DOI: 10.1002/ejoc.200500436

Syntheses, Structures and Electronic Properties of Cationic Hydroxy- and Methoxy-Substituted Tricarbonyl(tetracyclopropylcyclopentadienyl)iron Complexes

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Dedicated to Professor Roland Boese on the occasion of his 60th birthday

Keywords: Small rings / Carbonyl compounds / Iron complexes / Structural data / Cations

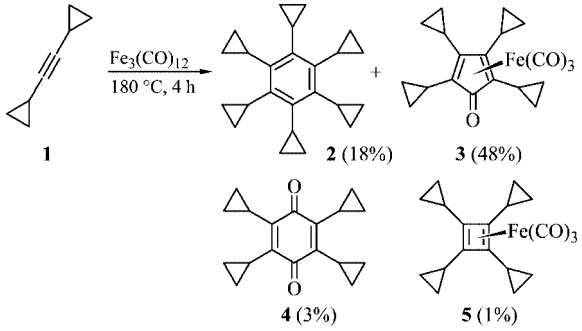
Tetracyclopropylcyclopentadienone, upon liberation from its previously known tricarbonyliron complex **3**, undergoes rapid [4+2] cyclodimerization to the highly congested 1,2,4,5,6,7,8,9-octacyclopropyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (**6**) which was characterized by an X-ray crystal structure analysis. Upon alkylation of **3** with Me_3OBF_4 as well as protonation with HBF_4 or CF_3SO_3H, the remarkably stable cationic tricarbonyl(tetracyclopropylcyclopentadienyl)-iron complexes **9**, **10** and **11**, **12**, respectively, were obtained in high yields (91, 87 and 74, 79%, respectively). X-ray crystal structural data for **11** and **12** as well as NMR- and IR spectroscopic evidences for all four new complexes **9**–**12** indicate that their positive charge predominantly rest on the tricarbonyliron fragments.

Introduction

Cationic tricarbonyl(cyclohexadienylium)iron and acyclic tricarbonylpentadienyliron complexes are quite common and have frequently been applied in organometallic chemistry towards organic synthesis.[1] A wide range of nucleophiles has been reported to readily react with these types of cationic species, in which the presence of the tricarbonyliron moiety is responsible for a high degree of control of the regio- and stereoselectivity. The structural and electronic properties of these complexes have also been well studied. In contrast, little is known about cationic tricarbonylcyclopentadienyliumiron complexes. In this report we describe the reaction of the previously known tricarbonyl(tetracyclopropylcyclopentadienone)iron complex **3** with Meerwein salts and with strong acids yielding remarkably stable new cationic tricarbonyl(cyclopentadienyl)iron complexes.

Results and Discussion

Cyclooligomerizations of alkynes under mediation or catalysis of transition metal carbonyl complexes provide the most efficient access to oligosubstituted oligounsaturated conjugated cyclic compounds. The reaction of neat dicyclopropylacetylene (**1**)[2] with dodecacarbonyltriiron in a sealed tube gave a mixture of products from which, after flash chromatography on silica gel, on top of the previously described hexacyclopropylbenzene (**2**),[3] and tricarbonyl(tetracyclopropylcyclopentadienone)iron (**3**),[3] tetracyclopropyl-*p*-benzoquinone (**4**)[4] and tricarbonyl(tetracyclopropylcyclobutadiene)iron (**5**)[5] were isolated in 3 and 1% yield, respectively (Scheme 1).



Scheme 1.

Uncomplexed cyclopentadienones are very reactive compounds, which are prone to immediately undergo [4+2] or [2+2] cyclodimerization[6] unless sufficiently sterically demanding substituents prevent it. Thus, tetraisopropyl-[7] tetra-*tert*-butoxy- and tetra-*tert*-butylcyclopentadienone[8] as well as four-, five- and six-ring-annelated 2,5-bis(tri-

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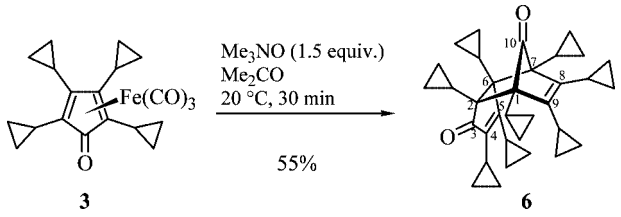
methylsilyl)cyclopentadienones[9] can be isolated as stable monomers. In order to test, whether the uncomplexed tetracyclopropylcyclopentadienone would also be stable enough and might be used as a precursor to tetra- and pentacyclopropylcyclopentadienyl cation species,[10] the tricarbonyliron complex **3** was treated with 1.5 equivalents of trimethylamine *N*-oxide as an oxidizing agent (acetone, 20 °C, 30 min), (Scheme 2). However, this did not lead to the free cyclopentadienone, but the [4+2] cyclodimer, which was isolated in 55% yield. This compound crystallized well from pentane/diethyl ether (3:1), and the colorless crystals were subjected to an X-ray crystal structure analysis to rigorously prove its configuration (Figure 1).[11] Apparently, the four cyclopropyl groups, which are only slightly bigger than four ethyl groups,[12] are not bulky enough to prevent tetracyclopropylcyclopentadienone from undergoing rapid [4+2] cyclodimerization.



