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THE FIRST CARBONYL IRON COMPLEXES WITH DIHYDROACEPENTALENE LIGANDS

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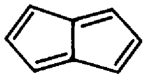
Abstract—1,4-Dibromo- (**8**) as well as 1,4,7-trichloro- (**11a**) and 1,4,7-tribromotriquinacene (**11b**) react with $Fe_2(CO)_9$ in THF to yield (dihydroacepentalene)hexacarbonyldiiron complexes **9** and **10**, the first representatives with a 7,10-dihydroacepentalene ligand. By reaction with $Fe_2(CO)_9$, the readily accessible 4,7-bis(dialkylamino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraenes **14**, derivatives of the unknown 4,7-dihydroacepentalene, were transformed into their tricarbonyliron complexes **15**. Upon reduction with sodium in THF, the η^4-(diene)tricarbonyliron **15** selectively gave the novel 1,10-η^2-(olefin)tricarbonylferrates(−2) **17** as a result of a twofold electron transfer. The intermediate green radical anion **16**, which is persistent in the absence of excess sodium, was characterized by its ESR signal. Complexes **17** are the first of their class with complete structural characterization by ^{1}H- and ^{13}C-NMR spectroscopy.

While pentalene (**1**) is a known molecule, albeit a highly reactive polyolefin with an extreme tendency to dimerize,[1] no reports have appeared as yet on attempted or even successful, generation of the etheno-bridged pentalene **2**. The so-called acepentalene (**2**) with its peri-anellated system of three 5-membered rings consists of three overlapping fulvene units. According to MO calculations, **2** should have a triplet ground state.[2] Even if this degeneracy were lifted by a possible Jahn–Teller distortion as in cyclobutadiene,[3] **2** would remain an extremely reactive polyolefin. It was therefore particularly challenging to test the concept of generating **2** within the ligand sphere of a transition metal, as has successfully been used to stabilize many elusive dienes and polyenes.[4] Indeed, acepentalene complexes of type **3** would be closed shell systems[5] and a binuclear complex such as **4** might also be a stable species. As triquinacene (**5**)[6,7] contains the same tricyclic skeleton as **2**, two strategies for the stepwise introduction of two additional double bonds were envisaged. The first one calls for the generation of a tetraene complex such as **6**, through some 1,4-elimination from appropriately 1,4-disubstituted triquinacene derivatives. This should be done most favourably by reaction with suitable metal carbonyls, as the free tetraene ligand in **6**, according to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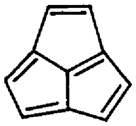
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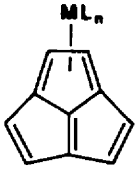
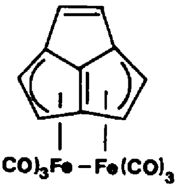

3 a) ML_n = CoCp
b) ML_n = Fe(CO)$_3$



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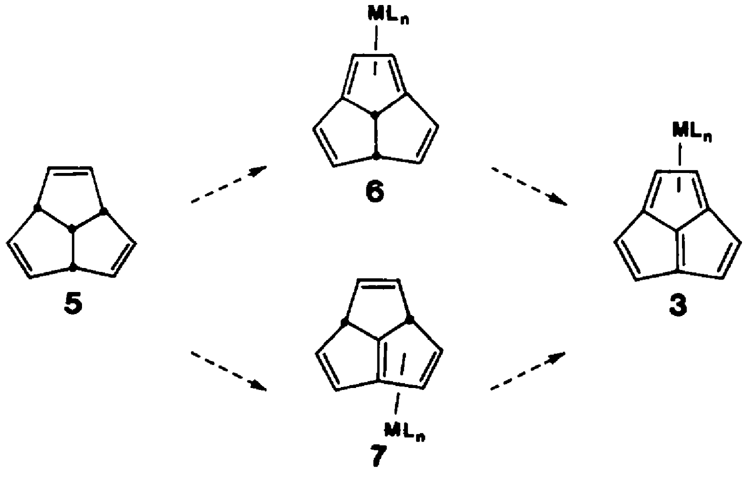


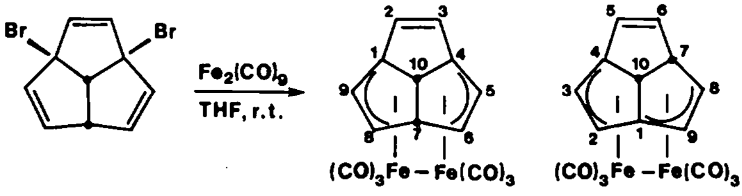
semiempirical MO and force field calculations,[8,9] is a highly strained twofold bridgehead olefin, probably too reactive to be isolated *per se*. The second concept is based on the surprisingly facile access to 4,7-bis(dialkylamino)tricyclo[5.2.1.0^{4,10}]deca - 1(10),2,5,8 - tetraenes (**14**),[9] which are derivatives of the dihydroacepentalene ligand in **7**. After protection of their cross-conjugated triene unit as in **7**, a suitable 1,4-elimination could lead to acepentalene complexes of type **3**. We here report the execution of both these strategies and the respective unforeseen results.

