126–7°. UV (isooctane): 215 (15800), 285 (2380). IR (KBr): 2980, 2920, 2900, 2040, 1980, 1960, 1740, 1410, 1145, 1100, 860. ^{1}H-NMR ($CDCl_3$): 3.23 (*t*, J = 2.5, 1H, H–C(1)); 2.93 (*m*, 1H, H–C(4)); 2.39 (*dd*, J = 19.0, 2, 1H, H_{exo}–C(3)); 2.31 (*ddd*, J = 19.0, 3.5, 1H, H_{endo}–C(3)); 2.3–1.9 (*m*, 4H); 1.9, 1.82, 0.32, 0.30 (4*d*, J = 2.5, 4H). ^{13}C-NMR: see *Table*. MS (70 eV): 282 (2), 260 (13), 232 (58), 204 (100), 176 (12), 174 (42), 160 (17), 148 (16). Anal. calc. for $C_{13}H_{12}FeO_4$ (288.084): C 54.20, H 4.20; found: C 54.23, H 4.20

*Tricarbonyl[(1RS,2RS,5RS)-C,5,6,C-η-(5,6-dimethylidene-2-*exo*-bicyclo[2.2.2]octanol)]iron* (**18**). $NaBH_4$ (55 mg) was added to a stirred solution of **7** (120 mg, 0.42 mmol) in anh. THF (3 ml). After heating under reflux for 12 h, the mixture was cooled to r.t., and H_2O was added (3 ml). The mixture was extracted with CH_2Cl_2 (10 ml, 2×), the org. extract washed with H_2O (10 ml, 2×) and dried ($MgSO_4$). After evaporation *i.v.*, the crude alcohol mixture was separated and purified by column chromatography on silica gel (AcOEt/hexane 1:4). The first fraction contained 35 mg (28.6%) of **3** and the second **18** which was recrystallized from Et_2O/hexane 1:4 yielding 35 mg (28.6%) of yellow crystals, m.p. 131–2°. UV (isooctane): 222 (20300), 294 (2300). IR (KBr): 3320, 2960, 2950, 2940, 2900, 2870, 2040, 1980, 1960, 1470, 1450, 1220, 1080, 1050, 1010. ^{1}H-NMR ($CDCl_3$): 4.32 (*m*, 1H); 2.5–1.2 (*m*, 4H); 1.9 (*m*, 1H); 1.78, 1.76, 0.24, 0.20 (4*d*, J = 2.5, 4H); 1.7–1.4 (*m*, 3H). ^{13}C-NMR: see *Table*. MS (70 eV): 291 (1.5), 290 (7), 262 (43), 234 (100), 207 (12), 206 (90), 205 (15), 204 (77), 186 (10), 178 (28), 162 (19), 160 (24). Anal. calc. for $C_{13}H_{14}FeO_4$ (290.10): C 53.82, H 4.86; found: C 53.69, H 4.87.

*Tricarbonyl[(1RS,2SR,5SR)-C,5,6,C-η-(5,6-dimethylidene-2-*endo*-bicyclo[2.2.2]octanol)]iron* (**19**). From **8** (276 mg, 0.96 mmol), as above for **18** from **7**: only one product which was recrystallized from Et_2O/hexane 1:4 yielding 190 mg (68%) of **19** as yellow crystals, m.p. 88–9°. UV (isooctane): 220 (17600), 296 (2300). IR (KBr): 3300, 2960, 2880, 2040, 1995, 1970, 1950, 1440, 1340, 1230, 1080, 1030. ^{1}H-NMR ($CDCl_3$): 4.08, 2.62, 2.55, 2.28 (4*m*, 4H); 1.9–1.6 (*m*, 4H); 1.37 (*m*, 1H); 1.78, 1.60, 0.19, 0.14 (4*d*, J = 2.5, 4H). ^{13}C-NMR: see *Table*. MS (70 eV): 290 (< 1), 262 (17), 234 (54), 207 (14), 206 (100) 189 (7), 188 (55), 186 (14), 178 (31), 160 (39). Anal. calc. for $C_{13}H_{14}FeO_4$ (290.10): C 53.82, H 4.86; found: C 53.87, H 4.79.