3 **6**

Scheme 2.

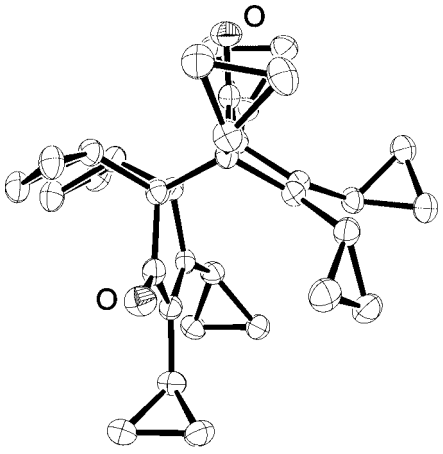
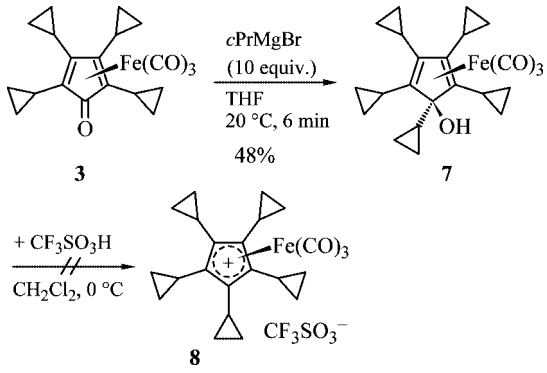


Figure 1. Structure of the tetracyclopropylcyclopentadienone dimer 1,2,4,5,6,7,8,9-octacyclopropyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (**6**) in the crystal. Selected bond lengths [pm]: C^2–C^6 157.9(3); C^1–C^2 159.5(3); C^1–C^{10} 153.9(3); C^6–C^{10} 153.9(3); C^6–C^7 160.7(3).[11]

However, the resulting tricycle **6** is the most sterically congested persubstituted cyclopentadienone [2+2] cyclodimer known to date, and this is reflected in its crystal structure. The carbon–carbon bonds C^1–C^2, C^2–C^6 and C^6–C^7 in the newly formed ring of the tricycle **6** are significantly (3–6 pm) longer than the corresponding ones in the previously described structure of diethyl 4,7-dimethyl-5,10-dioxo-*endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene-3,8-dicarboxylate[13] with the same tricyclic skeleton.

Since the uncomplexed tetracyclopropylcyclopentadienone thus could not be used for the intended transformations, an attempt was made to add organometallic reagents directly to the carbonyl group in the complex **3** and then liberate the ligand from the resulting cyclopentadienol complex. In fact, when **3** was treated with cyclopropyllithium, only decomposition was observed, but treatment of **3** with cyclopropylmagnesium bromide gave, after some optimization of the conditions, the tricarbonyl(pentacyclopropylcyclopentadienol)iron complex **7** in 48% yield (Scheme 3).



3 **7** **8**

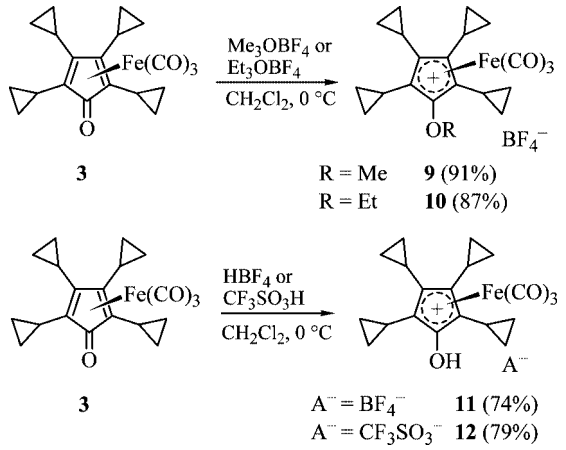
Scheme 3.

However, the product complex **7** was unstable at room temperature even under an inert atmosphere. It decomposed within a few hours, and the decomposition was not simply with liberation of the uncomplexed pentacyclopropylcyclopentadienol, at least the latter could not be isolated. Despite this instability, an attempt was made to generate the cationic tricarbonyl(pentacyclopropylcyclopentadienylium)iron complex **8** by treatment of **7** in dichloromethane at 0 °C with trifluoromethanesulfonic acid, but only decomposition was observed.

