148. The Reaction of Water with Iron- and Rutheniumcarbonyl Complexes of Polyolefins: 1,2- and 1,4-Hydrogenation of 1,3-Dienes. Hydrogenolysis of Allylic Ethereal Bonds and Deoxygenation of 7-Oxabicyclo[2.2.1]hept-2-enes

by **Shuki Araki**[1]), **Edia Bonfantini**[2]), and **Pierre Vogel***

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

(21.IV.88)

Under basic conditions, H_2O reacts with tricarbonyl[(1*R*,2*R*,3*S*,4*S*,5*R*,6*S*)-*C*,5,6,*C*-*η*-(2-*exo*,3-*exo*-bis(chloromethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane)]iron (**1**) and -ruthenium (**4**), with tricarbonyl[(1*R*,2*S*,3*R*,4*S*)-*C*,2,3,*C*-*η*-(2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane)]iron (**6**) and -ruthenium (**7**), and with *cis*-*μ*-[1*s*,2*S*,3*R*,4*s*,5*S*,6*R*)-*C*,2,3,*C*-*η* :*C*,5,6,*C*-*η*-(2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane)]bis(tricarbonyliron) (**11**) to give products of demetallation and 1,2- or/and 1,4-hydrogenation. Reductive demetallation of tricarbonyl[*C*,5,6,*C*-*η*-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohexa-1,3-diene)]iron (**14**) required heating under acidic conditions, giving 2,3-dimethylbenzaldehyde (**16**). H_2O reacted under neutral conditions with *cis*-heptacarbonyl-*μ*-[(1*RS*,2*SR*,3*RS*,4*SR*,5*RS*,6*SR*)-2,3-*η* :*C*,5,6,*C*-*η*-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]diiron (**17**) and with tricarbonyl[(1*RS*,4*RS*,5*SR*,6*RS*)-*C*,5,6,*C*-*η*-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]iron (**18**) to give the orthoquinodimethane complex **14** as major product. This reaction was accompanied by hydrogenolysis of the allylic ethereal C(4)–O(7) bond in **17** and **18** and gave tricarbonyl[(1*RS*,5*RS*,6*SR*)-*C*,5,6,*C*-*η*-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohex-2-en-1-ol)]iron (**21**) as minor product. The latter was not an intermediate of reaction **17**→**14**. Reactions with D_2O allowed one to discuss the possible mechanisms of this deoxygenation process. With *trans*-heptacarbonyl-*μ*-[(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*RS*)-2,3-*η* :*C*,5,6,*C*-*η*-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]diiron (**38**), the reaction with THF/H_2O gave **14** nearly quantitatively, with no D-incorporation in the presence of D_2O.

Introduction. – The $Fe(CO)_3$ group is a useful protecting or/and activating group of 1,3-diene functions [1]. Removal of the metallic moiety is generally achieved under mild conditions on oxidation with trimethylamine oxide [2], $FeCl_3$ [3], Ce(IV) salts [4], alcaline solution of H_2O_2 [5], *Collins* reagent [6], or *o*-chloranil [7]. In the presence of a strong *Lewis* acid such as $AlCl_3$, CO insertion can occur with formation of the corresponding cyclopent-3-enones [8]. The latter reaction can also be induced by $(NH_4)_2Ce(NO_3)_6$ in acetone in the case of tricarbonyl(*o*-quinodimethane)iron complexes giving the corresponding 2-indanones [9]. Ironcarbonyl complexes can also promote deoxygenation of amine oxides [2] [10], of nitro compounds [11], sulfoxides, *C*-nitroso compounds [12], and epoxides [13]. On heating tetracarbonyl(7-oxabicyclo[2.2.1]hept-2-ene)iron complexes, deoxygenation into the corresponding cyclohexa-1,3-dienes was observed [9] [14] [15]. Photoreduction of tricarbonyl(1,3-diene)iron complexes into the corresponding products of 1,2- and 1,4-hydrogenation has been reported by *Franck-Neumann* and coworkers [16].

---

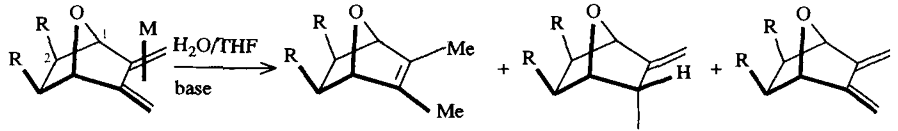
[1]) On leave of absence from the Department of Applied Chemistry, Nagoya Institute of Technology, Gokisu-cho, Showa-ku, Nagoya 466, Japan.

[2]) Part of the planned Ph. D. thesis of *E. Bonfantini*.

In the case of dienes substituted at the terminal C-centre by an electron-withdrawing group, 1,4-reduction was the favoured process.

We have found that tricarbonyl(1,3-diene)iron complexes can be demetallated by H_2O/THF to give reduced organic ligands. Depending on the structure of the complexed dienes, basic or acidic conditions are required to induce thermal 1,4- or 1,2-hydrogenation. In one instance, we have found that the selectivity between 1,4- and 1,2-hydrogenation products can be reversed by changing the metal from Fe to Ru. We shall show also that iron carbonyls are capable of reducing 7-oxabicyclo[2.2.1]hept-2-ene derivatives into the corresponding cyclohex-2-enols in the presence of H_2O. This reaction competes with the deoxygenation that leads to the corresponding cyclohexa-1,3-dienes.

Results and Discussion. – When the tricarbonyldieneiron complex **1** [17] was heated in wet tetrahydrofuran (THF) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), no elimination of HCl from the chloromethyl moieties was observed. A mixture of the uncomplexed monoolefins **2** and **3** was obtained instead in high yield *(Table)*. The 'reductive demetallation' was also good yielded when only a catalytical amount (0.1 mol-equiv.) of DBU was employed. The bases 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,4-diazabicyclo[2.2.2]octane (DABCO) also induced the hydrogenation *(Runs 4–6, Table)*. With DABCO, the reaction was slower than with DBU and DBN. In all cases, the product of 1,4-hydrogenation **2** was formed predominantly over the product of 1,2-hydrogenation **3**. Structures of **2** and **3** were given by their spectral data and elemental analyses *(Exper. Part)*. The ^{1}H-NMR spectrum of **3** confirmed the exclusive *exo*-face hydrogenation of the exocyclic double bond as a typical [18] vicinal coupling constant $^3J(H_{exo}-C(5), H-C(4)) = 4.5$ Hz was observed. Under the conditions of the above reactions, isomerization **2**$\rightleftarrows$**3** was not detected (by adding pure **2** or **3** to the reaction mixtures and prolonged heating) thus demonstrating that products **2** and **3** were obtained under conditions of kinetic control. When H_2O was replaced by D_2O, the corresponding dideuterated olefins (D_2)-**2** and (D_2)-**3** were obtained. Using various H_2O/D_2O ratios, the degree of deuteration of **2** and **3** (by 360-MHz ^{1}H-NMR and mass spectrometry) suggested that the isotopic effect k_H/k_D is near unity.



1 M = Fe(CO)$_3$
4 M = Ru(CO)$_3$

2 **3** **5**

R = CH_2Cl

No 'reductive demetallation' was detected on boiling **1** with DBN in dry THF, CCl_4, or wet MeOH for 2–3 days. In the presence of weaker bases such as Et_3N, pyridine, or imidazol, heating of **1** in wet THF did not affect the complex either. In the presence of KOH and in THF/H_2O, a 59:41 mixture **2**/**3** was obtained *(Run 7, Table)*. The latter reaction was at least 10 times slower than that using wet THF and DBU.

