166. Ironcarbonyl Complexes of 5,6-Dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene Derivatives. Synthesis of Substituted Tricarbonyl(*ortho*-quinodimethane)iron Complexes and 2-Indanones

by **Edia Bonfantini**[1]), **Jean-Luc Métral**[2]), and **Pierre Vogel***

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

(13.VII.1987)

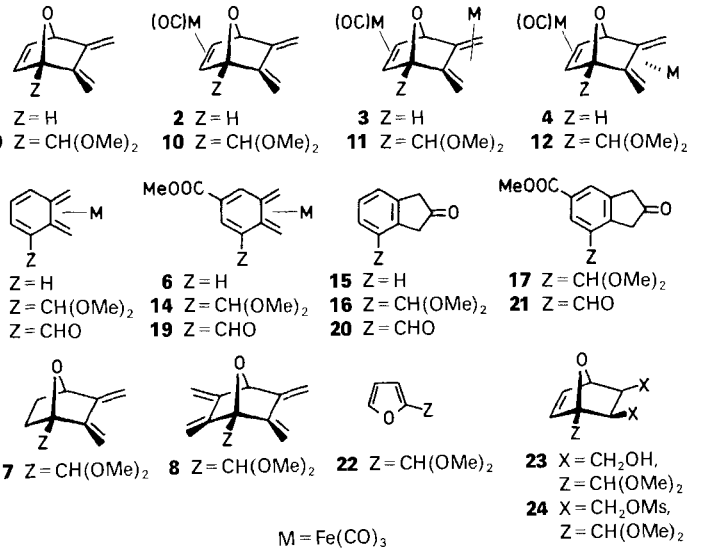
The 1-dimethoxymethyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**9**) has been prepared. On treatment with $Fe_2(CO)_9$, the endocyclic double bond C(2)=C(3) was coordinated first giving the corresponding *exo*-$Fe(CO)_4$ complex **10**. The latter reacted with $Fe_2(CO)_9$ and afforded *cis*-heptacarbonyl-μ-[(1*RS*,2*SR*,3*RS*,4*SR*,5*RS*,6*SR*)-2,3-η: *C*,5,6,*C*-η-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]diiron (**11**) as a major product. On heating, **11** underwent deoxygenation of the 7-oxabicyclo[2.2.1]heptene moiety yielding tricarbonyl[*C*,5,6,*C*-η-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohexa-1,3-diene)]iron (**13**). In MeOH, a concurrent, regioselective methoxycarbonylation was observed giving tricarbonyl[*C*,3,4,*C*-η-(methyl 5-(dimethoxymethyl)-3,4-dimethylidenecyclohexa-1,5-diene-1-carboxylate)]iron (**14**). Oxidative removal of the $Fe(CO)_3$ moiety in **13** and **14** did not afford the expected *ortho*-quinodimethane derivatives but led to CO insertions giving 2,3-dihydro-2-oxo-1*H*-indene-4-carbaldehyde (**20**) and methyl 7-formyl-2,3-dihydro-2-oxo-1*H*-indene-5-carboxylate (**21**), respectively.

Introduction. – The complexation of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**) by transition metals has been described recently [1] [2]. For various metalcarbonyls (Fe, Ru, Os, Cr, W) it was found that the endocyclic double bond between C(2) and C(3) in **1** is always coordinated faster than the exocyclic diene moiety, leading to the isolation of η^2-complexes **2** in good yield, provided the complexation reaction was carried out in a non-coordinating solvent. Prolonged exposure of **2** to metalcarbonyls gave the corresponding doubly complexed systems **3** and **4**. Depending on the nature of the metal, of the solvent, and the reaction temperature, condensation products were also formed which arose from a formal [4+2]-cyclodimerization of **2** [3] [4]. On heating the iron double complexes **3**/**4** in toluene, the *ortho*-quinodimethane complex **5** was obtained in 60% yield. Thermolysis of **3**/**4** in MeOH afforded instead the carboxylated derivative **6**.

Recently, we reported on the syntheses of the acetal derivatives **7** [5] and **8** [6] and on their *Diels-Alder* stereo- and regioselectivity. We have now prepared the corresponding triene-acetal **9** and report here on its reaction with $Fe_2(CO)_9$. We shall show that the corresponding complexes **10** and **11**/**12** can be prepared readily. The double complexes **11**/**12** can be transformed to the corresponding (*ortho*-quinodimethane)iron complexes **13** and **14** from which **18** and **19**, respectively, were obtained. Contrary to an earlier report [7], we have found that Ce(IV) can oxidize the metallic complexe **5**, leading to the

[1]) Part of the Ph. D. thesis of *E. Bonfantini*, in preparation.

[2]) Part of the Ph. D. thesis of *J.-L. Métral*, Ecole polytechnique fédérale de Lausanne, Dec. 1984. Present address: *Ciba-Geigy AG*, CH–1870 Monthey.



formation of 2-indanone (**15**). The same oxidative carbonylation process was observed with the substituted derivatives **13** and **14** (→**16** and **17**, resp.), thus opening a simple method for the synthesis of rare substituted 2-indanones such as **20** and **21**.

