

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

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The 1-dimethoxymethyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**9**) has been prepared. On treatment with $\text{Fe}_2(\text{CO})_9$, the endocyclic double bond $\text{C}(2)=\text{C}(3)$ was coordinated first giving the corresponding *exo*- $\text{Fe}(\text{CO})_4$ complex **10**. The latter reacted with $\text{Fe}_2(\text{CO})_9$ 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 $\text{Fe}(\text{CO})_3$ 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 metallocarbonyls (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 metallocarbonyls 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]-cycloaddimerization 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 $\text{Fe}_2(\text{CO})_9$. 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 complex **5**, leading to the

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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 Me₃NO [12], decomposition of **13** and **14** was observed as a slow reaction. In the presence of an excess of (NH₄)₂Ce(NO₃)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 from 1,4-dibromo-2,3-dimethylbenzene, [14]) with an excess of (NH₄)₂Ce(NO₃)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 AlCl₃. Under the latter conditions, the yield of **15** was only moderate in our hands. Furthermore, when derivatives **13** and **14** were treated with AlCl₃ in CH₂Cl₂, 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 AlCl₃ [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 1-substituted 5,6-dimethyldiene-7-oxabicyclo[2.2.1]hept-2-ene derivative.

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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 anhyd. pyridine (29 ml) at 0° and under N₂. 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 vigorously stirred ice-cold H₂O (2 l). The precipitate was collected by filtration and dissolved in CH₂Cl₂ (150 ml). After washing with H₂O and drying (MgSO₄), the solvent was evaporated. The residue was recrystallized from CH₂Cl₂ at -20°, yielding 10.06 g (60%) of colourless crystals. M.p. 118–120° (dec.). IR (CH₂Cl₂): 3060, 2970, 2940, 2840, 1360, 1340, 1175, 1105, 1080, 970, 945, 855, 805. ¹H-NMR (80 MHz, CDCl₃): 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), CH₂-C(5), CH₂-C(6)); 3.53 (s, 2 CH₃O); 3.0 (s, 2 CH₃S); 2.51–2.02 (m, H-C(5), H-C(6)). ¹³C-NMR (90 MHz, CDCl₃): 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, CH-C(1)); 91.4 (m, C(1)); 80.2 (d, ¹J(C,H) = 165, C(4)); 69.5, 67.3 (2t, ¹J(C,H) = 152, 2 CH₂O); 57.1, 56.6 (2qd, ¹J(C,H) = 142, ³J(C,H) = 5, 2 CH₃O); 41.7, 41.67 (2d, ¹J(C,H) = 140, C(5), C(6)); 37.5, 37.3 (2q, ¹J(C,H) = 139, 2 CH₃S). CI-MS (CH₄): 356 (2, M⁺ + H-OCH₃), 258 (10), 111 (12), 41 (37), 29 (100). Anal. calc. for C₁₃H₂₂O₉S₂ (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 N₂ to a stirred mixture of **24** (6 g, 15.5 mmol) and anhyd. DMF/HMPT 6:1 at 0°. After stirring at 0° for 2 h, H₂O (20 ml) was added and the mixture extracted with pentane (200 ml, 5 times). The org. extract was washed with H₂O and dried (MgSO₄). 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 (CH₂Cl₂): 3050, 2990, 2960, 2940, 2910, 2840, 1185, 1150, 1105, 1085, 1050, 1035, 985, 940, 930, 890, 820. ¹H-NMR (360 MHz, CDCl₃): 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 (4s, CH₂=C(5), CH₂=C(6)); 5.18 (br. s, H-C(4)); 4.83 (s, CH(OCH₃)₂); 3.6, 3.54 (2s, 2 CH₃O). ¹³C-NMR (90 MHz, C₆D₆): 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, CH-C(1)); 102.8, 101.0 (2 t, ¹J(C,H) = 158, CH₂=C(5), CH₂=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 CH₃O). CI-MS (CH₄): 195 (5, M⁺ + H), 163 (15), 135 (26), 131 (11), 75 (50), 57 (100). Anal. calc. for C₁₁H₁₄O₃ (194.232): C 68.02, H 7.27; found: C 67.95, H 7.27.