Heating the tricarbonyl(diene)ruthenium complex **4** [17] in wet THF with DBU for 20 h gave 5% of the uncomplexed diene **5** together with a 12:88 mixture of **2** and **3** (90%, isolated). Interestingly, the product ratio **2**/**3** so-obtained was inverse of that observed for

Table. *Reactions of Tricarbonyl(diene)iron and Ruthenium Complexes* **1** *and* **4** *with Wet THF* (*ca.* 2% H_2O)

Run	Complex	Base	Number of equiv. of base	Time[a]) [h]	Isolated yield	Product ratio **2**/**3**
1	**1**	DBU	5	5	98	89:11
2	**1**	DBU	5	98	98	87:13
3	**1**	DBU	0.1	15	90	86:14
4	**1**	DBN	5	15	82	93:7
5	**1**	DBN	0.1	15	93	88:12
6	**1**	DABCO	5	72	80	83:17
7	**1**	KOH[b])	5	45	43	59:41[c])
8	**4**	DBU	5	20	90	12:88[d])
9	**4**	DBU	5	88	93	18:82[d])

[a]) Heating under reflux.

[b]) In THF/H_2O 1:1.

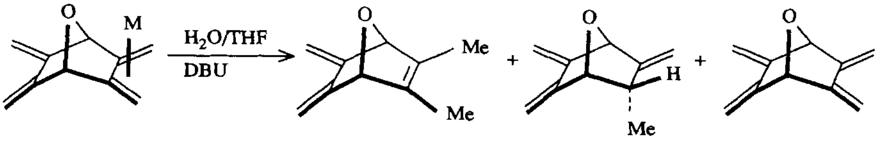
[c]) 41% of **1** was recovered.

[d]) Uncomplexed diene **5** was also formed (*ca.* 5%).

the 'reductive demetallation' of the iron complex **1** (*cf. Runs 1* and *8, Table*). No isomerization **2**⇄**3** could be evidenced on heating pure **2** or **3** under the reaction conditions of 'reductive demetallation' of **4**.

It is worth to compare the product ratio **2**/**3** obtained for the thermal 'reductive demetallations' of **1** and **4** with that of **1** under photochemical conditions. Irradiation at 20° (*Pyrex* reactor, high-pressure Hg lamp, N_2 bubbling) of **1** in AcOH [16] gave a 15:68:16 mixture of **2**/**3**/**5** in 90% yield.

In order to test the generality of the 'reductive demetallation' of tricarbonyl(1,3-diene)-iron and ruthenium complexes by basic H_2O/THF, we explored the reactivity of the monocomplexes **6** and **7** of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**10**) [17]. We have found complex **6** to be significantly less reactive than **1** toward DBU in wet THF. After 15 h of heating under reflux, and in the presence of 5 equiv. of the base, **6** afforded a 88:12 mixture of uncomplexed trienes **8** and **9** in 19% yield, together with 63% of recovered starting material. In this case also, the 1,4-hydrogenation product **8** predominated over the product **9** of 1,2-hydrogenation. The structures of **8** and **9** were established by their spectral data and elemental analyses (*Exper. Part*). On heating the ruthenium

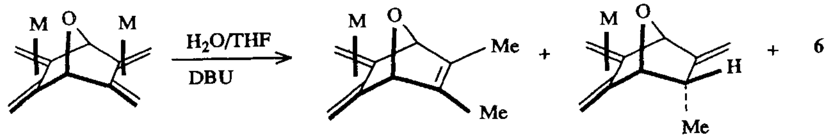


6 M = Fe(CO)$_3$
7 M = Ru(CO)$_3$

8

9

10



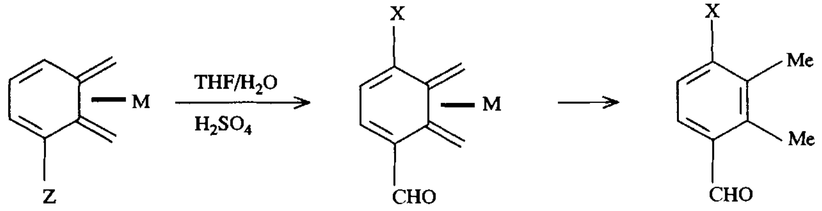
11 M = Fe(CO)$_3$

12 M = Fe(CO)$_3$

13 M = Fe(CO)$_3$

monocomplex **7** in wet THF with 5 equiv. of DBU, a 17:83:50 mixture of **8**, **9**, and uncoordinated tetraene **10** was obtained. Complete consumption of the starting material was observed after 15 h of boiling. As in the case of the 'reductive demetallation' of the ruthenium complex **4**, 1,2-hydrogenation was the favoured process, and it was *exo*-face selective.

The dinuclear complex **11** was significantly more reactive than the corresponding iron monocomplex **6**. In the presence of 10 equiv. of DBU, heating of **11** in wet THF for 5 h furnished **6**, **12**, and **13** in 20, 38, and 32% isolated yield, respectively. In this case, the selectivity between 1,4- and 1,2-hydrogenation was not as good as for the 'reductive demetallations' of the iron monocomplexes **1** and **6**.



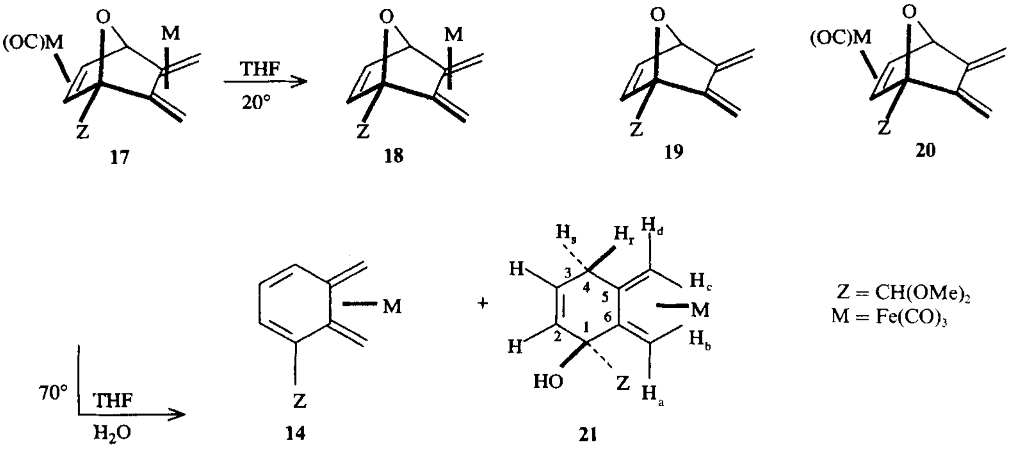
14 Z = $CH(OMe)_2$, M = $Fe(CO)_3$

15 X = H, M = $Fe(CO)_3$
24 X = D, M = $Fe(CO)_3$

16 X = H
25 X = D

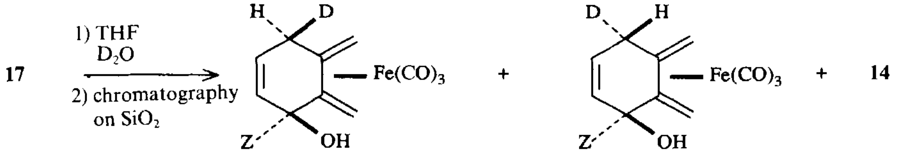
The tricarbonyl(*o*-quinodimethane)iron derivative **14** [9] was stable on heating in THF/H_2O with DBN, DBU, or KOH. However, 'reductive demetallation' of **14** was possible on heating in wet THF containing 3–10 equiv. of H_2SO_4. The reaction was competitive with hydrolysis of the dimethylacetal (**14**→**15**). After boiling for 2 days, 2,3-dimethylbenzaldehyde (**16**) was isolated in 89% yield together with 3% of complex **15** [9].

In the absence of air, the dinuclear iron complex **17** [9] was stable in anh. THF. In the presence of air and at 20°, **17** was slowly transformed into the corresponding tricarbonyldieneiron complex **18**. The same partial demetallation occurred also in degassed, anh.