Results. – The synthesis of triene **9** started with the *Diels-Alder* addition of maleic anhydride to 2-(dimethoxymethyl)furan (**22**) [8] [6b]. The corresponding adduct was reduced by $LiAlH_4$ to give the ene-diol **23**. Mesylation (MsCl/pyridine) gave the diester **24** which furnished **9** on treatment with *t*-BuOK in anh. dimethylformamide (DMF)/hexamethylphosphoric triamide (HMPT) 6:1.

On heating triene **9** in MeOH with an excess of $Fe_2(CO)_9$ (40–70°, Ar), the monocomplex **10** was formed first which was then transformed into a mixture of the dicomplexes **11** and **12**. Under these conditions, **10** gave also some products of condensation [9], and **11**/**12** were decomposed into a mixture of the substituted *ortho*-quinodimethane complexes **13** and **14**. The proportions of **10**/**11**/**12**/**13**/**14** varied with the concentrations of **9** and $Fe_2(CO)_9$, the temperature of the reaction, and the flow of Ar. These complexes were isolated by column chromatography on silica gel and identified easily by their mode of formation, their spectral data, and their elemental analyses (see *Exper. Part*).

The *exo* configuration of the $Fe(CO)_4$ moiety in **10**–**12** was established by the vicinal coupling constant $^3J < 1$ Hz observed between the bridgehead proton H–C(4) and the adjacent olefinic proton H–C(3) [1] [2] [10]. The distinction between the *exo*- and *endo*-η^4-dienc $Fe(CO)_3$ complexes **11** and **12** was based on the observation of a long-range coupling constant ^4J of 0.8 Hz between H–C(4) and the methylidene proton *trans* with respect to C(5)=C(6) in the 360-MHz ^{1}H-NMR spectrum of **11**. The latter coupling constant was < 0.4 Hz for the *endo*-isomer **12** [11].

On heating pure **11** in toluene (95°, 80 min), the *ortho*-quinodimethane complex **13** was obtained in 53% yield (isolated). Hydrolysis of **13** (THF/H_2O 1:1, *Nafion*-H^+, 20°, 1 d) gave the corresponding aldehyde **18** (93%). On heating **11** in MeOH (50–60°), a 14:1 mixture of **13** (63%) and of the carboxylated derivative **14** (4.4%) was obtained. Under bubbling of Ar, the thermal decomposition of **11** was complete after 5 d at 60° in MeOH,

whereas under 2.5 atmosphere of CO, the thermal decomposition of **11** was incomplete (*ca.* 80%) after 5 d at 60° in MeOH (see *Exper. Part*). No trace of an isomer of **14** could be detected in the crude reaction mixture, thus demonstrating the high regioselectivity of the methoxycarbonylation reaction **11**→**14**. The proportion of **14** was increased by applying a pressure of CO. Hydrolysis of **14** by the same procedure as for **13** yielded **19**.

All our attempts to generate the uncoordinated *ortho*-quinodimethanes by oxidation of the metal in complexes **13** and **14** failed. On heating with Me_3NO [12], decomposition of **13** and **14** was observed as a slow reaction. In the presence of an excess of $(NH_4)_2Ce(NO)_6$ in acetone [13] at 20°, however, **13** gave a mixture of products from which the 2-indanone derivative **20** was isolated in 65% yield. Control experiments confirmed that the primary product of reaction was the acetal **16**. Nevertheless, **16** was an unstable compound under our workup conditions, giving the corresponding carbaldehyde **20**. On treatment of complex **18** with Ce(IV) salt, **20** was also formed in 69% yield. Under the same conditions, complex **14** afforded the disubstituted 2-indanone derivative **21**, arising probably from acetal **17** which, as in the case of **16**, is expected to be hydrolysed rapidly under our workup conditions.

An earlier report [7] stated that the unsubstituted tricarbonyl(*ortho*-quinodimethane)iron **5** was inert toward oxidizing agents such as Ce(IV) salts. We have found, however, that the treatment of **5** (prepared form 1,4-dibromo-2,3-dimethylbenzene, [14]) with an excess of $(NH_4)_2Ce(NO_3)_6$ in acetone at 20° gave pure 2-indanone (**15**) in 90% isolated yield. The reaction **5**→**15** has been reported before [15] [16] to be induced by $AlCl_3$. Under the latter conditions, the yield of **15** was only moderate in our hands. Furthermore, when derivatives **13** and **14** were treated with $AlCl_3$ in CH_2Cl_2, very complicated mixtures of products were obtained in which only traces of the corresponding 2-indanones **20** and **21** could be detected.

Discussion. – At this stage of our investigations, no limiting mechanisms can be retained for the deoxygenation **11**→**13** and the carboxylation **11**→**14**. The deoxygenation of 7-oxabicyclo[2.2.1]hepta-2,5-diene derivatives complexed to $Fe(CO)_4$ is a known reaction [1] [17]. The concomitant carboxylation of the resulting cyclohexadiene product was first observed for the unsubstituted dicomplex **3** [1]. The high regioselectivity observed for reaction **11**→**14** is noteworthy but does not authorize to limit the number of mechanistic hypotheses. Since reactions **11**→**13** and **11**→**14** are both retarded on applying a CO pressure, it is probable that the first step of these two reactions implies the loss of a CO molecule from the $Fe(CO)_4$ moiety in **11**, followed by an oxidative addition of the metal into one of the two allylic C–O bonds [18] [19].