Complexation of **9** with Fe₂(CO)₉ (*Method A*). Fe₂(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 (CHCl₃): 3010, 2970, 2940, 2840, 2095, 2020, 2000, 1995, 1100, 1080. ¹H-NMR (360 MHz, CDCl₃): 5.45, 5.43, 5.33, 5.10 (4s, CH₂-C(5), CH₂-C(6)); 4.72 (br. H-C(4)); 4.54 (s, CH-C(1)); 3.60, 3.58 (2s, 2 CH₃O); 3.21, 3.12 (2d, ³J(H-C(2), H-C(3)) = 5.2, H-C(2), H-C(3)). ¹³C-NMR (90 MHz, CDCl₃): 210.2 (s, CO); 146.5, 144.3 (2m, C(5), C(6)); 105.0 (dm, ¹J(C,H) = 161, CH-C(1)); 104.2, 102.2 (2 t, ¹J(C,H) = 160, CH₂=C(5), CH₂=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 CH₃O); 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 C₁₅H₁₄FeO₇ (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. ¹H-NMR (360 MHz, CDCl₃): 4.79, 4.68 (2s, CH–C(1), H–C(4)); 3.60, 3.58 (2s, 2 CH₃O); 3.63, 3.48 (2d, 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 (2d, ²J = 2.5, H–C=C(5), H–C=C(6)). ¹³C-NMR (90 MHz, CDCl₃): 211.2, 209.0 (2s); 111.9, 110.8 (2s, C(5), C(6)); 104.3 (d, ¹J(C,H) = 160, CH–C(1)); 89.8 (s, C(1)); 82.2 (d, ¹J(C,H) = 170, C(4)); 57.6, 57.3 (2d, ¹J(C,H) = 170, C(2), C(3)); 58.3, 56.2 (2q, ¹J(C,H) = 142, CH₃O); 34.1, 33.0 (2t, ¹J(C,H) = 162, CH₂=C(5), CH₂=C(6)). CI-MS (CH₄): 502 (15, M⁺), 446 (58), 418 (100), 390 (30), 362 (30), 334 (33), 306 (51). Anal. calc. for C₁₈H₁₄Fe₂O₁₀ (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 (CHCl₃): 3010, 2965, 2940, 2840, 2055, 1995, 1470, 1350, 1120, 1075, 1060. ¹H-NMR (360 MHz, CDCl₃): 7.67–7.35 (H–C(2), H–C(3), H–C(4)); 5.39 (s, CH–C(1)); 3.43, 3.38 (2s, 2 CH₃O); 2.78, 2.47 (2d, ²J = 3.6, H–C=C(5), H–C=C(6) *trans* to C(5), C(6)); 0.25, 0.07 (2d, ²J = 3.6, H–C=C(5), H–C=C(6) *cis*). ¹³C-NMR (90 MHz, CD₂Cl₂): 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, CH–C(1)); 100.2, 100.1 (2s, C(5), C(6)); 54.5, 53.8 (2qd, ¹J(C,H) = 143, ³J(C,H) = 5, 2 CH₃O); 36.7, 33.3 (2t, 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 C₁₄H₁₃FeO₅ (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. ¹H-NMR (360 MHz, CDCl₃): 8.30, 8.13 (2s, H–C(2), H–C(6)); 5.39 (s, CH–C(5)); 3.97 (s, COOCH₃); 3.44, 3.40 (2s, 2 CH₃O); 2.89, 2.50 (2d, J = 3.5); 0.32, 0.15 (2d, J = 3.5, H–C=C(3), H–C=C(4) *cis* to C(3), C(4)). ¹³C-NMR (90 MHz, CDCl₃, –30°): 215.6, 206.6, 205.4 (3 br. s, CO); 166.1 (s, CH₃COO); 139.4, 125.6 (2d, ¹J(C,H) = 166, C(2), C(6)); 137.6, 128.4 (2s, C(1), C(5)); 101.8, 96.8 (2s, C(3), C(4)); 101.7 (d, ¹J(C,H) = 161, CH–C(5)); 53.8, 53.4 (2dq, ¹J(C,H) = 144, ³J(C,H) = 5, 2 CH₃O); 52.4 (q, ¹J(C,H) = 147, COOCH₃); 36.7, 33.5 (2t, ¹J(C,H) = 160, CH₂=C(3), CH₂=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 C₁₆H₁₆FeO₇ (376.144): C 51.09, H 4.29; found: C 51.13, H 4.18.