Since alkoxy and hydroxy groups are even better electron donors than a cyclopropyl substituent, alkoxy- and hydroxytetracyclopropylcyclopentadienylium complexes should be more stable than **8**, and they should be accessible by alkylation and protonation with strong electrophiles such as Meerwein salts and strong acids, respectively, of the carbonyl group in **3**. Indeed, treatment of **3** with trimethyl- and triethyloxonium tetrafluoroborate in dichloromethane at 0 °C gave, after evaporation of the solvent, the expected *O*-alkylated cationic complexes **9** and **10** in very high yields (91 and 87%, respectively). The structural assignments of these remarkably stable compounds rest on their NMR, IR and mass spectra (see below).

Treatment of **3** in dichloromethane at 0 °C with strong acids such as tetrafluoroboric or trifluoromethanesulfonic acid led to selective protonation of the carbonyl group in the five-membered ring and gave the hydroxy-substituted complexes **11** and **12** in 74 and 79% yield, respectively. Both the Meerwein salts and the protic acids had to be added in slightly substoichiometric amounts to prevent complete decomposition of the starting materials (Scheme 4).

In order to probe the electronic structure of these new cationic complexes, suitable crystals of the uncharged cyclopentadienone complex **3** (recrystallization from hexane) and of the protonated compounds **11** and **12** [recrystalli-



Scheme 4.

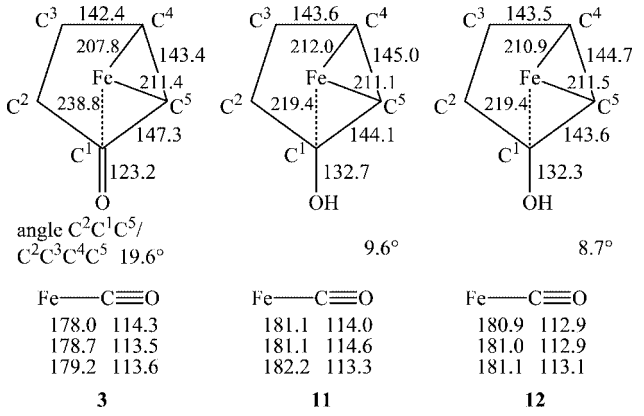


Figure 3. Comparison of X-ray crystal structural data of the neutral tricarbonyl(tetracyclopropylcyclopentadienone)iron complex **3** and the protonated species **11** and **12**.

zation from Et_2O/hexane (1:2)] were grown. X-ray crystal structure analyses were performed (Figure 2),[11,14] and NMR as well as IR data were collected.

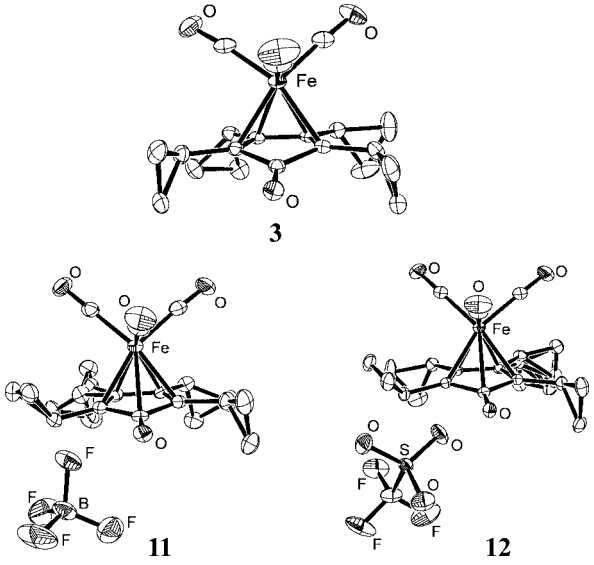


Figure 2. Structures of complexes **3**, **11** and **12** in the crystals (133 K).[11,14]

A comparison of the structural data (Figure 3) discloses a significant elongation (by 9.5 and 9.9 pm, respectively) of the C^1,O^1 bond in the five-membered ring on going from the neutral complex **3** to the cationic species **11** and **12**. In the latter, the bond order of this C,O bond apparently is between that of a single and a double bond, indicating that a considerable fraction of the positive charge remains on the oxygen atom, like in protonated dicyclopropyl ketone **13**, in which the C,O bond length is 129.0 pm indicating an even higher double bond character than in **11** and **12**.[15]

The five-membered ring in **3** is not planar with the ring carbonyl group being bent away from the $Fe(CO)_3$ moiety at an angle of 19.7° between the $C^2C^1C^5$ and the $C^2C^3C^4C^5$ plane. Upon protonation, the delocalization of the positive charge into the five-membered ring causes it to become more planar with an angle between the $C^2C^1C^5$ and the $C^2C^3C^4C^5$ plane of only 9.6° and 8.7° in **11** and **12**, respectively, and the distance between the iron and the carbonyl carbon atom to shorten from 238.8 to 219.7 and 219.4 pm, respectively. With the other four iron to carbon distances remaining virtually the same, the coordination hapticity of the iron atom changes from η^4 to almost η^5. The difference between the Fe–C^1 and the average distance Fe–C^2($C^3C^4C^5$) in **3** is 29.2 pm and in the protonated complexes only 8.1 pm and 8.2 pm in **11** and **12**, respectively.