Tricarbonyl(1,3-diene)iron derivatives are known to give the corresponding cyclopent-3-one derivatives on treatment with a strong *Lewis* acid such as $AlCl_3$ [15] [16] [20]. Anhydrous aluminium salts help the CO insertion reaction [21]. Under oxidizing conditions, some allyliron complexes have been reported to undergo CO insertion [22]. It is not clear yet whether it is the *Lewis* acid character of the Ce(IV) salt or its oxidation potential which is responsible of the smooth CO insertions **5**→**15**, **13**→**16**, and **18**→**20**. A clean CO insertion into cyclopentadienyl(*ortho*-quinodimethane)cobalt to give 2-indanone has been reported by *Hersch* and *Bergman* [23].

Conclusion. – An access to rare 4-substituted and 4,6-disubstituted 2-indanones has been developed from the ironcarbonyl complexes of a l-substituted 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene derivative.

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

General. See [6b].

*[(1RS,4SR,5SR,6RS)-1-(Dimethoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene-5-*exo*,6-*exo*-dimethyl] Dimethanesulfonate* (**24**). Methanesulfonyl chloride (17 ml, 218 mmol) was added dropwise to a stirred mixture of 1-(dimethoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene-5-*exo*,6-*exo*-dimethanol (**23** [6b]; 10 g, 43 mmol) and anh. pyridine (29 ml) at 0° and under N_2. After stirring at 0° for 1 h, the mixture was stored in a refrigerator at −10° for 4 d. The mixture was then poured into vigourously stirred ice-cold H_2O (2 l). The precipitate was collected by filtration and dissolved in CH_2Cl_2 (150 ml). After washing with H_2O and drying ($MgSO_4$), the solvent was evaporated. The residue was recrystallized from CH_2Cl_2 at −20°, yielding 10.06 g (60%) of colourless crystals. M.p. 118–120° (dec.). IR (CH_2Cl_2): 3060, 2970, 2940, 2840, 1360, 1340, 1175, 1105, 1080, 970, 945, 855, 805. ^{1}H-NMR (80 MHz, $CDCl_3$): 6.37 (br. *s*, H–C(2), H–C(3)); 4.9 (br. *s*, H–C(4)); 4.78–3.9 (*m*, CH–C(1), CH_2–C(5), CH_2–C(6)); 3.53 (*s*, 2 CH_3O); 3.0 (*s*, 2 CH_3S); 2.51–2.02 (*m*, H–C(5), H–C(6)). ^{13}C-NMR (90 MHz, $CDCl_3$): 137.1 (*d*, ^1J(C,H) = 178, C(2)); 135.3 (*d*, ^1J(C,H) = 177, C(3)); 103.7 (*dm*, ^1J(C,H) = 159, *C*H–C(1)); 91.4 (*m*, C(1)); 80.2 (*d*, ^1J(C,H) = 165, C(4)); 69.5, 67.3 (2*t*, ^1J(C,H) = 152, 2 CH_2O); 57.1, 56.6 (2*qd*, ^1J(C,H) = 142, ^3J(C,H) = 5, 2 CH_3O); 41.7, 41.67 (2*d*, ^1J(C,H) = 140, C(5), C(6)); 37.5, 37.3 (2*q*, ^1J(C,H) = 139, 2 CH_3S). CI-MS (CH_4): 356 (2, M^+ + H–OCH_3), 258 (10), 111 (12), 41 (37), 29 (100). Anal. calc. for $C_{13}H_{22}O_9S_2$ (386.341): C 40.41, H 5.74; found: C 40.38, H 5.62.