*Tricarbonyl[(1RS,2RS,5RS)-C,5,6,C-η-(5,6-dimethylidene-2-*exo*-bicyclo[2.2.2]octyl acetate)]iron* (**20**). From **18**, as above for **5** from **3**: 66% of **20**, yellow crystals, m.p. 88–90°. UV (isooctane): 220 (18950), 297 (2200). IR (KBr): 2960, 2880, 2040, 1990, 1960, 1730, 1470, 1450, 1380, 1350, 1250, 1080, 1050, 1020. ^{1}H-NMR ($CDCl_3$): 5.12, 2.73, 2.56, 2.34, 2.22, 1.90, 1.75, 1.58, 1.41 (9*m*, 9H); 2.03 (*s*, 3H); 1.80, 1.79, 0.29, 0.22 (4*d*, J = 2.5, 4H). ^{13}C-NMR: see *Table*. MS (70 eV): 332 (1), 304 (18), 277 (8), 276 (53), 248 (39), 220 (27), 192 (12), 188 (46), 184 (15), 174 (9), 162 (17), 160 (12), 105 (92), 91 (92), 56 (100). Anal. calc. for $C_{15}H_{16}FeO_5$ (332.137): C 54.24, H 4.85; found: C 54.11, H 4.86.

*Tricarbonyl[(1RS,2SR,5SR)-C,5,6,C-η-(5,6-dimethylidene-2-*endo*-bicyclo[2.2.2]octyl acetate)]iron* (**21**). From **19**, as above for **5** from **3**: 77% of **21**, yellow crystals, m.p. 76–7°. UV (isooctane): 225 (19250), 295 (2200). IR (KBr): 3040, 2980, 2950, 2920, 2890, 2870, 2040, 1970, 1740, 1475, 1370, 1240, 1060, 1045, 1020. ^{1}H-NMR ($CDCl_3$): 5.0, 2.79, 2.60, 2.37, 1.47 (5*m*, 5H); 2.0 (*s*, 3H); 2.0–1.6 (*m*, 4H); 1.80, 1.62, 0.20, 0.12 (4*d*,

J = 2.5, 4H). ^{13}C-NMR: see *Table*. MS (70 eV): 332 (1), 304 (6), 276 (41), 249 (16), 248 (100), 221 (14), 220 (94), 218 (7), 205 (8), 188 (58), 186 (26), 174 (16), 162 (11), 161 (10), 160 (23). Anal. calc. for $C_{15}H_{16}FeO_5$ (332.137): C 54.24, H 4.85; found: C 54.18, H 4.84.

*Tricarbonyl[(1*RS,*2*SR,*5*RS)-C,*5,6,*C-*η*-*(5,6-dimethylidene-2-*endo-*bicyclo[2.2.2]octyl methanesulfonate)]-iron* (**5′**). Methanesulfonyl chloride (434 mg, 3.68 mmol) was added to a stirred solution of **3** (1 g, 3.44 mmol) in anh. pyridine (20 ml). After stirring at r.t. and under N_2 for 3 min, CH_2Cl_2 (50 ml) was added. The solution was washed with 1N HCl (20 ml, 3×) and then with H_2O (20 ml, 2×). After drying ($MgSO_4$), the solvent was evaporated *i.v.* and the crude ester recrystallized from Et_2O/hexane 1:4 yielding 1.09 g (86%) of yellow crystals, m.p. 104–5°. UV (isooctane): 220 (19400), 293 (2200). IR (KBr): 3040, 2980, 2940, 2020, 1980, 1955, 1460, 1310, 1175, 1160, 960, 930, 910. ^{1}H-NMR ($CDCl_3$): 5.33, 3.0, 2.7, 2.56 (4*m*, 4H); 3.02 (*s*, 3H); 1.95–1.45 (*m*, 5H); 1.83, 0.32 (2*m*, 4H). ^{13}C-NMR ($CDCl_3$): 210.1 (*s*), 111.6 (*s*, C(5)); 106.3 (*s*); 79.7 (*d*, J = 156, C(2)); 39.3 (*d*, J = 140, C(1)); 38.9 (*q*, J = 140, CH_3); 38.3 (*t*, J = 160, CH_2=C(6)); 37.0 (*t*, J = 160, CH_2=C(5)); 36.9 (*t*, J = 132, C(2)); 33.4 (*d*, J = 140, C(4)); 27.7 (*t*, J = 132, C(7)); 25.9 (*t*, J = 132, C(8)). MS (70 eV): 368 (5), 341 (6), 340 (35), 312 (13), 285 (16), 284 (100), 282 (8), 257 (14), 256 (79), 254 (5), 245 (9), 243 (5), 217 (10), 205 (22), 189 (10), 188 (34). Anal. calc. for $C_{14}H_{16}FeO_6S$ (368.185): C 45.67, H 4.38; found: C 45.47, H 4.36.