Along the same line of evidence, the average of the bond lengths C^2–C^3; C^3*–C^4; C^4–C^5 (143.0 pm) in the neutral complex **3** are significantly shorter than those between between C^2 as well as C^1 and C^5 (147.3 pm), whereas all five bond lengths in the cationic complexes **11** (144.1, 145.0 143.6) and **12** (143.6, 144.7, 143.5 pm) are very similar.

On the other hand, the average distance between the iron atom and the three CO ligands changes from 178.6 pm in **3** to 181.5 and 181.0 pm, respectively, in **11** and **12**, indicating that the iron atom in the latter is fulfilling an increased electron demand from the cationic cyclopentadienylium ligand.

In view of the electron demand of the central five-membered ring, the orientation of the four cyclopropyl substituents in **11**, **12** and **3** is also important, since the cyclopropyl groups can exert their particularly good electron donor ability only in the bisected conformation. In **11**, the dihedral angles are 77.7 (at C^2), 73.5 (16.8° for the disordered species, at C^3), 63.7 (at C^4) and 22.8° (at C^5) out of the bisected conformation.[16] Similarly, these angles in **12** are 81.7 (at C^2), 48.1 (at C^3), 10.3 (76.8° for the disordered species, at C^4) and 21.0° (at C^5). Similar dihedral angles were observed for the neutral complex **3** (19.1, 81.9, 37.6 and 42.0°). Thus, two out of four cyclopropyl groups in all three complexes can act as significant electron donors, and the positive charge in the five-membered rings of the cationic complexes **11** and **12** does not cause any significant change in the orientation of the cyclopropyl substituents.

In line with this, the bond lengths between the cyclopropyl substituents and the five-membered ring carbon atoms as well as within the three-membered rings virtually do not change on going from **3** to the protonated complexes **11**

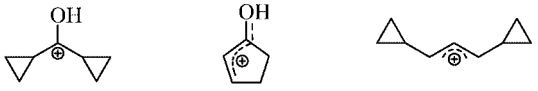
Table 1. Selected ^{1}H and ^{13}C NMR chemical shifts (in ppm) of complexes **3**, **9**, **10**, **11** and **12**.

	3 $CDCl_3$	**3** [D$_6$]DMSO	**9** [D$_6$]DMSO	**10** [D$_6$]DMSO	**11** $CDCl_3$	**12** $CDCl_3$
H_α (m)	0.68–1.78	0.64–1.86	1.63–1.81	1.60–1.85	1.52–1.69	1.47–1.75
H_β (m)	not separated	not separated	0.88–1.16	0.82–1.25	1.00–1.20	0.97–1.26
C-cPr	7.0–8.2	6.7–8.4	6.2–9.4	6.2–9.2	5.5–8.9	5.8–9.1
C^2–C^5	85.6	85.2	96.2	96.0	92.8	93.1
C^3–C^4	104.2	104.7	106.1	106.1	105.7	105.6
C=O	170.3	169.8	139.1	138.6	142.6	142.9
$Fe(CO)_3$	209.6	210.3	205.3	205.3	204.6	204.7

and **12**, whereas the bond lengths between the cyclopropyl groups and the carbonyl carbon in protonated dicyclopropyl ketone is shortened by 4.5 pm.[15]

The lack of delocalization of the positive charge into the cyclopropyl groups in the cationic complexes **11** and **12** as well as in **9** and **10** is also evident in the ^{1}H- and ^{13}C-NMR spectroscopic data. The signals of the protons on the cyclopropyl groups as well as the carbon atoms in them are not shifted to lower fields on going from the neutral **3** to the cationic complexes (Table 1).

For comparison, the corresponding signals of the methyne groups in protonated dicyclopropyl ketone **13** and 1,3-dicyclopropylallyl cation **15**[17] occur at δ = 3.60 and 2.70 ppm, respectively (Figure 4).



13
H_α 3.60
H_β 1.98

C_α 18.3, 27.6
C_β 25.5, 24.9
CO 235.9

14

C^1 230.6
C^2 132.7
C^3 182.0

15
H_α 2.70
H_β 2.14, 2.43

C_α 32.9
C_β 23.4
C^1/C^2 211.3
C^2 135.6

Figure 4. ^{1}H- and ^{13}C-NMR chemical shifts (in ppm) of protonated dicyclopropyl ketone **13**, protonated cyclopent-2-enone **14** and 1,3-dicyclopropylallyl cation **15**.[17–18,19]

The signals of the five-membered ring carbon atoms C^2 and C^5 in the cationic complexes **9**–**12** were observed between δ = 92.8 and 96.2 ppm, i.e. shifted by about 7–10 ppm to lower field than in **3**. The signals of C^3 and C^4 were only shifted downfield by about 1.5 ppm. Yet, with chemical shifts of about 106 ppm, these signals appear at much higher field than those of the corresponding carbon atoms in protonated cyclopentenone **14**, for which the resonances of C^2 and C^3 were observed at 132.7 and 182 ppm, respectively. These small changes in chemical shifts also indicate that only a minor fraction of the positive charge is delocalized into the five-membered rings of the cationic complexes **9**–**12**.