1-(Dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**9**). *t*-BuOK. (18 g, 160 mmol) was added portionwise under N_2 to a stirred mixture of **24** (6 g, 15.5 mmol) and anh. DMF/HMPT 6:1 at 0°. After stirring at 0° for 2 h, H_2O (20 ml) was added and the mixture extracted with pentane (200 ml, 5 times). The org. extract was washed with H_2O and dried ($MgSO_4$). The solvent was distilled off (*Vigreux* column) and the residue bulb-to-bulb distilled (*Büchi*), giving 1.96 g (65%) of a colourless liquid. B.p. 90°/0.5 Torr. UV (isooctane): 233 (9000), 229 (sh, 9100), 223 (sh, 9700), 205 (14200). UV (95% EtOH): 228 (8700), 223 (sh, 8600), 220 (sh, 9400), 204 (13100). IR (CH_2Cl_2): 3050, 2990, 2960, 2940, 2910, 2840, 1185, 1150, 1105, 1085, 1050, 1035, 985, 940, 930, 890, 820. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.52–6.43 (*m*, ^3J(H–C(2), H–C(3)) = 5.6, ^3J(H–C(3), H–C(4)) = 1.6, ^4J(H–C(2), H–C(4)) = 0.5, ^5J(H–C(3), H–C(5)) = 0.6, H–C(2), H–C(3)); 5.36, 5.26, 5.25, 5.08 (4*s*, CH_2=C(5), CH_2=C(6)); 5.18 (br. *s*, H–C(4)); 4.83 (*s*, *C*H$(OCH_3)_2$); 3.6, 3.54 (2*s*, 2 CH_3O). ^{13}C-NMR (90 MHz, C_6D_6): 145.6 (*m*, C(5)); 144.1 (*m*, C(6)); 136.2, 135.2 (2 *dm*, ^1J(C,H) = 179, ^2J(C,H) = 3.5, C(2), C(3)); 103.7 (*dm*, *C*H–C(1)); 102.8, 101.0 (2 *t*, ^1J(C,H) = 158, *C*H_2=C(5), *C*H_2=C(6)); 92.0 (*m*, C(1)); 82.5 (*dm*, ^1J(C,H) = 166, C(4)); 55.4, 55.36 (2 *qd*, ^1J(C,H) = 144, ^3J(C,H) = 5, 2 CH_3O). CI-MS (CH_4): 195 (5, M^+ + H), 163 (15), 135 (26), 131 (11), 75 (50), 57 (100). Anal. calc. for $C_{11}H_{14}O_3$ (194.232): C 68.02, H 7.27; found: C 67.95, H 7.27.

Complexation of **9** *with* $Fe_2(CO)_9$ *(Method A).* $Fe_2(CO)_9$ (13.4 g, 36.8 mmol) was added portionwise to a soln. of **9** (4 g, 20.6 mmol) in MeOH (110 ml) and heated to 70° under Ar bubbling. After 26 h, the mixture was filtered and the solvent evaporated. The residue was filtered through a short column of silica gel (AcOEt/petroleum ether 1:4) and then chromatographed on silica gel (type *C* column, *Lobar*, AcOEt/petroleum ether 1:5), yielding three *Fractions A, B*, and *C*. *Fraction A* was chromatographed on a silica-gel column (type *C*, *Lobar*, AcOEt/petroleum ether 1:15) giving successively fractions containing **11**, **10**, and **13**. *Fraction B* was chromatographed on a silica-gel column (type *B*, *Lobar*, AcOEt/petroleum ether 1:5) giving successively fractions containing **13** and **14**. All the fractions were recrystallized from MeOH at −20°. Complex **12** was present in less than 1% in the final reaction mixture. Under the conditions used here, it probably isomerized into **11** or/and was transformed into **13**/**14**.

Tetracarbonyl[(1RS,2SR,3RS,4RS)-2,3-η-(1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]-hept-2-ene)]iron (**10**). Yield 470 mg (6.3%), yellow needles. M.p. 68–69°. UV (isooctane): 264 (sh, 8500), 216 (sh, 35400), 205 (36900). UV (95% EtOH): 265 (sh, 8200), 215 (sh, 34400), 206 (36000). IR ($CHCl_3$): 3010, 2970, 2940, 2840, 2095, 2020, 2000, 1995, 1100, 1080. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.45, 5.43, 5.33, 5.10 (4*s*, CH_2–C(5), CH_2–C(6)); 4.72 (br. H–C(4)); 4.54 (*s*, CH–C(1)); 3.60, 3.58 (2*s*, 2 CH_3O); 3.21, 3.12 (2*d*, ^3J(H–C(2), H–C(3)) = 5.2, H–C(2), H–C(3)). ^{13}C-NMR (90 MHz, $CDCl_3$): 210.2 (*s*, CO); 146.5, 144.3 (2*m*, C(5), C(6)); 105.0 (*dm*, ^1J(C,H) = 161, *C*H–C(1)); 104.2, 102.2 (2 *t*, ^1J(C,H) = 160, *C*H_2=C(5), *C*H_2=C(6)); 89.9 (*m*, C(1)); 82.9 (*dm*, ^1J(C,H) = 166, C(4)); 57.6, 56.6 (*qd*, ^1J(C,H) = 143, ^3J(C,H) = 5, 2 CH_3O); 56.5, 54.5 (*d*, ^1J(C,H) = 174, C(2), C(3)). MS (70 eV): 278 (100), 250 (49), 235 (23), 220 (46), 218 (55), 205 (18), 203 (18), 190 (55), 188 (59), 162 (58), 160 (35), 147 (56), 132 (28), 91 (19), 75 (24). Anal. calc. for $C_{15}H_{14}FeO_7$ (362.122): C 49.75, H 3.90; found: C 49.88, H 3.90.