*Tricarbonyl[(1*RS,*2*RS,*5*SR)-C,*5,6,*C-*η*-*(5,6-dimethylidene-2-*exo-*bicyclo[2.2.2]octyl methanesulfonate)]-iron* (**6′**). From **4** (1 g, 3.44 mmol), as above for **5′** from **3**: 988 mg (78%) of **6′**, yellow crystals, m.p. 112–3°. UV (isooctane): 220 (20800), 290 (2180). IR (KBr): 3040, 3020, 2980, 2960, 2940, 2880, 2020, 2000, 1985, 1960, 1350, 1180, 1160, 970, 950, 925, 870. ^{1}H-NMR ($CDCl_3$): 4.75, 2.9, 2.63, 2.41 (4*m*, 4H); 3.01 (*s*, 3H); 2.2 (*m*, 2H); 1.8–1.6 (*m*, 3H); 1.84, 1.78, 0.33, 0.28 (4*d*, J = 2.5, 4H). ^{13}C-NMR ($CDCl_3$): 210.3 (*s*); 109.8 (*s*, C(5)); 103.4 (*s*, C(6)); 79.6 (*d*, J = 154, C(2)); 38.2 (*q*, J = 138, CH_3); 38.2 (*d*, J = 140, C(1)); 37.8 (*t*, J = 160, CH_2=C(6)); 37.3 (*t*, J = 132, C(3)); 37.2 (*t*, J = 160, CH_2=C(5)); 33.9 (*d*, J = 140, C(4)); 26.0 (*t*, J = 132, C(7)); 19.2 (*t*, J = 132, C(8)). MS (70 eV): 368 (1.5), 340 (14), 312 (8), 284 (100), 258 (31), 198 (39), 132 (41). Anal. calc. for $C_{14}H_{16}FeO_6S$ (368.185): C 45.67, H 4.38; found: C 45.87, H 4.41.

General Technique for the Iron Oxidations in Complexes **5–9**, **20**, *and* **21**. Freshly sublimed trimethylamine oxide (340 mg, 4.5 mmol) was added portionwise to a stirred solution of 0.1 mmol of $Fe(CO)_3$ complex in anh. acetone (30 ml). After disappearance of the complex (2–15 h, control by TLC), H_2O (50 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 50 ml). The org. extract was washed with H_2O (3 × 50 ml) and dried ($MgSO_4$). The solvent was removed by distillation under reflux. Complexes **5** and **21** gave the acetate **14**; **6** and **20** gave the isomer **15**; **7** and **8** were oxidized into dienone **22** [6].

*Tricarbonyl[(1*RS,*3*RS,*5*SR)-C,*5,6,*C-*η*-*(5,6-dimethylidene(3-*exo-$^2H_1$)-2-bicyclo[2.2.2]octanone)]iron* (**32**). A 1M solution of MeONa in CD_3OD (0.34 ml) was added dropwise to a stirred solution of **8** (100 mg, 0.347 mmol) in CD_2Cl_2 (2.7 ml) and CD_3OD (1 ml). After stirring at r.t. for 24 h, the solvent was evaporated *i.v.* and the residue taken up in CH_2Cl_2 (10 ml). The solution was filtered through a short column of silica gel (1 g). After evaporation *i.v.*, the crude **32** was recrystallized from Et_2O/hexane 1:4 giving 72 mg (71.7%) of yellow crystals, m.p. 127°. IR (KBr): 3020, 2960, 2400, 2040, 1980, 1960, 1730, 1410, 1200, 920. ^{1}H-NMR ($CDCl_3$): 3.23 (*t*, J = 2.5, 1H, H–C(1)); 2.94 (*q*, 1H, H–C(4)); 2.28 (*m*, 1H, H_{endo}–C(3)); 2.3–1.9 (*m*, 4H); 1.9, 1.82, 0.32, 0.30 (4*d*, J = 2.5, 4H). MS (70 eV): 290 (3.5), 289 (13.4), 288 (0.5), 262 (13.9), 261 (37), 260 (1), 234 (19), 233 (64), 232 (2), 206 (31), 205 (100). Anal. calc. for $C_{13}H_{11}DFeO_4$ (289.09): C 54.01, H 3.83; found: C 53.96, H 3.84.