Surprisingly, the peaks of C^1 in the cationic complexes **9**–**12** appear around 140 ppm, i.e. shifted by about 30 ppm to higher field compared to the corresponding signal for **3** (δ =170 ppm), whereas the carbonyl carbon signal of protonated dicyclopropyl ketone **13**[18] (δ = 235.9 ppm) and of protonated cyclopentenone **14**[19] (δ = 230.6 ppm) are drastically shifted to lower fields. Thus, the positive charges in **9**–**12** must, to a large extent, rest on the tricarbonyliron fragment.

This is in the line with IR spectroscopic evidence. While the stretching vibrations of the three CO ligands in the neutral complex **3** were observed at 2049 and 1979 cm^{-1}, those of the protonated complex **11** are shifted significantly to higher frequencies (at, 2095 and 2027 cm^{-1}). The higher positive charge at the iron lowers its ability to back bind to the carbon atoms of the CO ligands, and this results in stronger CO bonds (Fe=C=O → Fe–C≡O), because a free electron pair of the oxygen now contributes some electron density into the C,O bond.

Conclusions

Stable tricarbonyl(alkoxy)- and tricarbonyl(hydroxytetracyclopropylcyclopentadienyl)iron complexes **9**, **11** and **11**, **12** have been obtained by alkylation and protonation, respectively, of tricarbonyl(tetracyclopropylcyclopentadienyl)iron (**3**). The observed planarization of the five-membered ring, the shortening of the Fe–C^1 distance and the change of the hapticity all corroborate a delocalization of the positive charge to the metal center. The lacking influence of the charge on the chemical shifts of C^2, C^3, C^4 and C^5 as well as the cyclopropylic protons and carbons, and the predominating non-bisected orientation of the cyclopropyl substituents are evidence against any delocalization of the positive charge into the cyclopropyl groups. Thus, these cationic complexes are stabilized mainly by delocalization to the tricarbonyliron fragment and oxygen substituents.

Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AM 250 (250 and 62.9 MHz) or Bruker AMX 300 (300 and 75 MHz). IR: Bruker IFS 66 (FT-IR). Low-resolution EI-MS: Finnigan MAT 95, ionizing voltage 70 eV. High resolution MS were obtained with a Finnigan MAT 95. HRMS: preselected ion peak matching at R = ca. 10000 to be within ±2 ppm of the exact masses. X-ray crystal structure determination: The data were collected on a Stoe-Siemens-AED diffractometer. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analyses: Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen. Chromatography: Merck silica gel 60 (230–400 mesh) or ICN neutral alumina (Super I, Activity II).

Tricarbonyl(η⁴-2,3,4,5-tetracyclopropylcyclopenta-2,4-dienone)iron (3): A mixture of 300 mg (0.596 mmol) of dodecacarbonyltriiron and 1.60 g (15.1 mmol) of dicyclopropylacetylene (**1**) in a sealed tube was heated at 180–190 °C for 2 h. After cooling down, 300 mg (0.596 mmol) of $Fe_3(CO)_{12}$ was added, and the mixture heated for an additional 2 h. The reaction mixture was filtered through 10 g of Celite (CH_2Cl_2), and the solvent was removed in vacuo. After chromatography on 60 g of silica gel (column 3×40 cm), eluting with light petroleum (PE)/Et_2O/CH_2Cl_2 (2:1:1) 656 mg (48%) of **3** (R_f = 0.18 in PE/Et_2O, 5:1) was isolated as yellow crystals, m.p. 90 °C. IR (KBr): $\tilde{\nu}$ = 3012 cm^{-1} (C–H), 2049 (C=O), 1979 (C=O), 1635 (C=O), 1437, 1027, 623, 592. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.68–0.92 (m, 2 H, *c*Pr-H), 0.94–1.05 (m, 2 H, *c*Pr-H), 1.08–1.24 (m, 6 H, *c*Pr-H), 1.30 (m_c, 4 H, *c*Pr-H), 1.78 (m_c, 6 H, *c*Pr-H). ^1H NMR (250 MHz, [D_6]DMSO): δ = 0.64–0.82 (m, 4 H, *c*Pr-H), 0.84–0.94 (m, 2 H, *c*Pr-H), 0.99–1.08 (m, 8 H, *c*Pr-H), 1.13–1.26 (m, 4 H, *c*Pr-H), 1.86 (m_c, 2 H, *c*Pr-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 7.00, 7.14, 7.67, 7.79 (–, *c*Pr-C), 7.91, 8.24 (+, *c*Pr-C), 85.59 [C_{quat}, C-2(5)], 104.24 [C_{quat}, C-3(4)], 170.29 (C_{quat}, C-1), 209.61 [C_{quat}, $Fe(CO)_3$]. ^{13}C NMR (62.9 MHz, [D_6]-DMSO, add. DEPT): δ = 6.70, 7.24, 7.62 (–, *c*Pr-C), 7.74 (+, *c*Pr-C), 7.84 (–, *c*Pr-C), 8.36 (+, *c*Pr-C), 85.20 [C_{quat}, C-2(5)], 104.74 [C_{quat}, C-3(4)], 169.80 (C_{quat}, C-1), 210.27 (C_{quat}, [$Fe(CO)_3$]). MS (70 eV), *m*/*z* (%): 380 (16) [M^+], 352 (52) [M^+ – CO], 324 (19) [M^+ – 2 CO], 296 (64) [M^+ – 3 CO], 240 (100) [M^+ – 3 CO – Fe], 236 (27), 56 (12) [Fe^+]. $C_{20}H_{20}FeO_4$ (380.2): 380.0710 (correct HRMS); calcd. C 63.18, H 5.30; found C 63.42, H 5.32.