cis-*Heptacarbonyl-μ-[(1RS,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* (**11**). Yield 145 mg (1.4%), yellow crystals. M.p. 99–100°. UV (isooctane): 300 (7900). IR (KBr): 3020, 2970, 2940, 2890, 2840, 2090, 2030, 2020, 2010, 1995, 1980, 1950, 1450, 1400, 1330, 1215, 1190, 1150, 1110, 1075, 980, 950, 935, 835. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.79, 4.68 (2*s*, CH–C(1), H–C(4)); 3.60, 3.58 (2*s*, 2 CH_3O); 3.63, 3.48 (2*d*, ^3J(H–C(3), H–C(2)) = 5, H–C(3), H–C(2)); 2.21 (*dd*, ^2J = 2.5, ^4J(H–C(4), H–C=C(5)) = 0.8, H–C=C(5) *trans* to C(5)=C(6)); 2.04 (*d*, ^2J = 2.5, H–C=C(6) *trans* to C(5),C(6)); 0.54, 0.47 (2*d*, ^2J = 2.5, H–C=C(5), H–C=C(6)). ^{13}C-NMR (90 MHz, $CDCl_3$): 211.2, 209.0 (2*s*); 111.9, 110.8 (2*s*, C(5), C(6)); 104.3 (*d*, ^1J(C,H) = 160, *C*H–C(1)); 89.8 (*s*, C(1)); 82.2 (*d*, ^1J(C,H) = 170, C(4)); 57.6, 57.3 (2*d*, ^1J(C,H) = 170, C(2),C(3)); 58.3, 56.2 (2*q*, ^1J(C,H) = 142, CH_3O); 34.1, 33.0 (2*t*, ^1J(C,H) = 162, CH_2=C(5), CH_2=C(6)). CI-MS (CH_4): 502 (15, M^+), 446 (58), 418 (100), 390 (30), 362 (30), 334 (33), 306 (51). Anal. calc. for $C_{18}H_{14}Fe_2O_{10}$ (501.994): C 43.07, H 2.81; found: C 42.87, H 2.79.

Tricarbonyl[C,5,6,C-η-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohexa-1,3-diene)]iron (**13**). Yield 1.57 g (24%), yellow crystals. M.p. 70–73°. UV (95% EtOH): 255 (7900), 199 (33800). IR ($CHCl_3$): 3010, 2965, 2940, 2840, 2055, 1995, 1470, 1350, 1120, 1075, 1060. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.67–7.35 (H–C(2), H–C(3), H–C(4)); 5.39 (*s*, CH–C(1)); 3.43, 3.38 (2*s*, 2 CH_3O); 2.78, 2.47 (2 *d*, ^2J = 3.6, H–C=C(5), H–C=C(6) *trans* to C(5),C(6)); 0.25, 0.07 (2*d*, ^2J = 3.6, H–C=C(5), H–C=C(6) *cis*). ^{13}C-NMR (90 MHz, CD_2Cl_2): 211.0 (*s*, CO); 139.2 (*m*, C(1)); 134.2 (*dm*, ^1J(C,H) = 165, C(2)); 103.2 (*dm*, ^1J(C,H) = 160, ^3J(C,H) = 5, *C*H–C(1)); 100.2, 100.1 (2*s*, C(5),C(6)); 54.5, 53.8 (2*qd*, ^1J(C,H) = 143, ^3J(C,H) = 5, 2 CH_3O); 36.7, 33.3 (2*t*, ^1J(C,H) = 160, *C*=C(5), *C*=C(6)). MS (70 eV): 318 (13, M^+), 262 (17), 234 (33), 216 (13), 204 (15), 188 (17), 174 (100), 132 (54), 115 (30), 103 (43), 91 (30), 77 (44). Anal. calc. for $C_{14}H_{15}FeO_5$ (318.112): C 52.86, H 4.44; found: C 52.70, H 4.36.

Tricarbonyl[C,3,4,C-η-(methyl-5-(dimethoxymethyl)-3,4-dimethylidenecyclohexa-1,5-diene-1-carboxylate)]-iron (**14**). Yield 116 mg (1.5%), yellow crystals. M.p. 81–82°. UV (isooctane): 386 (3200), 266 (13000), 222 (sh, 26800), 202 (43000). IR (KBr): 3000, 2950, 2830, 2040, 1980, 1960, 1710, 1430, 1360, 1290, 1240, 1225, 1130, 1070, 1050. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.30, 8.13 (2*s*, H–C(2), H–C(6)); 5.39 (*s*, CH–C(5)); 3.97 (*s*, $COOCH_3$); 3.44, 3.40 (2*s*, 2 CH_3O); 2.89, 2.50 (2*d*, *J* = 3.5); 0.32, 0.15 (2*d*, *J* = 3.5, H–C=C(3), H–C=C(4) *cis* to C(3),C(4)). ^{13}C-NMR (90 MHz, $CDCl_3$, – 30°): 215.6, 206.6, 205.4 (3 br. *s*, CO); 166.1 (*s*, CH_3OOC); 139.4, 125.6 (2*d*, ^1J(C,H) = 166, C(2), C(6)); 137.6, 128.4 (2*s*, C(1), C(5)); 101.8, 96.8 (2*s*, C(3), C(4)); 101.7 (*d*, ^1J(C,H) = 161, *C*H–C(5)); 53.8, 53.4 (2*dq*, ^1J(C,H) = 144, ^3J(C,H) = 5, 2 CH_3O); 52.4 (*q*, ^1J(C,H) = 147, $COOCH_3$); 36.7, 33.5 (2*t*, ^1J(C,H) = 160, CH_2=C(3), CH_2=C(4)). MS (70 eV): 376 (29), 348 (23), 320 (15), 292 (73), 262 (81), 232 (65), 204 (100), 174 (79), 146 (55), 131 (47), 115 (49), 103 (50). Anal. calc. for $C_{16}H_{16}FeO_7$ (376.144): C 51.09, H 4.29; found: C 51.13, H 4.18.