Complexation of 9 with Fe₂(CO)₉ (Method B). A mixture of **9** (2.3 g, 11.84 mmol), anh. MeOH (130 ml), and Fe₂(CO)₉ (7.5 g, 20.6 mmol) was stirred at 20° under vigorous bubbling with Ar. Fe₂(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. H₂O (10 ml) was added and the mixture extracted with CH₂Cl₂ (40 ml, 3 times). After drying (MgSO₄), 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,6SR)-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. ¹H-NMR (360 MHz, CDCl₃): 5.15, 4.67 (2s, CH–C(1), H–C(4)); 3.66, 3.62 (2s, 2 CH₃O); 3.60, 3.48 (2d, ³J(H–C(3), H–C(2)) = 5, H–C(3), H–C(2)); 2.43, 2.16 (2d, ²J = 3, H–C=C(5), H–C=C(6) *trans* to C(5), C(6)); 0.74, 0.69 (2d, ²J = 3, H–C=C(5), H–C=C(6)). ¹³C-NMR (90 MHz, CDCl₃): 209.6 (s, CO of Fe(CO)₃ and Fe(CO)₄); 118.6, 117.6 (2s, C(5), C(6)); 105.8 (d, ¹J(C,H) = 160, CH–C(1)); 92.0 (s, C(1)); 83.0 (d, ¹J(C,H) = 170, C(4)); 61.2, 59.9 (2d, ¹J(C,H) = 174, C(2), C(3)); 58.04, 57.17 (2q, ¹J(C,H) = 143, 2 CH₃O); 34.37, 34.03 (2t, ¹J(C,H) = 162, CH₂=C(5), CH₂=C(6)). CI-MS (CH₄): 474 (4, M⁺ – CO), 446 (40), 418 (100), 390 (11), 362 (15), 334 (21), 306 (41). Anal. calc. for C₁₈H₁₄Fe₂O₁₀ (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/H₂O 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 CH₂Cl₂ (30 ml). After drying (MgSO₄), the solvent was evaporated and the residue purified by filtration through a short column of silica gel (AcOEt/CH₂Cl₂ 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. ¹H-NMR (360 MHz, CDCl₃): 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, 2*H*); 0.34, 0.14 (2*d*, *J* = 3.5, 2*H*). ¹³C-NMR (90 MHz, CDCl₃): 209.5 (CO); 191.4 (*d*, ¹*J*(C,H) = 174, CHO); 141.3, 138.9 (2*d*, ¹*J*(C,H) = 160, C(2), C(4)); 126.8 (*d*, ¹*J*(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*, ¹*J*(C,H) = 160, CH₂=C(5), CH₂=C(6)). MS (70 eV): 272 (31), 244 (27), 216 (44), 189 (82), 160 (20), 133 (84), 103 (28), 77 (27). Anal. calc. for C₁₂H₈FeO₄ (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. ¹H-NMR (360 MHz, CDCl₃): 10.18 (*s*, CHO); 8.60, 8.49 (2*s*, H–C(2), H–C(6)); 4.02 (*s*, CH₃OOC); 4.00, 2.49 (2*d*, ²*J* = 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, 2*H*). ¹³C-NMR (90 MHz, CDCl₃): 209.0 (*s*, CO), 191.3 (*d*, ¹*J*(C,H) = 178, CHO); 165.2 (*s*, COOCH₃); 145.2, 138.3 (2*d*, ¹*J*(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*, CH₃O); 37.3, 35.7 (2*t*, ¹*J*(C,H) = 160, CH₂=C(3), CH₂=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 C₁₄H₁₀FeO₆ (330.075): C 50.94, H 3.05; found: C 51.10, H 3.08.

2-Indanone (15). Anh. (NH₄)₂Ce(NO₃)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 (NH₄)₂Ce(NO₃)₆ were added and after 70 min, 100 mg of (NH₄)₂Ce(NO₃)₆. After 100 min of reaction and addition of H₂O (120 ml), the mixture was extracted with CH₂Cl₂ (150 ml, 4 times). The extract was dried (MgSO₄), the solvent evaporated, and the residue purified by filtration through a short column of silica gel (CH₂Cl₂): 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. (NH₄)₂Ce(NO₃)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 (NH₄)₂Ce(NO₃)₆, respectively, were added. After 95 min, pentane (100 ml) was added and the mixture filtered. The solution was washed with H₂O (70 ml), the aq. phase extracted with CH₂Cl₂ (100 ml, 4 times), the combined org. phase dried (MgSO₄) and evaporated, and the residue purified by column chromatography on silica gel (AcOEt/CH₂Cl₂ 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. ¹H-NMR (360 MHz, CDCl₃): 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*, CH₂(1), CH₂(3)). ¹³C-NMR (90 MHz, CDCl₃): 213.6 (*s*, CO); 191.9 (*d*); 139.6, 139.0, 132.5 (3*s*); 131.6, 130.2, 127.9 (3*d*, ¹*J*(C,H) = 160); 43.9, 42.9 (2*t*, ¹*J*(C,H) = 135). MS (70 eV): 160 (11), 132 (48), 104 (78), 78 (44), 70 (50), 61 (80), 45 (100). Anal. calc. for C₁₀H₈O₂ (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. $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (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 ($\text{AcOEt}/\text{CH}_2\text{Cl}_2$ 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. $^1\text{H-NMR}$ (360 MHz, CDCl_3): 10.16 (s, CHO); 8.46, 8.25 (2s, H–C(4), H–C(6)); 3.99 (s, COOCH_3); 3.95, 3.63 (2s, $\text{CH}_2(1)$, $\text{CH}_2(3)$). MS (70 eV): 218 (23, M^+), 190 (100), 187 (21), 162 (22), 159 (15), 146 (15), 131 (32), 119 (10), 103 (69), 102 (50), 77 (84). HR-MS (ref.: iodotoluene): $(\text{C}_{12}\text{H}_{10}\text{O}_4)^+$, 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°. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 8.25, 8.12 (2s, H–C(4), H–C(6)); 5.47 (s, CH–C(7)); 4.02 (s, COOCH_3); 3.75, 3.67 (2s, $\text{CH}_2(1)$, $\text{CH}_2(3)$); 3.40 (s, 2 CH_3O).

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