Z = $CH(OMe)_2$
M = $Fe(CO)_3$

THF in the presence of DBN. Its rate depended on the relative amount of the base. The monocomplex **18** had never been made before. Indeed, direct complexation of triene **19** with $Fe_2(CO)_9$ or $Fe(CO)_5$ gives first the tetracarbonyliron complex **20** which is slowly transformed into **17** in the presence of an excess of iron carbonyls [9]. The mononuclear iron complex **18** could be obtained in 83% yield by treatment of **17** at 20° in anh. THF containing 0.6 equiv. of DBN. These results suggested that **17** equilibrates with **18** and $Fe(CO)_4(THF)$ at 20°, the latter complex being slowly decomposed by air. In the presence of DBN, the concurrent equilibrium **17**⇄**18** + $Fe(CO)_4(DBN)$ might intervene and accelerate the reactions of **17**.



22 (major) **23** (minor)

On heating **17** in degassed and wet THF (*ca.* 2% H_2O) under reflux for 24 h, a mixture was obtained from which **14** and the allylic alcohol **21** were isolated in 55 and 14% yield, respectively. The outcome of that partial demetallation and reduction process was not affected in a significant fashion by addition of 0.2 equiv. of DBN. In the presence of KOH, the same products were obtained (THF/H_2O 5:1, 70°, 20 h) but in lower yields. On heating mononuclear complex **18** in wet THF containing 0.7 equiv. of DBU, a slower reaction than that of **17** was observed. After 29 h, *ca.* 50% of **18** were consumed giving **14**, the uncoordinated triene **19**, and the allylic alcohol **21** in 7, 8, and 7.5% isolated yield, respectively. The observations that the partial demetallation and reductions of the dinuclear iron complex **17** were slightly faster processes than the demetallation and reductions of the corresponding mononuclear iron complex **18** suggested that reactions **17**→**14** + **21** and **18**→**14** + **21** imply the intermediacy of an ironhydride coordinated to the endocyclic monoolefin moiety (see below). Alternatively, the reductions could be due to an intermolecular process involving hydrido species derived form $Fe(CO)_4(THF)$, $Fe(CO)_3(THF)_2$, $Fe_2(CO)_9$, $Fe_2(CO)_8(THF)$, *etc.* The latter are more abundant when using **17** than **18** as starting material; they are known to engender hydrides in the presence of H_2O [19]3).

When pure **21** was heated (70°) in THF/H_2O, with or without DBN, no reaction was detected after 36 h. Similarly, after heating **21** in toluene to 100° for 24 h, **21** was recovered unchanged. In the presence of H_2SO_4, however, the allylic alcohol **21** eliminated 1 equiv. of H_2O giving the (*o*-quinodimethane)iron complex **15** which was then transformed into **16**. When D_2O (30 equiv.) replaced H_2O in wet THF, heating of **17** gave the undeuterated (by 360-MHz ^1H-NMR and mass spectrometry) (*o*-quinodimethane)iron complex **14** and the deuterated allylic alcohols **22**/**23** in proportions similar to those observed for the

---

3) Disproportion of transition-metalcarbonyls under basic conditions is a well known phenomenon, also for $Fe(CO)_5$ [20].

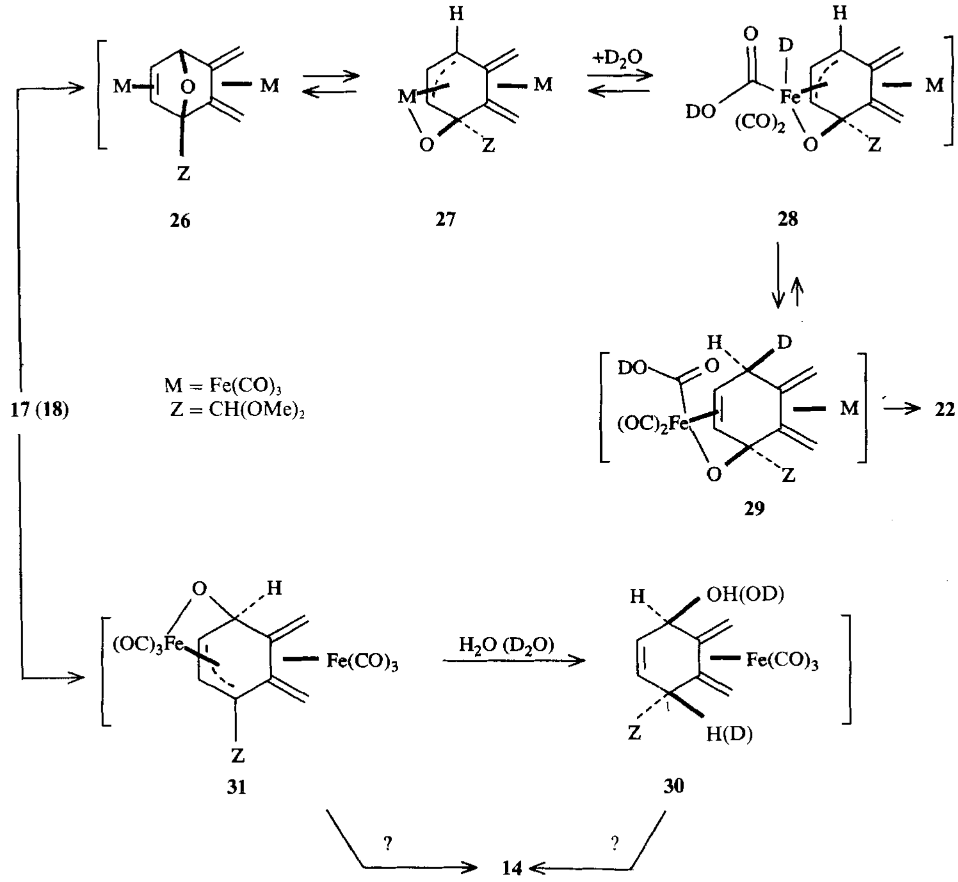
reductive demetallation of **17** in THF/H_2O. The 360-MHz ^1H-NMR spectrum showed that deuteration at C(4) was not stereospecific, the isomeric ratio **22**/**23** being 4.5:1. Heating pure **22**/**23** in THF/H_2O/H_2SO_4 led to the deuterated tricarbonyl(*o*-quinodimethane)iron derivative **24** which was then slowly demetallated giving 2,3-dimethyl[4-D]benzaldehyde (**25**). Based on 360-MHz ^1H-NMR analysis, the degree of deuteration of **24** and **25** was 81 ± 3%. These experiments demonstrated that the allylic alcohol **21** is not an intermediate of the direct deoxygenation of the 7-oxabicyclo[2.2.1]hept-2-ene derivatives **17** and **18** to the corresponding *o*-quinodimethane complex **14**. The 'reductive demetallations' **17**→**14** and **17**→**21** are thus parallel processes.

The structure of the allylic alcohol **21** (and **22**/**23**) was deduced from its elemental analysis and spectral data (*Exper. Part*). The relative configurations of the $Fe(CO)_3$ moiety, of protons H_r and H_s at C(4) and of OH at C(1) were suggested by the 360-MHz ^1H-NMR spectrum and by double-irradiation experiments, including nuclear *Overhauser* effect (NOE) measurements. For instance, irradiation of the *s* at 2.79 ppm attributed to the OH group led to the observation of NOE's at 4.31 (CH–C(1)) and 2.08 ppm (H_a of CH_2=C(6), *trans* to C(5)). A NOE was also observed for the pair H_r–C(4)/H_d(H of CH_2=C(5) *trans* to C(6)). This confirmed the '*syn*' relationship between H_r–C(4) and the $Fe(CO)_3$ moiety which makes proton H_d to bend above the butadiene plane toward H_r–C(4) and H_c(H of CH_2=C(5) *cis* to C(6); 0.24 ppm) to be more or less aligned with H_s–C(4) (3.36 ppm; H *trans* to OH). This hypothesis was confirmed by the observation of a coupling constant $^4J = 1$ Hz between the two latter protons.

Alcohol **21** derives from hydrogenolysis of the C(4)–O(7) allylic-ether bond of **17** (and **18**). The major mode of reduction **17**→**22** can be interpreted in terms of an intramolecular hydrogenolysis involving the hypothetical intermediates of type **26**⇄**27**⇄**28**⇄**29**. The minor mode of reductive deuteration **17**→**23** can be explained by the intervention of a concurrent S_N2 displacement at C(4) of the secondary allylic ether by an iron-deuteride species.