*Tricarbonyl[(1*RS,*5*RS)-C,*5,6,*C-*η*-*(5,6-dimethylidene(3,3,-$^2H_2$)-2-bicyclo[2.2.2]octanone)]iron* (**35**). From **7** (100 mg, 0.347 mmol), as above for **32** from **8**: 75 mg (74.4%) of **35**, yellow crystals, m.p. 97°. IR (KBr): 3040, 3000, 2980, 2960, 2400, 2040, 1990, 1980, 1730, 1460, 1450, 1220. ^{1}H-NMR ($CDCl_3$): 3.08 (*m*, 1H, H–C(1)); 2.94 (*m*, 1H, H–C(4)); 2.2.–1.7 (*m*, 4H); 1.86, 1.79, 0.38, 025 (4*d*, J = 2.5, 4H). MS (70 eV): 291 (1.5), 290 (10), 289 (1), 235 (10), 234 (68), 233 (7), 232 (4), 208 (1.7), 207 (13), 206 (99), 205 (10), 204 (7), 179 (2), 178 (18), 176 (28), 56 (100). Anal. calc. for $C_{13}H_{10}D_2FeO_4$ (290.095): C 53.82, H 3.47; found: C 53.85, H 3.58.

*Tricarbonyl[(1*RS,*5*RS)-C,*5,6,*C-*η*-*(5,6-dimethylidene-2-bicyclo[2.2.1]heptanone)]iron* (**41**). CrO_3 (3 g, 30 mmol) was added portionwise to a stirred mixture of anh. pyridine (4.75 g, 60 mmol) and CH_2Cl_2 (150 ml) cooled to 0° and under Ar. After stirring at r.t. for 1 h, 50 ml of this solution was added dropwise to a stirred solution of **39** [4c] (0.3 g, 1.08 mmol) in anh. CH_2Cl_2 (5 ml). After stirring at r.t. for 1 h, the mixture was filtered and the residue washed with CH_2Cl_2 (10 ml, 5×). The org. solution was washed successively with 5% aq. NaOH (50 ml, 3×), 5% aq. HCl (50 ml, 8×) and sat. aq. $NaHCO_3$ (50 ml, 2×). After drying ($MgSO_4$), a mixture of **41** (40%), **39** (20%), uncomplexed 5,6-dimethylidene-2-*exo*-bicyclo[2.2.1]heptanol (20%) and uncomplexed 5,6-dimethylidene-2-bicyclo[2.2.1]heptanone (20%) was obtained. Better yield of **41** was obtained by treatment of 5,6-dimethylidene-2-bicyclo[2.2.1]heptanone (0.5 g, 3.7 mmol) [17] with $Fe_2(CO)_9$ (1.5 g, 4.1 mmol) in anh. MeOH at 45° under Ar for 5 h. After cooling to r.t., more $Fe_2(CO)_9$ (0.5 g, 1.4 mmol) was added and the mixture stirred overnight at r.t. under Ar bubbling. The precipitate was removed by filtration and the solvent