Complexation of **9** *with* $Fe_2(CO)_9$ *(Method B).* A mixture of **9** (2.3 g, 11.84 mmol), anh. MeOH (130 ml), and $Fe_2(CO)_9$ (7.5 g, 20.6 mmol) was stirred at 20° under vigourous bubbling with Ar. $Fe_2(CO)_9$ (twice 3.5 g, 9.6 mmol) was added after 20 h and 28 h of reaction. After 50 h at 20°, the mixture was filtered on a short column of silica gel (AcOEt/petroleum ether 1:8). The yellow fraction was collected and evaporated. After addition of acetone (5 ml) and 1N HCl (3 ml), the mixture was allowed to stay at 20° for 15 h. This acidic treatment was required to hydrolyze **13** quantitatively into **18**. Under these conditions, acetals **9**–**12** were not hydrolyzed. H_2O (10 ml) was added and the mixture extracted with CH_2Cl_2 (40 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated and the residue separated by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:20), yielding successively 690 mg (11.6%) of **11**, 180 mg, (4.2%) of **10**, 529 mg (8.9%) of **12** and 357 mg (11.1%) of **18**.

trans-*Heptacarbonyl-μ-[(1RS,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* (**12**). Yellow crystals. M.p. 82–83°. UV (isooctane): 310 (6820). IR (KBr): 3020, 2950, 2850, 2090, 2040, 2020, 2010, 1990, 1975, 1965, 1445, 1390, 1360, 1330, 1210, 1190, 1080, 970, 935, 910. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.15, 4.67 (2*s*, CH–C(1), H–C(4)); 3.66, 3.62 (2*s*, 2 CH_3O); 3.60, 3.48 (2*d*, ^3J(H–C(3), H–C(2)) = 5, H–C(3), H–C(2)); 2.43, 2.16 (2*d*, ^2J = 3, H–C=C(5), H–C=C(6) *trans* to C(5),C(6)); 0.74, 0.69 (2*d*, ^2J = 3, H–C=C(5), H–C=C(6)). ^{13}C-NMR (90 MHz, $CDCl_3$): 209.6 (*s*, CO of $Fe(CO)_3$ and $Fe(CO)_4$); 118.6, 117.6 (2*s*, C(5), C(6)); 105.8 (*d*, ^1J(C,H) = 160, *C*H–C(1)); 92.0 (*s*, C(1)); 83.0 (*d*, ^1J(C,H) = 170, C(4)); 61.2, 59.9 (2*d*, ^1J(C,H) = 174, C(2), C(3)); 58.04 57.17 (2*q*, ^1J(C,H) = 143, 2 CH_3O); 34.37, 34.03 (2*t*, ^1J(C,H) = 162, CH_2=C(5), CH_2=C(6)). CI-MS (CH_4): 474 (4, M^+ – CO), 446 (40), 418 (100), 390 (11), 362 (15), 334 (21), 306 (41). Anal. calc. for $C_{18}H_{14}Fe_2O_{10}$ (501.994): C 43.07, H 2.81; found: C 42.89, H 2.79.

Thermal Decomposition of **11** *in an Open Flask. A.* A soln. of **11** (76 mg, 0.15 mmol) in toluene (6 ml) was heated to 95° for 80 min. After solvent evaporation and purification of the residue by column chromatography on silica gel (5 g, AcOEt/petroleum ether 1:7), 30 mg (53%) of **13** were obtained. *B.* A soln. of **11** (107 mg, 0.21 mmol) in MeOH (20 ml) was heated to 50° for 5 d, then to 60° for 1 d, under bubbling of Ar. After filtration on *Florisil* (AcOEt/petroleum ether 1:4), a 15:1 mixture **13**/**14** was obtained. Chromatography on silica gel (*Lobar, column*

type *B*, AcOEt/petroleum ether 1:7) gave a 1st fraction containing 30 mg (63%) of **13** and a 2nd fraction yielding 2.5 mg (4.4%) of **14**.

Thermal Decomposition of **11** *in a Sealed Vessel.* A soln. of **11** (253 mg, 0.5 mmol) in MeOH (45 ml) was heated to 60° for 5 d in a sealed, round-bottom flask. The mixture was filtered on a short column of silica gel (AcOEt/petroleum ether 1:4). After solvent evaporation, the residue was purified by medium-pressure chromatography on silica gel (*Lobar*, column type *B*, AcOEt/petroleum ether 1:10), yielding successively 90 mg (56%) of **13** and 31 mg (16%) of **14**. Product ratio **13**/**14** 3.5:1.