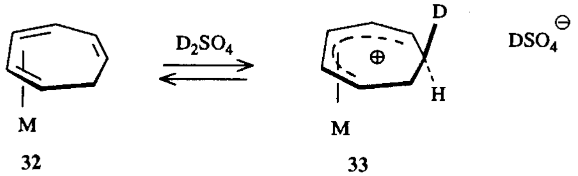
The non-observation of isomeric, secondary allylic alcohols **30** resulting from the hydrogenolysis of the C(1)–O(7) bonds in **17** and **18** might appear as a surprise. If a mechanism involving oxidative addition (**26**→**27**) of a tricarbonyliron moiety into the C(4)–O(7) bond is operative, it should be competitive with the oxidative addition into the C(1)–O(7) bond, the latter being not significantly stronger than the former [21]. It is thus possible that **30** is in fact the major product of 'reductive partial demetallation' of **17** and **18**, but is unstable under the conditions of its formation, undergoing a fast 1,4-elimination of H_2O to give the major product isolated, *i.e.* **14**. This hypothesis is consistent with the higher acidity expected for the H–C(1) bond in **30** than that of the H–C(4) bonds in **21** because of the inductive effect of the adjacent dimethyl-acetal moiety and with the easier heterolysis of the OH group in **30** than in **21**. One can thus envision that the deoxygenation of the 7-oxabicyclo[2.2.1]hept-2-ene moiety into the corresponding cyclohexa-1,3-diene system in aqueous or alcoholic solvents [9] [14] [15] follows a mechanism analogous to **18**⇄**17**→**31**→**30**→**14**. This hypothesis is consistent with our observation that **17** gave exclusively undeuterated *o*-quinodimethane complex **14** when the 'reductive demetallation' was carried out in THF/D_2O. On heating **17** in anh. toluene (95°, 80 min), **14** was obtained in 53% yield (isolated) [9]. Under these conditions, hydrolysis of **31** is not possible. Thus one must admit that **31** can undergo a direct elimination of $FeO(CO)_3$ to give **14**, concurrently with reaction **31**→**30**→**14**.

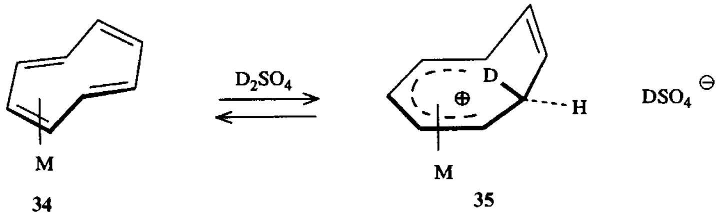
The acid-catalyzed H_2O elimination from **22**/**23** (4.5:1) gave a *ca.* 4.4:1 mixture **24**/**15** (and then **25**/**16**; 81 ± 3% deuteration at C(4), see above). This result is consistent with

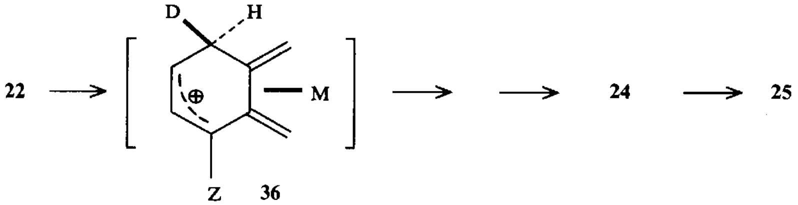


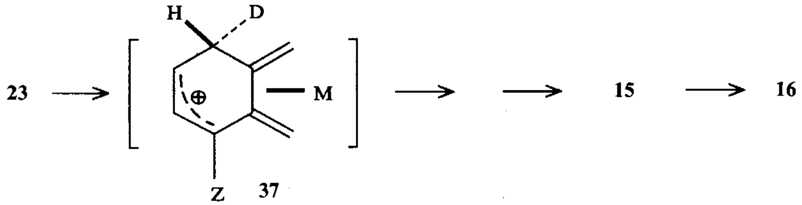
the observation that reversible protonation (deuteration) of an olefinic moiety adjacent to a tricarbonyl(diene)iron function is highly stereoselective and occurs on the face *'anti'* to the metal atom, as reported for **32**⇄**33** and **34**⇄**35** [22]. Heterolysis of alcohols **22** and **23** are assumed to generate the allylic cation intermediate **36** and **37**, respectively, which are stabilized by participation of the tricarbonyl(diene)iron group [23]. Elimination of the proton *'anti'* to the metal atom leads to the deuterated *o*-quinodimethane complex **24** (after hydrolysis of the acetal) and to the undeuterated complexes **14**→**15**, respectively, thus explaining the similitude of the product ratios **22**/**23** and **24**/**15**.

We have also examined the reaction of the *exo,endo*-dinuclear complex **38** [9] with H_2O. On heating **38** in THF (70°) containing 1 equiv. of H_2O and 0.1 equiv. of DBN, a nearly quantitative yield of **14** was obtained. The reaction was complete in less than 5 h, whereas, under the same conditions, **17** required 27 h for a complete transformation. When using D_2O instead of H_2O, no D-incorporation in **14** could be detected by 360-MHz ^{1}H-NMR. The higher reactivity of **38** in THF/H_2O compared with that of **17** is difficult to explain. It can be attributed, tentatively, to a difference in steric effects: the *exo*-Fe(CO)$_3$ moiety in **17** is expected to perturb the hydrogenolysis of the allylic ether more than the *endo*-Fe(CO)$_3$ moiety in **38**. This hypothesis, however, does not explain yet

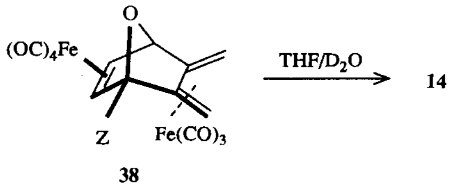








M = $Fe(CO)_3$, Z = $CH(OMe)_2$



the non-observation of allylic alcohols isomeric of **21** (and **30**) during the reaction of **38** with THF/H_2O.

Conclusion. – Water reacts with tricarbonyliron and tricarbonylruthenium complexes of exocyclic 1,3-dienes to give products of 1,4- or/and 1,2-hydrogenation. Depending on the nature of the skeleton of the dienes, a base or an acid is required for the demetallation.

Under neutral conditions, H_2O reacts with heptacarbonyl(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)diiron derivatives yielding the corresponding tricarbonyl(*o*-quinodimethane)iron complexes. This process is accompanied by the formation of products arising from the hydrogenolysis of the allylic etheral bonds of the 7-oxabicyclo-[2.2.1]hept-2-ene moiety.

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

Experimental Part

1. *General*. See [24].

2. a) *Syntheses of Complexes* **1**, **6**, *and* **11**, see [17].

b) *Tricarbonyl[(1*R*,2*R*,3*S*,4*S*,5*R*,6*S*)-C,5,6,C-η-(2-*exo*,3-*exo-bis(chloromethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane)]ruthenium* (**4**). For 3 h, 2-*exo*,3-*exo*-bis(chloromethyl)-5,6-dimethylidene-7-oxabicyclo-[2.2.1]heptane [25] (**5**; 657 mg, 3 mmol) and octacarbonylbis(triethylsilyl)diruthenium [26] (1.97 g, 3 mmol) were heated under reflux in CH_3CN (35 ml). After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2) to give 326 mg (27%), colourless crystals. M.p. 98.5–99°. UV (isooctane): 203 (15400), 278 (sh, 3100). IR (KBr): 2054, 1980, 1953, 1280, 998, 906, 840, 773, 671. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.59 (*d*, *J* = 3); 2.13 (*d*, *J* = 3); 2.68 (*m*, H–C(2), H–C(3)); 3.6, 3.85 (2*m*, 2 CH_2Cl); 4.73 (*s*, H–C(1), H–C(4)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 25.0 (CH_2=); 43.5 (CH_2Cl); 46.6 (C(2), C(3)); 81.0 (C(1), C(4)); 109.5 (C(5), C(6)). MS (70 eV): 404 (1, M^+, $C_{13}H_{12}{}^{35}Cl_2O_4{}^{102}Ru$), 376 (9), 348 (5), 320 (8), 91 (100). Anal. calc. for $C_{13}H_{12}Cl_2O_4Ru$ (404.21): C 38.63, H 2.99; found: C 38.79, H 3.09.