evaporated *i.v.* The crude complex mixture was taken up with 100 ml hexane/Et_2O 9:1 and stirred with acidic Al_2O_3 at r.t. for 12 h. The mixture was purified by column chromatography on *Florisil* (60 cm × 1.5 cm; hexane, then hexane/Et_2O 9:1). The first fraction (after $Fe_3(CO)_{12}$) contained **41** which yielded 0.46 g (44%) of yellow crystals, m.p. 87–8°. The second fraction contained the *endo*-complex **42** which yielded 0.23 g (22%) of yellow crystals, m.p. 94–5°. Data of **41**: IR (hexane): 2050, 1975, 1960, 1750. ^{1}H-NMR ($CDCl_3$): 3.07 (*m*, 1H, H–C(4)); 2.95 (br. *s*, 1H, H–C(1)); 2.41 (*dm*, J = 13, H_{exo}–C(3)); 2.26 (*dm*, J = 13, H_{endo}–C(3)); 2.25, 2.07 (2 br. *d*, J = 10, 2H, CH_2(7)); 2.0, 1.95, 0.55, 0.44 (4*d*, J = 2.7, 4H). ^{13}C-NMR ($CDCl_3$): 211.9 (*s*, C(2)); 208.1 (*s*, $Fe(CO)_3$); 114.1, 105.6 (2*s*, C(5), C(6)); 54.5, 39.2 (2*d*, J = 156, C(1), C(4)); 45.6 (*t*, J = 138, C(7)); 38.6 (*t*, J = 135, C(3)); 34.7, 34.65 (2*t*, J = 156, CH_2=C(5), CH_2=C(6)). MS (70 eV): 274 (6), 246 (51), 218 (89), 190 (100). Anal. calc. for $C_{12}H_{10}FeO_4$ (274.05): C 52.59, H 3.68; found: C 52.75, H 3.67.

Tricarbonyl[(1RS,5SR)-C,5,6,C-η-(5,6-dimethylidene-2-bicyclo[2.2.1]heptanone)]iron (**42**). As described above for **41**: The *Collins* oxidation of **40** [4c] gave a mixture of **42** (35%), unreacted **40** (18%), and of the corresponding uncomplexed ligands due to iron oxidation (35%).

Data of **42**: IR (hexane): 2050, 1975, 1960, 1750. ^{1}H-NMR ($CDCl_3$): 3.28 (br. *s*, 1H, H–C(1)); 3.24 (*m*, 1H, H–C(4)); 2.59, 2.26 (2 *dm*, J = 17, 2H, CH_2(3)); 3.10, 2.59 (2 br. *d*, J = 9.5, 2H, CH_2(7)); 2.02, 1.94, 0.55, 0.50 (4*d*, J = 3.1, 4H). ^{13}C-NMR ($CDCl_3$): 209.0 (*s*, C(2)); 208.1 (*s*, $Fe(CO)_3$); 121.3, 110.5 (2*s*, C(5), C(6)); 57.0 (*t*, J = 138, CH_2(7)); 56.4, 39.3 (2*d*, J = 152, C(1), C(4)); 47.3 (*t*, J = 133, C(3)); 34.4, 33.8 (2*t*, J = 160, CH_2=C(5), CH_2=C(6)). MS (70 eV): 274 (3), 246 (19), 218 (62), 190 (100). Anal. calc. for $C_{12}H_{10}FeO_4$ (274.05): C 52.59, H 3.68; found: C 52.49, H 3.83.

Tricarbonyl[(1RS,5RS)-C,5,6,C-η-(5,6-dimethylidene(3,3-$^2H_2$)-2-bicyclo[2.2.1]heptanone)]iron (**46**). A solution of **41** (50 mg, 0.18 mmol) in CH_3OD was added to a solution of CH_3ONa (*ca.* 30 mmol) in CH_3OD (1 ml). After stirring at r.t. for 4 h, D_2O (1 ml) was added dropwise and the mixture extracted with $CDCl_3$ (1 ml, 2×). After drying ($MgSO_4$), the solvent was evaporated *i.v.* and the crude ketone purified by column chromatography on *Florisil* (20 cm × 1 cm; hexane/Et_2O 9:1): 45 mg (90%) of yellow crystals, m.p. 87–8°. IR (hexane): 2065, 1990, 1975. ^{1}H-NMR ($CDCl_3$): 3.06 (br. *s*, 1H, H–C(4)); 2.96 (*s*, 1H, H–C(1)); 2.25, 2.08 (2*d*, J = 10, CH_2(7)); 2.01, 1.96, 0.56, 0.45 (4*d*, J = 2.8, 4H), no peak observed for CH_2(3). ^{13}C-NMR ($CDCl_3$): 212.0 (*s*, C(2)); 208.9 (*s*, $Fe(CO)_3$); 114.0, 105.5 (2*s*, C(5), C(6)); 54.5, 39.1 (2*d*, J = 157, C(1), C(4)); 45.5 (*t*, J = 138, C(7)); 38.3 (*tt*, J = 20, C(3)); 34.7 (2*t*, J = 156, CH_2=C(5), CH_2=C(6)). MS (70 eV): 276 (9, M^+), 248 (56), 220 (100), 192 (93). Anal. calc. for $C_{12}H_8D_2FeO_4$ (276.07): C 52.21, H 3.65; found: C 53.04, H 3.76.