Thermal Decomposition of **11** *under CO Pressure.* A soln. of **11** (100 mg, 0.2 mmol) in MeOH (19 ml) was degassed under vacuum and then pressurized with CO (2.5 atm). After heating to 60° for 5 d, the mixture was filtered on a short column of silica gel (AcOEt/petroleum ether 1:4) and purified by medium-pressure chromatography on silica gel (*Lobar*, column type *A*, AcOEt/petroleum ether 1:15). The 1st fraction yielded 20.5 mg (20.4%) of **11**. A 2nd fraction gave 1 mg (1.8%) of **18** (derived from hydrolysis of **13**). A 3rd fraction yielded 6 mg (7.9%) of **14**. Product ratio **18**/**14** 0.23:1. Complex **14** was less sensitive than **13** toward acid-catalyzed hydrolysis of the acetal function (the ester group in **14** destabilizes the benzyl-cation intermediate).

Tricarbonyl[C,5,6,C-η-(5,6-dimethylidenecyclohexa-1,3-diene-1-carbaldehyde)]iron (**18**). A mixture of **13** (202 mg, 0.63 mmol), THF/H_2O 1:1 (3 ml) and *Nafion*-H^+ (18 mg) was stirred at 20° for 1 d. After filtration, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (30 ml). After drying ($MgSO_4$), the solvent was evaporated and the residue purified by filtration through a short column of silica gel (AcOEt/CH_2Cl_2 1:50). Recrystallization from MeOH at −20° yielded 159 mg (93%) of yellow-orange crystals. M.p. 67–68°. UV (dioxane): 397 (4100), 304 (7900), 269 (sh, 10800), 214 (34500). IR (KBr): 3070, 2840, 2740, 2040, 1990, 1970, 1690, 1540, 1470, 1230, 1170, 1090, 960, 900, 780. ^{1}H-NMR (360 MHz, $CDCl_3$): 10.17 (*s*, CHO); 7.93 (*d*, *J* = 7.5, H–C(2)); 7.85 (*d*, *J* = 9, H–C(4)); 7.54 (*dd*, *J* = 7.5, 9, H–C(3)); 3.90, 2.48 (2*d*, *J* = 3.5, 2H); 0.34, 0.14 (2*d*, *J* = 3.5, 2H). ^{13}C-NMR (90 MHz, $CDCl_3$): 209.5 (CO); 191.4 (*d*, ^1J(C,H) = 174, CHO); 141.3, 138.9 (2*d*, ^1J(C,H) = 160, C(2), C(4)); 126.8 (*d*, ^1J(C,H) = 165, C(3)); 136.8 (*s*, C(1)); 98.7, 97.9 (2*s*, C(5), C(6)); 36.5, 34.2 (2*t*, ^1J(C,H) = 160, CH_2=C(5), CH_2=C(6)). MS (70 eV): 272 (31), 244 (27), 216 (44), 189 (82), 160 (20), 133 (84), 103 (28), 77 (27). Anal. calc. for $C_{12}H_8FeO_4$ (271.919): C 52.98, H 2.96; found: C 52.94, H 2.94.

Tricarbonyl[C,3,4,C-η-(methyl-5-formyl-3,4-dimethylidenecyclohexa-1,5-diene-1-carboxylate)]iron (**19**). Same procedure as for **18**, starting with **14**. Yield 90%, yellow-orange crystals. M.p. 123–124°. UV (dioxane): 420 (3300), 312 (sh, 4600), 268 (11200), 222 (28800), 214 (28700). IR (KBr): 3060, 3000, 2960, 2820, 2740, 2060, 1980, 1720, 1690, 1440, 1310, 1240, 1215, 1100, 1000, 765. ^{1}H-NMR (360 MHz, $CDCl_3$): 10.18 (*s*, CHO); 8.60, 8.49 (2*s*, H–C(2), H–C(6)); 4.02 (*s*, CH_3OOC); 4.00, 2.49 (2*d*, ^2J = 3.6, H–C=C(3), H–C=C(4), *trans* to C(3), C(4)); 0.38, 0.30 (2*d*, *J* = 3.6, 2H). ^{13}C-NMR (90 MHz, $CDCl_3$): 209.0 (*s*, CO), 191.3 (*d*, ^1J(C,H) = 178, CHO); 165.2 (*s*, $COOCH_3$); 145.2, 138.3 (2*d*, ^1J(C,H) = 164, C(2), C(6)); 136.8, 128.7 (2*s*, C(1), C(5)); 100.5, 96.7 (2*s*, C(3), C(4)); 52.8 (*q*, CH_3O); 37.3, 35.7 (2*t*, ^1J(C,H) = 160, CH_2=C(3), CH_2=C(4)). MS (70 eV): 330 (30), 302 (30), 274 (43), 246 (84), 218 (61), 216 (72), 188 (75), 160 (23), 132 (53), 103 (33), 77 (42), 56 (100). Anal. calc. for $C_{14}H_{10}FeO_6$ (330.075): C 50.94, H 3.05; found: C 51.10, H 3.08.