3. *Demetallation of* **1** *and* **4** *with H_2O; General Procedure*. A mixture of **1** or **4** (0.2 mmol) and of a base in freshly dist. THF (15 ml; containing *ca.* 2% H_2O, by the *Karl-Fischer* method) was heated under reflux for various reaction times. After cooling to 20°, the solvent was evaporated and the residue purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 gradient) giving mixtures **2**/**3** whose ratio was given by 360-MHz ^{1}H-NMR (see the *Table*). The experiment using D_2O employed freshly dist. THF over $LiAlH_4$ to which various amounts of D_2O were added. Pure samples of **2** and **3** were obtained by repetitive chromatography on silica gel (petroleum ether/CH_2Cl_2).

5-*exo*,6-*exo-Bis(chloromethyl)-2,3-dimethyl-7-oxabicyclo[2.2.1]hept-2-ene* (**2**). Colourless crystals. M.p. 83.5–84° (petroleum ether). UV (isooctane): 204 (4400). IR (KBr): 2964, 1670, 1440, 1284, 1000, 957, 897, 833, 812, 777, 705. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.7 (*s*, 2 Me); 2.08 (*m*, H–C(5), H–C(6)); 3.48, 3.73 (2*m*, 2 CH_2Cl); 4.63 (*s*, H–C(1), H–C(4)). ^{13}C-NMR ($CDCl_3$): 9.6 (Me); 44.4 (CH_2Cl); 46.0 (C(5), C(6)); 85.8 (C(1), C(2)); 136.8 (C(2), C(3)). MS (70 eV): 220 (1, M^+), 205 (1), 185 (5), 96 (100), 91 (6), 77 (7), 68 (8), 67 (18). Anal. calc. for $C_{10}H_{14}Cl_2O$ (221.13): C 54.32, H 6.38; found: C 54.37, H 6.45.

2-*exo*,3-*exo-Bis(chloromethyl)-5-*endo*-methyl-6-methylidene-7-oxabicyclo[2.2.1]heptane* (**3**). Colourless oil. UV (isooctane): 202 (3300). IR (CCl_4): 3065, 2955, 1665, 1445, 1280, 1245, 995, 960, 885, 710. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.1 (*d*, *J* = 7.2, Me); 2.34, 2.60 (2*m*, H–C(2), H–C(3)); 2.74 (*m*, ^3J = 7.2, 4.5, H_{exo}–C(5)); 3.48, 3.63 (2*m*, 2 CH_2Cl); 4.44 (*d*, ^3J = 4.5, H–C(4)); 4.76 (*s*, H–C(1)); 4.81, 5.03 (2*d*, *J* = 2.3, CH_2=C(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 13.4 (Me); 41.9, 43.3 (C(2), C(3)); 42.6, 43.0 (2 CH_2Cl); 51.5 (C(5)); 84.7 (C(1), C(4)); 103.1 (CH_2=C(6)); 154.4 (C(6)). MS (70 eV): 223 (1), 222 (4), 221 (3), 220 (6, M^+), 219 (5), 187 (33), 186 (10), 185 (100), 171 (10), 157 (23), 133 (10), 131 (44), 121 (38), 107 (29), 105 (45), 96 (37), 95 (59), 93 (77), 91 (96), 79 (62), 77 (66), 67 (91), 65 (53), 55 (65), 53 (79). Anal. calc. for $C_{10}H_{14}Cl_2O$ (221.13): C 54.32, H 6.38; found: C 54.47, H 6.23.

4. *Tricarbonyl[(1*R*,2*S*,3*R*,4*S*)-C,2,3,C-η-(2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane)]ruthenium* (**7**). A mixture of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane [27] (**10**; 438 mg, 3 mmol) and octacarbonylbis(triethylsilyl)diruthenium (1.97 g, 3 mmol) in CH_3CN (35 ml) was heated under reflux for 2 h. After cooling to 20°, the solvent was evaporated and the residue purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2), yielding 335 mg (34%), colourless crystals. M.p. 94–95° (petroleum ether). UV (isooctane): 204 (20600), 230 (13500), 238 (13700), 289 (6300). IR (KBr): 2060, 1985, 1970, 975, 890, 840, 765, 650. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.65, 2.13 (2*d*, *J* = 3.0, 4 H); 4.9 (*s*, H–C(1), H–C(4)); 5.33, 5.53 (2*s*, CH_2=C(5), CH_2=C(6)).

^{13}C-NMR (90.55 MHz, $CDCl_3$): 25.5 (Ru···CH_2=C); 81.9 (C(1), C(4)); 104.5 (CH_2=C(5), CH_2=C(6)); 110.3 (C(2), C(3)); 143.3 (C(5), C(6)). MS (70 eV): 332 (23, M^+, $C_{13}H_{10}O_4{}^{102}Ru$), 304 (100), 276 (40), 248 (75). Anal. calc. for $C_{13}H_{10}O_4Ru$ (331.29): C 47.13, H 3.04; found: C 47.24, H 3.12.

5. *Demetallation of* **6** *with H_2O.* A mixture of **6** (572 mg, 2 mmol) and DBU (1.52 ml, 10 mmol) in THF/H_2O 98:2 (50 ml) was heated under reflux for 15 h. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2). The 1st fraction gave 360 mg of **6** (63%). The 2nd fraction contained 58 mg (19%) of a 88:12 mixture **8**/**9** (by 360-MHz ^{1}H-NMR) and a small amount (*ca.* 1%) of **10**. Repeated column chromatography on silica gel (petroleum ether/CH_2Cl_2) gave pure samples of **8** and **9**.

2,3-Dimethyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**8**). Colourless crystals. M.p. 54.5–55° (pentane). UV (isooctane): 208 (11900), 226 (sh, 7800), 234 (7200), 243 (sh, 5600). IR (KBr): 3066, 2901, 1658, 1438, 981, 973, 943, 899, 875, 835, 760. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.73 (*s*, 2 Me); 4.84 (*s*, H–C(1), H–C(4)); 5.04, 5.21 (2*s*, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 9.9 (Me); 87.0 (C(1), C(4)); 100.5 (CH_2=); 137.6 (C(2), C(3)); 144.4 (C(5), C(6)). MS (70 eV): 149 (6), 148 (16, M^+), 120 (9), 119 (60), 105 (13), 96 (81), 95 (21), 91 (29), 81 (12), 79 (15), 77 (24), 70 (13), 68 (11), 67 (21), 43 (100). Anal. calc. for $C_{10}H_{12}O$ (148.20): C 81.04, H 8.16; found: C 81.05, H 8.13.

*2-*endo*-Methyl-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane* (**9**). Colourless oil. UV (isooctane): 220 (7000), 227 (6700), 248 (7300), 279 (4100). IR (CCl_4): 3070, 2985, 1665, 1415, 965, 930, 885. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.03 (*d*, ^3J = 7, CH_3); 2.80 (*m*, H–C(2)); 4.71 (*d*, ^3J = 5.2, H–C(1)); 4.81 (*dd*, ^2J = 2.5, 1.1); 5.08 (*dd*, *J* = 2.5, 0.8, CH_2=C(3)); 4.96 (*s*, H–C(4)); 4.99, 5.01, 5.23, 5.43 (4*s*, CH_2=C(5), CH_2=C(6)). MS (70 eV): 149 (2), 148 (5), 147 (1), 133 (4), 131 (2), 119 (4), 105 (7), 96 (5), 95 (3), 93 (2), 43 (100). Anal. calc. for $C_{10}H_{12}O$ (148.20): C 81.04, H 8.16; found: C 80.94, H 7.97.