***endo*-1,2,4,5,6,7,8,9-Octacyclopropyltricyclo[5.2.1.0^{2,6}]deca-8,8-diene-3,10-dione (6):** To a solution of 2.50 g (6.58 mmol) of **3** in 30 mL of acetone was added at room temp. 741 mg (9.49 mmol) of trimethylamine *N*-oxide, the mixture was stirred for 30 min and then filtered through 5 g of Celite (Et_2O). After chromatography on 20 g of silica gel (column 1×20 cm) eluting with pentane/CH_2Cl_2 (3:1) 876 mg (55%) of **6** (R_f = 0.85, pentane/Et_2O = 3:1) was isolated as colorless crystals, m.p. 119 °C. IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1} (C–H), 3010 (C–H), 1756, 1706, 1604, 1379, 1173, 1059, 1029, 957, 900, 820. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.14 (m_c, 1 H, *c*Pr-H), 0.26 (m_c, 1 H, *c*Pr-H), 0.40–0.59 (m, 9 H, *c*Pr-H), 0.60–0.82 (m, 11 H, *c*Pr-H), 0.88–1.11 (m, 6 H, *c*Pr-H), 1.12–1.49 (m, 9 H, *c*Pr-H), 1.63 (m_c, 2 H, *c*Pr-H), 1.82 (m_c, 1 H, *c*Pr-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 2.90 (–, *c*Pr-C), 3.37 (–, 2 *c*Pr-C), 4.44 (–, *c*Pr-C), 4.95 (–, 2 *c*Pr-C), 5.12, 5.25, 5.38 (–, *c*Pr-C), 5.44 (–, 2 *c*Pr-C), 6.42 (–, *c*Pr-C), 6.75 (+, *c*Pr-C), 7.38, 7.86 (–, *c*Pr-C), 9.26, 9.37, 9.90 (+, *c*Pr-C), 10.26, 10.99 (–, *c*Pr-C), 11.06, 12.56, 15.75, 16.43 (+, *c*Pr-C), 59.39, 61.96, 63.40, 63.42 (C_{quat}, C-3a, C-4, C-7, C-7a), 141.40, 142.67, 142.85 (C_{quat}, C-2, C-5, C-6), 173.93 (C_{quat}, C-3), 200.78 (C_{quat}, C-8), 204.43 (C_{quat}, C-1). MS (70 eV), *m*/*z* (%): 480 (2) [M^+], 318 (33), 277 (100), 256 (33), 240 (28) [M^+ – $C_{17}H_{20}O$], 212 (28), 203 (29), 183 (17), 165 (18), 155 (16), 141 (18), 129 (19), 91 (22). – DCI-MS (200 eV), *m*/*z* (%): 498 (10) [$C_{34}H_{40}O_2^+$ + NH_3], 481 (9), 258 (38), 241 (100) [$C_{16}H_{20}O^+$ + H]. $C_{34}H_{40}O_2$ (480.7): calcd. 480.3028, 240.1514 (correct HRMS).