2-Indanone (**15**). Anh. $(NH_4)_2Ce(NO_3)_6$ (990 mg, 1.8 mmol) was added portionwise to a stirred soln. of **5** (0.2 g, 0.82 mmol) in anh. acetone (30 ml). After 50 min, 145 mg (0.26 mmol) of $(NH_4)_2Ce(NO_3)_6$ were added and after 70 min, 100 mg of $(NH_4)_2Ce(NO_3)_6$. After 100 min of reaction and addition of H_2O (120 ml), the mixture was extracted with CH_2Cl_2 (150 ml, 4 times). The extract was dried ($MgSO_4$), the solvent evaporated, and the residue purified by filtration through a short column of silica gel (CH_2Cl_2): 98 mg (90%) of white crystals. M.p. 54–55° ([24]: 54–56°).

*2,3-Dihydro-2-oxo-1*H*-indene-4-carbaldehyde* (**20**). Anh. $(NH_4)_2Ce(NO_3)_6$ (950 mg, 1.73 mmol) was added portionwise to a stirred soln. of **13** (250 mg, 0.78 mmol) in anh. acetone (40 ml) at 20°. After 45 min and 60 min of stirring at 20°, 170 mg (0.31 mmol) and 160 mg (0.29 mmol) of $(NH_4)_2Ce(NO_3)_6$, respectively, were added. After 95 min, pentane (100 ml) was added and the mixture filtered. The solution was washed with H_2O (70 ml), the aq. phase extracted with CH_2Cl_2 (100 ml, 4 times), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on silica gel (AcOEt/CH_2Cl_2 1:50), yielding, after recrystallization from toluene, 81 mg (65%) of yellowish crystals. M.p. 95–96°. Sublimation (70°/11 Torr) yielded pure, white crystals. M.p. 101–102°. UV (dioxane): 300 (2200), 253 (11600), 247 (10900), 212 (15500). IR (KBr): 2900, 2870, 2850, 2770, 1740, 1685, 1590, 1395, 1235, 1145, 995, 785, 775, 745. ^{1}H-NMR (360 MHz, $CDCl_3$): 10.12 (*s*, CHO); 7.77, 7.58 (2*d*, *J* = 7.6, H–C(5), H–C(7)); 7.51 (*t*, *J* = 7.6, H–C(6)); 3.93, 3.58 (2*s*, CH_2(1), CH_2(3)). ^{13}C-NMR (90 MHz, $CDCl_3$): 213.6 (*s*, CO); 191.9 (*d*); 139.6, 139.0, 132.5 (3*s*); 131.6, 130.2, 127.9 (3*d*, ^1J(C,H) = 160); 43.9, 42.9 (2*t*, ^1J(C,H) = 135). MS (70 eV): 160 (11), 132 (48), 104 (78), 78 (44), 70 (50), 61 (80), 45 (100). Anal. calc. for $C_{10}H_8O_2$ (160.172): C 74.99, H 5.03; found: C 75.05, H 4.98.

Under the same conditions as for the transformation of **13** into **20**, **18** gave **20** in 69% yield.

Methyl 7-Formyl-2,3-dihydro-2-oxo-1H-indene-5-carboxylate (**21**). Anh. $(NH_4)_2Ce(NO_3)_6$ (403 mg, 0.73 mmol) was added portionwise to a stirred soln. of **14** (78 mg, 0.21 mmol) in anh. acetone (8 ml). After 50 min at 20°, H_2O (10 ml) was added and the mixture extracted with CH_2Cl_2 (20 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated and the residue purified by chromatography on a column of silica gel ($AcOEt/CH_2Cl_2$ 1:10), yielding 22.5 mg (32%) of yellowish crystals. M.p. 136–150° (dec.). UV (dioxane): 307 (3400), 299 (3400), 258 (sh, 8300), 252 (sh, 10400), 223 (30700). IR (KBr): 3000, 2960, 1740, 1710, 1680, 1580, 1430, 1390, 1380, 1340, 1300, 1260, 1220, 1100, 1010, 980, 965. ^{1}H-NMR (360 MHz, $CDCl_3$): 10.16 (*s*, CHO); 8.46, 8.25 (2*s*, H–C(4), H–C(6)); 3.99 (*s*, $COOCH_3$); 3.95, 3.63 (2*s*, CH_2(1), CH_2(3)). MS (70 eV): 218 (23, $M^{+\cdot}$), 190 (100), 187 (21), 162 (22), 159 (15), 146 (15), 131 (32), 119 (10), 103 (69), 102 (50), 77 (84). HR-MS (ref.: iodotoluene): $(C_{12}H_{10}O_4^{+\cdot}$, calc. 218.0579); 218.0575–218.0597.

In some runs, the methyl acetal **17** of **21** was isolated as a minor compound, which was hydrolyzed into **21** on standing in $CDCl_3$ soln. **17**: White crystals. M.p. 102–104°. ^{1}H-NMR (80 MHz, $CDCl_3$): 8.25, 8.12 (2*s*, H–C(4), H–C(6)); 5.47 (*s*, CH–C(7)); 4.02 (*s*, $COOCH_3$); 3.75, 3.67 (2*s*, CH_2(1), CH_2(3)); 3.40 (*s*, 2 CH_3O).

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