6. *Demetallation of* **7** *with H_2O.* A mixture of **7** (33 mg, 0.1 mmol) and DBU (76 µl, 0.5 mmol) in THF/H_2O 98:2 (3 ml) was heated under reflux for 15 h. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2) giving 5 mg (30%) of a 17:83:49 mixture **8**/**9**/**10**.

7. *Partial Demetallation of* cis-*µ-[(1*s*,2*S*,3*R*,4*s*,5*S*,6*R*)-C,2,3,C-η:C,5,6,C-η-(2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane)]bis(tricarbonyliron)* (**11**) *with H_2O.* A mixture of **11** (113 mg, 0.27 mmol) [17], DBU (0.41 g, 2.7 mmol), and THF/H_2O 98:2 (15 ml) was heated under reflux for 5 h. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 gradient) giving 29 mg (38%) of **12**, 25 mg (32%) of **13**, and 15 mg (20%) of **6**.

*Tricarbonyl[(1*R*,4*S*,5*R*,6*S*)-C,5,6,C-η-(2,3-dimethyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]iron* (**12**). Yellow crystals. M.p. 119.5–120° (petroleum ether). UV (isooctane): 209 (29400), 293 (3700). IR (KBr): 2036, 1952, 1433, 970, 846, 620, 602. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.56 (*d*, *J* = 2.6, 2 H); 1.90 (*s*, 2 Me); 2.18 (*d*, *J* = 2.6, 2 H); 4.98 (*s*, H–C(1), H–C(4)). MS (70 eV): 288 (3, M^+), 260 (15), 232 (71), 204 (28), 189 (16), 176 (59), 174 (99), 169 (20), 148 (24), 146 (24), 134 (14), 119 (19), 105 (30), 91 (29), 84 (22), 81 (17), 79 (13), 77 (21), 65 (12), 56 (100). Anal. calc. for $C_{13}H_{12}FeO_4$ (288.08): C 54.20, H 4.20; found: C 54.24, H 4.34.

*Tricarbonyl[(1*RS*,2*SR*,4*SR*,5*RS*,6*SR*)-C,5,6,C-η-(2-*endo*-methyl-3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptane)]iron* (**13**). Yellow crystals. M.p. 60–61° (petroleum ether). UV (isooctane): 207 (33400), 290 (4100). IR (KBr): 2030, 1955, 970, 890, 840, 630, 610. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.38, 0.50 (2*d*, *J* = 2.6, 2 H); 1.18 (*d*, *J* = 7.4, Me–C(2)); 2.05, 2.10 (2*d*, *J* = 2.6, 2 H); 3.08 (*dq*, *J* = 7.4, 5.0, H–C(2)); 4.78 (*d*, *J* = 5.0, H–C(1)); 4.91 (*s*, H–C(4)); 5.10, 5.35 (2*d*, *J* = 2.0, 2 H). MS (70 eV): 288 (3, M^+), 260 (28), 232 (78), 204 (100), 202 (96), 189 (57), 176 (30), 174 (62), 164 (27), 148 (75), 134 (27), 108 (29), 105 (26), 96 (19), 95 (18), 91 (29). Anal. calc. for $C_{13}H_{12}FeO_4$ (288.08): C 54.20, H 4.20; found: C 54.27, H 4.09.

8. *Reductive Demetallation of Tricarbonyl[C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohexa-1,3-diene)]iron* (**14**). A mixture of **14** [9] (65 mg, 0.2 mmol), THF/H_2O 98:2 (6 ml), and conc. H_2SO_4 soln. (300 mg) was heated under reflux for 2 days. After cooling to 20°, H_2O (20 ml) was added and the mixture extracted with CH_2Cl_2 (30 ml, 3 times). After drying ($MgSO_4$), and evaporation, the residue was purified by chromatography on silica gel (AcOEt/petroleum ether 1:10), yielding 24 mg (89%) of *2,3-dimethylbenzaldehyde* (**16**) [28] and 1.5 mg (2.7%) of *tricarbonyl[C,5,6,C-η-(5,6-dimethylidene-1,3-cyclohexadiene-1-carbaldehyde)]iron* (**15**) [9].

9. *Tricarbonyl[(1*RS*,4*RS*,5*SR*,6*RS*)-C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]iron* (**18**). A mixture of **17** [9] (200 mg, 0.4 mmol), anh. THF (10 ml), and DBN (30 µl, 0.24 mmol) was allowed to stand at 20° for 6 days (control of the disparation of **17** by TLC on silica gel, AcOEt/petroleum ether 1:7). After evaporation, the residue was purified by column chromatography on silica gel (AcOEt/petroleum ether 1:7), yielding 111 mg (83%), yellow oil which crystallized from MeOH at –20°. M.p. 47–48°. IR

(film): 2990, 2930, 2830, 2040, 1955, 1465, 1445, 1270, 1210, 1190, 1110, 1080, 935. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.53, 0.55 (2*d*, $^2J = 2.5$); 2.13 (*d*, $^2J = 2.5$, H of CH_2=C(6) *trans* to C(5), C(6)); 2.23 (*dd*, $^2J = 2.5$, $^4J = 1$, H of CH_2=C(5) *trans* to C(5), C(6)); 3.6, 3.58 (2*s*, 2 MeO); 4.85 (*d*, ^5J(CH–C(1), H–C(3)) = 1, CH–C(1)); 5.26 (br. *d*, $^3J = 2$, H–C(4)); 7.11 (*ddd*, $^3J = 5.5$, 2, $^5J = 1$, H–C(3)); 7.17 (*d*, $^3J = 5.5$, H–C(2)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 34.3, 34.7 (2*t*, ^1J(C,H) = 162, *C*H_2=C(5), *C*H_2=C(6)); 56.0, 57.0 (2*q*, ^1J(C,H) = 142, 2 MeO); 81.2 (*d*, ^1J(C,H) = 170, C(4)); 92.5 (*s*, C(1)); 103.0 (*d*, ^1J(C,H) = 160, CH–C(1)); 114.2, 116.7 (2*s*, C(5), C(6)); 142.5 (*d*, ^1J(C,H) = 180, C(2), C(3)); 211.5 (*s*, 3 CO). MS (70 eV): 306 (2, $M^+ - CO$), 278 (7), 250 (9), 218 (9), 188 (12), 162 (13), 160 (9), 147 (16), 132 (8), 111 (13), 104 (14), 91 (28), 75 (53), 56 (100). Anal. calc. for $C_{14}H_{14}FeO_6$ (334.107): C 50.33, H 4.22; found: C 50.38, H 4.23.

10. *Reaction of* cis-*Heptacarbonyl-μ-[(1*RS,2SR,3RS,4SR,5RS,6SR*)-2,3-η:C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]diiron* (**17**) *with* H_2O. A mixture of **17** (385 mg, 0.76 mmol) in anh. THF (17.5 ml), H_2O (400 μl, 22.2 mmol), and DBN (10 μl, 0.08 mmol) was heated to 70° for 27 h. After cooling to 20°, the solvent was evaporated and the residue filtered through silica gel (AcOEt/petroleum ether 1:4). The mixture was separated and purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:8) yielding 134 mg (55%) of **14** and 37 mg (14%) of **21**.

Following the same procedure, trans-*heptacarbonyl-μ-[(1*RS,2SR,3RS,4SR,5SR,6RS*)-2,3-η:C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]diiron* (**38**) gave **14** (*ca.* 100%) after 5 h reaction.