Tricarbonyl[(1RS,3RS,5SR)-C,5,6,C-η-(5,6-dimethylidene(3-exo-$^2H_1$)-2-bicyclo[2.2.1]heptanone)]iron (**43**). From **42** (100 mg, 0.36 mmol), as described above for **46** from **41**: 95 mg (95%) of **43**, yellow crystals, m.p. 101–2°. No trace of dideuterated ketone **44** was detected (^{1}H-NMR and MS) after 1 week, 30°. IR (hexane): 2065, 1990, 1975. ^{1}H-NMR ($CDCl_3$): 3.29 (*dd*, J = 1.5, 1.7, 1H, H–C(1)); 3.24 (*dd*, J = 1.3, 1.5, 1H, H–C(4)); 3.10 (*dddd*, J = 10.0, 1.7, 1.5, 5, H_{anti}–C(7)); 2.60 (*d*, J = 10, H_{syn}–C(7)); 2.25 (*m*, 1H, H_{endo}–C(3)); 2.03, 1.95, 0.55, 0.51 (4*d*, J = 3.1, 4H). ^{13}C-NMR ($CDCl_3$): 208.9 (*s*, C(2)); 208.0 (*s*, $Fe(CO)_3$); 121.2, 110.5 (2*s*, C(5), C(6)); 56.9 (*t*, J = 137, C(7)); 56.4, 39.2 (2*d*, J = 155, 149, C(1), C(4)); 47.0 (*dt*, J = 141, $J_{C,D}$ = 20, C(3)); 34.4, 33.8 (2*t*, J = 161, CH_2=C(5), CH_2=C(6)). Anal. calc. for $C_{12}H_9DFeO_4$ (275.07): C 52.40, H 3.66; found: C 52.60, H 3.74.

Tricarbonyl[(1RS,2RS,5RS)-C,5,6,C-η-(5,6-dimethylidene-2-exo-bicyclo[2.2.1]heptyl methanesulfonate)]-iron (**50**). Methanesulfonyl chloride (520 mg, 4.6 mmol) was added dropwise to a stirred solution of **39** [4c] (1 g, 3.6 mmol) in anh. pyridine (10 ml) at 0°. After stirring at r.t. and under N_2 for 2 h, CH_2Cl_2 (50 ml) was added. The solution was washed with 1N HCl (3 × 20 ml) and then with H_2O (2 × 20 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* and the crude ester recrystallized from Et_2O/hexane 1:4 yielding 1.03 g (81%) of yellow crystals, m.p. 61–2°. IR (CH_2Cl_2): 2060, 1980, 1970. ^{1}H-NMR ($CDCl_3$): 5.08 (br. *d*, 1H, H–C(2)); 3.08 (*s*, 3H, CH_3); 3.05 (br. *s*, 1H, H–C(1)); 2.82 (*d*, J = 3.9, 1H, H–C(4)); 2.29 (*m*, 1H, H_{endo}–C(3)); 2.12 (*m*, 1H, H_{exo}–C(3)); 1.92, 1.87, 0.37, 0.33 (4*d*, J = 2.6, 4H); 1.87, 1.86 (2*d*, J = 10.0, 2H, CH_2(7)). ^{13}C-NMR ($CDCl_3$): 209.7 (*s*, $Fe(CO)_3$); 114.6, 105.7 (2*s*, C(5), C(6)); 81.2 (*d*, J = 153, C(2)); 47.8, 40.2 (2*d*, J = 154, 151, C(1), C(4)); 42.0 (*t*, J = 138, C(7)); 38.5 (*q*, J = 137, CH_3); 37.2 (*t*, J = 136, C(3)); 34.4, 34.0 (2*t*, J = 162, CH_2=C(5), CH_2=C(6)). MS (70 eV): 354 (6), 326 (23), 298 (21), 270 (52), 231 (10), 206 (16), 174 (38), 120 (95), 92 (100). Anal. calc. for $C_{13}H_{14}FeO_6S$ (354.10): C 44.10, H 3.96; found: C 44.27, H 3.99.