Tricarbonyl(η⁴-1,2,3,4,5-pentacyclopropylcyclopenta-2,4-dienol)iron (7): To a solution of 711 mg (1.87 mmol) of **3** in 30 mL of anhydrous Et_2O was added with stirring at room temp. cyclopropylmagnesium bromide (13.2 mL, 18.7 mmol, 1.42 M in Et_2O). After 6 min at room temp., 30 mL of water and 100 mL of Et_2O were added, the organic layer was dried with $MgSO_4$, and the solvent was evaporated in vacuo. Flash chromatography under an inert atmosphere on 40 g of aluminum oxide, activity grade II (column 2×40 cm), eluting with PE/Et_2O, 10:1 to Et_2O yielded 381 mg (48%) of **7** as a yellow, rapidly decomposing oil (R_f = 0.62, PE/Et_2O, 3:1). ^1H NMR (250 MHz, C_6D_6): δ = 0.49–0.72 (m, 14 H, *c*Pr-H), 0.86–0.90 (m, 2 H, *c*Pr-H), 1.05–1.27 (m, 8 H, *c*Pr-H), 2.60 (m_c, 1 H, *c*Pr-H), 10.70 (s, 1 H, OH). ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 6.52 (+, 2 C, *c*Pr-C), 7.11 (–, 2 C, *c*Pr-C), 7.24 (–, 2 C, *c*Pr-C), 7.31 (+, 2 C, *c*Pr-C), 7.51 (–, 2 C, *c*Pr-C), 8.11 (–, 2 C, *c*Pr-C), 12.38 (–, 2 C, *c*Pr-C), 40.30 (+, *c*Pr-C), 95.04, 100.54 [C_{quat}, C-2(5), C-3(4)], 126.00 (C_{quat}, C-1), 217.53 [C_{quat}, $Fe(CO)_3$]. MS (70 eV), *m*/*z* (%): 422 (1) [M^+], 394 (52) [M^+ – CO], 366 (10) [M^+ – 2 CO], 338 (100) [M^+ – 3 CO], 282 (14) [M^+ – $Fe(CO)_3$], 252 (42), 240 (46), 165 (51), 153 (46), 128 (42), 56 (20) [Fe^+].

Tricarbonyl(η⁵-1-methoxy-2,3,4,5-tetracyclopropylcyclopenta-2,4-dienylium)iron Tetrafluoroborate (9): To a solution of 150 mg (0.395 mmol) of **3** in 30 mL of anhydrous CH_2Cl_2 was added at 0 °C 55.4 mg (0.375 mmol) of trimethyloxonium tetrafluoroborate, and the mixture was stirred for 1 h. After removal of the solvent in vacuo and recrystallization [Et_2O/hexane (1:2)], 165 mg (91%) of **9** was isolated as a yellow solid, m.p. 158 °C. IR (KBr): $\tilde{\nu}$ = 3018 cm^{-1} (C–H), 2098 (C=O), 2037 (C=O), 1718, 1611, 1491, 1402, 1256, 1055, 622, 575. ^1H NMR (250 MHz, [D_6]DMSO): δ = 0.88–1.16 (m, 16 H, *c*Pr-H), 1.63–1.81 (m, 4 H, *c*Pr-H), 4.21 (s, 3 H, CH_3). ^{13}C NMR (62.9 MHz, [D_6]DMSO, add. DEPT): δ = 6.15, 7.19 (+, *c*Pr-C), 8.37, 8.98, 9.19, 9.40 (–, *c*Pr-C), 63.57 (+, OCH_3), 96.23 [C_{quat}, C-2(5)], 106.05 [C_{quat}, C-3(4)], 139.12 (C_{quat}, C-1), 205.26 [C_{quat}, $Fe(CO)_3$]. MS (70 eV), *m*/*z* (%): 380 (13) [M^+ – BF_4 – CH_3], 352 (51) [M^+ – BF_4 – CH_3 – CO], 324 (14) [M^+ – BF_4 – CH_3 – 2 CO], 296 (65) [M^+ – BF_4 – CH_3 – 3 CO], 268 (25) [M^+ – BF_4 – CH_3 – $Fe(CO)_2$], 240 (100) [M^+ – BF_4 – CH_3 – $Fe(CO)_3$]. $C_{21}H_{23}BF_4FeO_4$ (482.1): calcd. C 52.32, H 4.81; found C 52.33, H 4.75.