*Tricarbonyl[(1*RS,5RS,6SR*)-C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohex-2-en-1-ol)]iron* (**21**). Yellow oil which crystallizes from Et_2O at −20°. M.p. 83–84°. UV (dioxane): 220 (20000), 285 (sh, 2200). IR (KBr): 3485, 3045, 2995, 2965, 2925, 2865, 2835, 2045, 1975, 1960, 1455, 1405, 1385, 1325, 1070. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.0 (*d*, $^2J = 2.5$, H of CH_2=C(6) *cis* to C(5)); 0.24 (*dd*, $^2J = 2.5$, $^4J = 1$ (coupling with H of CH_2(4) *trans* to OH), H of CH_2=C(5) *cis* to C(6)); 1.80 (*d*, $^2J = 2.5$, H of CH_2=C(5) *trans* to C(6)); 2.08 (*d*, $^2J = 2.5$, H of CH_2=C(6) *trans* to C(5)); 2.62 (*dd*, $^2J = 20.5$, $^3J = 5.5$, H of CH_2(4) *cis* to OH); 2.79 (*s*, OH); 3.36 (*dm*, $^2J = 20.5$, H of CH_2(4) *trans* to OH); 3.54, 3.59 (2*s*, 2 MeO); 4.31 (*s*, CH–C(1)); 5.88 (*dd*, $^3J = 10$, $^4J = 2.7$, H–C(2)); 6.12 (*ddd*, ^3J(H–C(2), H–C(3)) = 10, ^3J(H–C(3),H_{cis}–C(4)) = 5.5, ^3J(H–C(3),H_{trans}–C(4)) = 1.7, H–C(3)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 32.2 (*t*, ^1J(C,H) = 128, C(4)); 34.1, 39.1 (2*t*, ^1J(C,H) = 160, CH_2=C(5), CH_2=C(6)); 58.4 (*q*, ^1J(C,H) = 142, 2 MeO); 72.7 (*s*, C(1)); 102.7, 105.2 (2*s*, C(5), C(6)); 112.1 (*d*, ^1J(C,H) = 162, CH–C(1)); 126.6, 130.2 (2*d*, ^1J(C,H) = 160, C(2), C(3)); 211.2 (*s*, 3 CO). MS (70 eV): 336 (2, M^+), 308 (3), 280 (12), 252 (12), 220 (10), 177 (9), 148 (100), 117 (37), 75 (46). Anal. calc. for $C_{14}H_{16}FeO_6$ (336.123): C 50.02, H 4.80; found: C 50.10, H 4.82.

*Tricarbonyl[(1*RS,4RS,5SR,6RS*)- and (1*RS,4SR,5SR,6RS*)-C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidene(4-^{2}H)cyclohex-2-en-1-ol)]iron* (**22/23**), *4.5:1 Mixture*. Same procedure as for the preparation of **21**, using D_2O instead of H_2O. Yield 15%, yellow crystals. M.p. 83–83.5°. UV (dioxane): 220 (20400), 285 (sh, 2200). IR (KBr): 3480, 3030, 2990, 2960, 2930, 2860, 2830, 2040, 1985, 1960, 1730, 1650, 1465, 1440, 1390, 1330, 1150, 1070, 980. ^{1}H-NMR (360 MHz, $CDCl_3$): nearly the same spectrum as for **21**, except for 2.61 (br. *s*, H of CH_2(4) *cis* to OH, 19 ± 3% of H); 3.35 (br. *s*, H of CH_2(4) *trans* to OH, 81 ± 3% of H); 6.12 (br. *dd*, $^3J = 10$, 1.8, H–C(3), lacks the coupling with H of CH_2(4) *cis* to OH). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 31.8 (*dt*, ^1J(C,H) = 128, ^1J(C,D) = 19.5, C(4)); 34.1, 39.10 (2*t*, ^1J(C,H) = 160); 58.5 (*q*, ^1J(C,H) = 140); 72.6 (*s*, C(1)); 102.6, 105.0 (2*s*, C(5), C(6)); 112.0 (*d*, ^1J(C,H) = 162); 126.7, 130.0 (2*d*, ^1J(C,H) = 160, C(2), C(3)); 211.2 (*s*). MS (70 eV): 337 (1, M^+), 309 (2), 281 (7), 253 (6), 221 (5), 149 (23), 118 (7), 86 (15), 84 (19), 57 (10), 49 (38), 43 (100). Anal. calc. for $C_{14}H_{15}DFeO_6$ (337.129): C 49.88, H 4.48, D 0.60; found: C 49.84, H 4.86.

11. *Acid-Catalyzed* H_2O *Elimination from* **22/23**. A 4.5:1 mixture **22/23** (20 mg, 0.059 mmol) in THF (3 ml) and conc. H_2SO_4 soln. (100 mg) was heated under reflux for 24 h. Control by TLC on silica gel showed the formation of **24** first, which was then converted to **25**. After cooling to 20°, H_2O (10 ml) was added and the mixture extracted with CH_2Cl_2 (15 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated and the residue separated and purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:8, column type *A*) yielding 6 mg (75%) of **25** and 2.5 mg (15%) of **24**.

Tricarbonyl[C,5,6,C-η-(5,6-dimethylidene[4-^{2}H]cyclohexa-1,3-diene-1-carbaldehyde)]iron (**24**). ^{1}H-NMR (360 MHz, $CDCl_3$): 10.17 (*s*, CHO); 7.95 (*d*, $^3J = 7$, H–C(2)); 7.55 (*dm*, $^3J = 7$, H–C(3)); 3.9, 2.47 (2*d*, $^2J = 3.5$); 0.33, 0.15 (2*d*, $^2J = 3.5$); 7.86 (*d*, $^3J = 8.5$, H–C(4); 1:(5.4 ± 0.8) the intensity of the signal at 7.95 ppm (H–C(2)), *i.e.* 81 ± 3% deuteration at C(4)). ^{1}H-NMR of non-deuterated **15**, see [9].

2,3-Dimethyl[4-^{2}H]benzaldehyde (**25**). ^{1}H-NMR (360 MHz, $CDCl_3$): 10.21 (*s*, CHO); 7.66 (*d*, $^3J = 7.7$, H–C(6)); 7.28 (*dm*, $^3J = 7.7$, H–C(5)); 2.58, 2.35 (2*s*, 2 Me); 7.42 (*d*, $^3J = 7.5$, H–C(4); 1:(5.4 ± 0.8) the intensity of the signal at 7.66 ppm (H–C(6)), *i.e.* 81 ± 3% deuteration at C(4)) [28].

REFERENCES

[1] J.J. Alexander, *J. Organomet. Chem.* **1984,** *274,* 331; *ibid.* **1985,** *283,* 415; A.J. Pearson, in 'Metalloorganic Chemistry', J. Wiley & Sons, New York, 1985, pp. 254 and ref. cit. therein; R.B. King, in 'The Organic Chemistry of Iron', Eds. E. Koerner von Gustorf, F.-W. Grevels, and I. Fischler, Academic Press, New York, 1978, Vol. 1, pp. 397–623; S.G. Davies, in 'Organotransition Metal Chemistry: Application to Organic Synthesis', Pergamon Press, Oxford, 1982; A.J. Pearson, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F.G.A. Stone, and E.W. Abel, Pergamon Press, Oxford, 1982, Vol. 8, Chapt. 58, p. 939; J.C. Zwick, P. Vogel, V. Mange, G. Chapuis, *Helv. Chim. Acta* **1987,** *70,* 1231 and ref. cit. therein.

[2] Y. Shvo, E. Hazum, *J. Chem. Soc., Chem. Commun.* **1974,** 336.

[3] D.H.R. Barton, A.A.L. Gunatilaka, T. Nakanishi, H. Patin, D.A. Widdowson, B.R. Worth, *J. Chem. Soc., Perkin Trans. 1* **1976,** 821; G. Evans, B.F.G. Johnson, J. Lewis, *J. Organomet. Chem.* **1975,** *102,* 507.

[4] G.F. Emerson, J.E. Mahler, R. Kochhar, R. Pettit, *J. Org. Chem.* **1964,** *29,* 3620; C.H. Mauldin, E.R. Biehl, P.C. Reeves, *Tetrahedron Lett.* **1972,** 2955.

[5] M. Franck-Neumann, M.P. Heitz, D. Martina, *Tetrahedron Lett.* **1983,** *24,* 1615.

[6] E.J. Corey, G. Moinet, *J. Am. Chem. Soc.* **1973,** *95,* 7185.