Reduction of **50**. A solution of **50** (200 mg, 0.56 mmol) and $NaBH_4$ (1 g, 26 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (30 ml) was heated for 4 h at 80°. After cooling to r.t., the solution was stirred for 12 h. H_2O (100 ml) was added and the mixture extracted with CH_2Cl_2 (4 × 30 ml). After drying ($MgSO_4$), the solvent was evaporated *i.v.* The residue was taken up in Et_2O/hexane 1:3 and filtered on *Florisil* yielding 20 mg of yellow oil containing the reduced complex and traces of $CF_3CH(OH)CF_3$. The reduction product was identified by its

1H- and ^{13}C-NMR which were identical with those of *tricarbonyl[(1RS,2RS)-C,2,3,C-η-(2,3-dimethylidenebicyclo[2.2.1]heptane)]iron* (**51**) [2] (uncorrectly reported with the *endo*-$Fe(CO)_3$ configuration by *Hansen et al.*).

REFERENCES

[1] *P.A. Carrupt & P. Vogel*, Helv. Chim. Acta, in preparation.

[2] *U. Steiner, H.-J. Hansen, K. Bachmann & W. von Philipsborn*, Helv. Chim. Acta *60*, 643 (1977).

[3] a) *Ph. Narbel, A.A. Pinkerton, E. Tagliaferri, J. Wenger, R. Roulet, R. Gabioud, P. Vogel & D. Schwarzenbach*, J. Organomet. Chem. *208*, 335 (1981); b) *E. Tagliaferri, R. Roulet, D. Schwarzenbach, R. Gabioud & P. Vogel*, in preparation.

[4] a) *R. Pettit, G. Emerson & J. Mahler*, J. Chem. Educ. *40*, 175 (1963); *H.D. Murdoch & E. Weiss*, Helv. Chim. Acta *45*, 1156 (1962); *iidem*, ibid. *46*, 1588 (1963); b) *D.F. Hunt, C.P. Lillya & M.D. Rausch*, J. Am. Chem. Soc. *90*, 2561 (1968); c) *Ch. Barras, L.G. Bell, R. Roulet & P. Vogel*, Helv. Chim. Acta *64*, 2841 (1981).

[5] *Y. Shvo & E. Hazum*, J. Chem. Soc., Chem. Commun. *1974*, 336; *A.P. Humphries & S.A.R. Knox*, J. Chem. Soc., Dalton Trans. *1978*, 1514.

[6] *M. Avenati, O. Pilet, P.-A. Carrupt & P. Vogel*, Helv. Chim. Acta *65*, 178 (1982).

[7] *R. Gabioud & P. Vogel*, Tetrahedron Lett. *24*, 1983 (1983).

[8] *R. Gabioud*, Dissertation, University of Lausanne, 1982.

[9] *A.A. Pinkerton, G. Chapuis, P. Vogel, U. Hänisch, Ph. Narbel, T. Boschi & R. Roulet*, Inorg. Chim. Acta *35*, 197 (1979).

[10] *J. Wenger, N.H. Thuy, T. Boschi, R. Roulet, A. Chollet, P. Vogel, A.A. Pinkerton & D. Schwarzenbach*, J. Organomet. Chem. *174*, 89 (1979).

[11] *Ch. Barras, R. Roulet, E. Vieira, P. Vogel & G. Chapuis*, Helv. Chim. Acta *64*, 2328 (1981).

[12] *Ch. Barras*, Dissertation, University of Lausanne, 1983.

[13] *J. Toullec*, Adv. Phys. Org. Chem. *18*, 1 (1982); *G. Lamaty*, in 'Isotopes in Organic Chemistry', Vol. 2, eds. E. Buncel and C.C. Lee, Elsevier, Amsterdam, 1976.

[14] *G.A. Abad, S.P. Jindal & T.T. Tidwell*, J. Am. Chem. Soc. *95*, 6326 (1973).

[15] *T.T. Tidwell*, J. Am. Chem. Soc. *92*, 1448 (1970); *N.H. Werstiuk & R. Taillefer*, Can. J. Chem. *48*, 3966 (1970).

[16] *D.N. Butler & R.A. Snow*, Can. J. Chem. *52*, 447 (1974); *iidem*, ibid. *53*, 256 (1975).

[17] *A. Chollet, C. Mahaim, C. Foetisch, M. Hardy & P. Vogel*, Helv. Chim. Acta *60*, 59 (1977).