Tricarbonyl(η⁵-1-ethoxy-2,3,4,5-tetracyclopropylcyclopenta-2,4-dienylium)iron Tetrafluoroborate (10): To a solution of 150 mg (0.395 mmol) of **3** in 30 mL of anhydrous CH_2Cl_2 was added at 0 °C 71.2 mg (0.375 mmol) of triethyloxonium tetrafluoroborate, and the mixture was stirred for 1 h. After removal of the solvent in vacuo and recrystallization [Et_2O/hexane (1:2)] 161 mg (87%) of **10** was isolated as a yellow solid, m.p. 173 °C. IR (KBr): $\tilde{\nu}$ = 3014 cm^{-1} (C–H), 2098 (C=O), 2038 (C=O), 1965 (C=O), 1446, 1385, 1340, 1035, 962, 872, 621, 576, 492. ^1H NMR (250 MHz, [D_6]DMSO): δ = 0.82–1.25 (m, 16 H, *c*Pr-H), 1.30 (t, ^3J = 7.6 Hz, 3 H, OCH_2CH_3), 1.60–1.85 (m, 4 H, *c*Pr-H), 4.35 (q, ^3J = 7.6 Hz, 2 H, OCH_2CH_3). ^{13}C NMR (62.9 MHz, [D_6]DMSO, add. DEPT): δ = 6.22, 7.17 (+, *c*Pr-C), 8.34, 8.94, 9.04, 9.18 (–, *c*Pr-C), 15.28 (+, OCH_2CH_3), 72.67 (–, OCH_2CH_3), 95.96 [C_{quat}, C-2(5)], 106.11 [C_{quat}, C-3(4)], 138.60 (C_{quat}, C-1), 205.30 [C_{quat}, $Fe(CO)_3$].

Tricarbonyl(η⁵-1-hydroxy-2,3,4,5-tetracyclopropylcyclopenta-2,4-dienylium)iron Tetrafluoroborate (11): To a solution of 150 mg (0.395 mmol) of **3** in 30 mL of anhydrous CH_2Cl_2 was added at 0 °C HBF_4·Et_2O (54%, 48.8 μL, 0.357 mmol), and the mixture was stirred for 30 min. After removal of the solvent in vacuo and recrystallization [Et_2O/hexane (1:2)] 123 mg (74%) of **11** was isolated as a yellow solid, m.p. 146 °C. IR (KBr): $\tilde{\nu}$ = 2095 cm^{-1} (C≡O), 2027 (C≡O), 1520 (C=O), 1460, 1363, 1084, 953, 822, 761, 699, 619, 566. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.20 (m, 16 H, *c*Pr-H), 1.56 (m_c, 2 H, *c*Pr-H), 1.65 (m_c, 2 H, *c*Pr-H), 6.80 (br. s, 1 H, OH). ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 5.45, 7.27 (+, *c*Pr-C), 8.63 (–, 2 C, *c*Pr-C), 8.89, 8.92 (–, *c*Pr-C), 92.75 [C_{quat}, C-2(5)], 105.68 [C_{quat}, C-3(4)], 142.63 (C_{quat}, C-1), 204.61 [C_{quat}, $Fe(CO)_3$].

Tricarbonyl(1-hydroxy-2,3,4,5-tetracyclopropylcyclopenta-2,4-dienylium)iron Trifluoromethanesulfonate (12): To a solution of 260 mg (0.684 mmol) of **3** in 30 mL of anhydrous CH_2Cl_2 was added at 0 °C 58.0 μL (0.655 mmol) trifluoromethansulfonic acid in Et_2O,

and the mixture was stirred for 30 min. After removal of the solvent in vacuo and recrystallization [Et_2O/hexane (1:2)] 274 mg (79%) of **12** was isolated as a yellow solid, m.p. 164 °C. IR (KBr): $\tilde{\nu}$ 2098 cm^{-1} (C≡O) 2035 (C≡O), 1521 (C=O), 1471, 1363, 1224, 1071, 959, 813. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.97–1.26 (m, 16 H, *c*Pr-H), 1.61 (m_c, 4 H, *c*Pr-H), 6.95 (br. s, 1 H, OH). ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 5.76 (+, 2 C, *c*Pr-C), 7.16 (+, 2 C, *c*Pr-C), 8.62 (–, 2 C, *c*Pr-C), 8.71 (–, 2 C, *c*Pr-C), 8.86 (–, 2 C, *c*Pr-C), 9.13 (–, 2 C, *c*Pr-C), 93.08 [C_{quat}, 2 C, C-2(5)], 105.56 [C_{quat}, 2 C, C-3(4)], 120.21 (d, ^1J(C,F) = 319.5 Hz, C_{quat}, CF_3), 142.85 (C_{quat}, C-1), 204.72 [C_{quat}, 3 C, $Fe(CO)_3$]. MS (70 eV), *m*/*z* (%): 380 (11) [$M^+ - CF_3SO_3H$], 352 (40) [$M^+ - CF_3SO_3H$ – CO], 324 (7) [$M^+ - CF_3SO_3H$ – 2 CO], 296 (54) [$M^+ - CF_3SO_3H$ – 3 CO], 268 (21), 240 (100) [$M^+ - CF_3SO_3H - Fe(CO)_3$]. $C_{21}H_{21}F_3FeO_7S$ (530.3): calcd. C 47.56, H 3.99; found C 47.34, H 3.74.

Acknowledgments

This work was supported by the State of Niedersachsen as well as the Fonds der Chemischen Industrie. The authors are grateful to Dr. Burkhardt Knieriem, Göttingen, for his careful proofreading of the final manuscript.

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Received: June 16, 2005
Published Online: October 25, 2005