[7] T. Ban, K. Nagai, Y. Miyamoto, K. Harano, M. Yasuda, K. Kanematsu, *J. Org. Chem.* **1982,** *47,* 110.

[8] B.F.G. Johnson, J. Lewis, D.J. Thompson, *Tetrahedron Lett.* **1974,** 3789; C.W. Yip, P. Au, T.-Y. Luh, S.W. Tam, *J. Organomet. Chem.* **1979,** *175,* 221; B.F.G. Johnson, J. Lewis, D.J. Thompson, B. Heil, *J. Chem. Soc., Dalton Trans.* **1975,** 567; B.F.G. Johnson, D.D. Karlin, J. Lewis, *J. Organomet. Chem.* **1978,** *145,* C 23; B.F.G. Johnson, K.D. Karlin, J. Lewis, *ibid.* **1979,** *174,* C 29; R.F. Heldeweg, H. Hogeveen, *J. Am. Chem. Soc.* **1976,** *98,* 6040; P. Eilbracht, R. Jelitte, P. Trabold, *Chem. Ber.* **1986,** *119,* 169; M. Franck-Neumann, *Pure Appl. Chem.* **1983,** *55,* 1715.

[9] E. Bonfantini, J.-L. Métral, P. Vogel, *Helv. Chim. Acta* **1987,** *70,* 1791.

[10] A. Dondoni, G. Barbaro, *J. Chem. Soc., Chem. Commun.* **1975,** 761.

[11] H. de Abbayes, H. Alper, *J. Am. Chem. Soc.* **1977,** *99,* 98; K. Cann, T. Cole, W. Slegeir, R. Pettit, *ibid.* **1978,** *100,* 3969.

[12] H. Alper, in 'Organic Synthesis via Metal Carbonyls', Eds. I. Wender and P. Pino, Wiley-Interscience, New York, 1977, Vol. 2, p. 545.

[13] H. Alper, D.D. Roches, *Tetrahedron Lett.* **1977,** 4155; see also: Y. Takegami, Y. Watanabe, T. Misudo, H. Masada, *Bull. Soc. Chem. Jpn.* **1969,** *42,* 202.

[14] A.A. Pinkerton, P.-A. Carrupt, P. Vogel, T. Boschi, N.H. Thuy, R. Roulet, *Inorg. Chim. Acta* **1978,** *28,* 123.

[15] L. Lombardo, D. Wege, S.P. Wilkinson, *Aust. J. Chem.* **1974,** *27,* 143; see also: H. Hart, G. Nwokogu, *J. Org. Chem.* **1981,** *46,* 1251.

[16] M. Franck-Neumann, D. Martina, F. Brion, *Angew. Chem.* **1978,** *90,* 736.

[17] E. Meier, O. Cherpillod, T. Boschi, R. Roulet, P. Vogel, C. Mahaim, A.A. Pinkerton, D. Schwarzenbach, G. Chapuis, *J. Organomet. Chem.* **1980,** *186,* 247.

[18] D. Gagnaire, E. Payo-Subiza, *Bull. Soc. Chim. Fr.* **1963,** 2627; C.K. Ramey, D.C. Lini, *J. Magn. Reson.* **1970,** *3,* 94; W.L. Nelson, D.R. Alten, *J. Heterocycl. Chem.* **1972,** *9,* 561; F. Kienzle, *Helv. Chim. Acta* **1975,** *58,* 1180; C. Mahaim, P. Vogel, *ibid.* **1982,** *65,* 866.

[19] W.F. Edgell, M.T. Yang, B.J. Bulkin, R. Bayer, N. Koizumi, *J. Am. Chem. Soc.* **1965,** *87,* 3080; H.C. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann, R. Pettit, *ibid.* **1977,** *99,* 8323; P.C. Ford, R.G. Rinker, C. Ungermann, R.M. Laine, V. Landis, S.A. Moya, *ibid.* **1978,** *100,* 4595.

[20] H.W. Sternberg, R.A. Friedel, S.L. Shufler, I. Wender, *J. Am. Chem. Soc.* **1955,** *77,* 2675.

[21] K.W. Egger, A.T. Cocks, *Helv. Chim. Acta* **1973,** *56,* 1516; 1537; H.E. O'Neal, S.W. Benson, in 'Free Radicals', Ed. J.K. Kochi, J. Wiley and Sons, New York, 1973.

[22] M. Brookhardt, K.J. Karel, L.E. Nance, *J. Organomet. Chem.* **1977,** *140,* 203; G.A. Olah, G. Liang, S. Yu, *J. Org. Chem.* **1977,** *42,* 4262; see also: B.F.G. Johnson, J. Lewis, G.L.P. Randall, *J. Chem. Soc., Chem. Commun.* **1969,** 1273; B.F.G. Johnson, J. Lewis, A.W. Parkins, G.L.P. Randall, *ibid.* **1969,** 595; H.J. Dauben, Jr., D.J. Bertelli, *J. Am. Chem. Soc.* **1961,** *83,* 497.

[23] E.O. Fischer, R.D. Fischer, *Angew. Chem.* **1960,** *72,* 919; R. Burton, L. Pratt, G. Wilkinson, *J. Chem. Soc.* **1961,** 594; A.J. Birch, M.A. Haas, *J. Chem. Soc. (C)* **1971,** 2465; S. Winstein, H.D. Kaesz, C.G. Kreiter, E.C. Friedrich, *J. Am. Chem. Soc.* **1965,** *87,* 3267; T.N. Margulis, L. Schiff, M. Rosenblum, *ibid.* **1965,** *87,* 3269; E.J. Reardon, Jr., M. Brookhart, *ibid.* **1973,** *95,* 4311; A. Eisenstadt, J.M. Guss, R. Mason, *J. Organomet. Chem.* **1974,** *80,* 245; J. Evans, B.F.G. Johnson, J. Lewis, D.J. Yarrow, *J. Chem. Soc., Dalton Trans.* **1974,** 2375; M. Cooke, P.T. Draggett, M. Green, B.F.G. Johnson, J. Lewis, D.J. Yarrow, *J. Chem. Soc., Chem. Commun.* **1971,** 621; M. Brookhart, E.R. Davis, D.L. Harris, *J. Am. Chem. Soc.* **1972,** *94,* 7853;

P. A. Dobosh, D. G. Gresham, C. P. Lillya, E. S. Magyar, *Inorg. Chem.* **1976,** *15,* 2311; A. J. Birch, P. W. Westerman, A. J. Pearson, *Aust. J. Chem.* **1976,** *29,* 1671; C. P. Lewis, W. Kitching, A. Eisenstadt, M. Brookhart, *J. Am. Chem. Soc.* **1979,** *101,* 4896; G. A. Olah, S. H. Yu, G. Liang, *J. Org. Chem.* **1976,** *41,* 2383; J. W. Burrill, B. R. Bonazza, D. W. Garrett, C. P. Lillya, *J. Organomet. Chem.* **1976,** *104,* C 37; P. A. Dobosh, D. G. Gresham, D. J. Kowalski, C. P. Lillya, E. S. Magyar, *Inorg. Chem.* **1978,** *17,* 1775; P. McArdle, H. Sherlock, *J. Chem. Soc., Dalton Trans.* **1978,** 1678; P. A. Dobosh, C. P. Lillya, E. S. Magyar, G. Scholes, *Inorg. Chem.* **1980,** *19,* 228.

[24] J. Wagner, E. Vieira, P. Vogel, *Helv. Chim. Acta* **1988,** *71,* 624.

[25] C. Mahaim, P. Vogel, *Helv. Chim. Acta* **1982,** *65,* 866.

[26] S. A. R. Knox, F. G. A. Stone, *J. Chem. Soc. (A)* **1969,** 2559.

[27] C. Mahaim. P.-A. Carrupt, J. P. Hagenbuch, A. Florey, P. Vogel, *Helv. Chim. Acta* **1980,** *63,* 1149.

[28] A. Chollet, J. P. Hagenbuch, P. Vogel, *Helv. Chim. Acta* **1979,** *62,* 511.