Reactions of 1,4-*dihalo- and* 1,4,7-*trihalotriquinacenes with* $Fe_2(CO)_9$

In analogy to 1,4-dehalogenations with $Fe_2(CO)_9$ known for primary or secondary bisallylic halides[10] 1,4-dibromotriquinacene (**8**) was treated with a 7.5 fold molar excess of $Fe_2(CO)_9$ in tetrahydrofuran (THF).[11] After 24 h at 25° the originally purple mixture had turned deep red. After a total of 48 h a red, non-crystalline compound was isolated (15%) by column chromatography. Its IR spectrum showed five absorptions at 1957, 1990, 2020, 2040, and 2057 cm^{-1} characteristic of terminal carbonyl ligands, which evidenced a dinuclear carbonyl iron complex. This was confirmed by the mass spectrum with a series of peaks corresponding to a molecular ion (m/e = 408) and the successive loss of six carbonyl ligands, as well as two iron atoms. The remaining organic ligand with m/e = 128 then must have been a dihydroacepentalene, indicating that 1,4-debromination of **8** with *in situ* complexation had taken place. The product was unequivocally proved by its five-signal ^{1}H-NMR spectrum (see Table 1) to be the C_s-symmetrical dihydroacepentalene complex **9**. Coupling correlations were identified by double resonance experiments; irradiation at the resonance frequency of 7-H largely simplified the spectrum, as couplings to 5(9)-H, 6(8)-H, and 10-H were eliminated.

Surprisingly, in one run, reaction of **8** with a 5 fold excess of $Fe_2(CO)_9$ under otherwise identical conditions yielded a product with additional ^{1}H-NMR signals, but almost identical IR and mass spectra. Careful inspection of the ^{1}H-NMR data led to the conclusion that a 1 : 2 mixture of **9** and most likely the less symmetrical **10** had been formed (yield 15%).

Although all coupling relationships could be established for **10**, it is inconsistent that the signal assigned to 3-H is at relatively high field with a rather small $^3J_{2,3}$ = 3.0 Hz. It is not yet understood why different product compositions were obtained in the two runs differing only in the $Fe_2(CO)_9$ excess. To exclude a dynamic process,[4b,12] which could mask the absence of a plane of symmetry in **9**, ^{1}H-NMR spectra were recorded at temperatures down to −100°, without any significant changes observable. In addition, the spectrum of **9** remained unchanged up to 73°, thus excluding an isomerization process of **9** to **10** up to this temperature. It was not tested if **10** conversely rearranges to the more symmetrical **9** at elevated temperatures. By analogy to this reaction of **8**, 1,4,7-trihalotriquinacenes **11** should lead to the corresponding 7-halodihydroacepentalene complexes, which would be ideal precursors to acepentalene complexes of type **4**.



8 **9** **10**

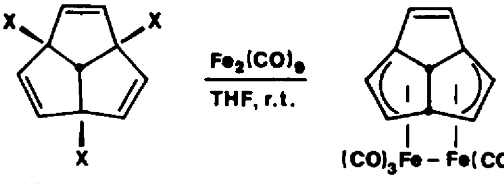
Upon reaction of 1,4,7-tribromotriquinacene (**11b**) with $Fe_2(CO)_9$, however, the same dihydroacepentalene complex **9** was obtained, even with a slightly

Table 1. ^{1}H-NMR data of 1,8,9η^3; 4-6η^3-(tricyclo[5.2.1.0^{4,10}]deca-1,3,5,8-tetraene)hexacarbonyldiiron(Fe—Fe) (**9**) and 1,8,9η^3; 2-4η^3-(tricyclo[5.2.1.0^{4,10}]deca-1,3,5,8-tetraene)hexacarbonyldiiron(Fe—Fe) (**10**) (270 MHz, C_6D_6)

Compound	δ_{TMS}	M	H	Coupling constants [Hz]	
9	2.72	dt	10-H	$^3J_{7,10} = 7.5$	$^4J_{2(3),10} = 1.1$
	3.35	dtt	7-H	$^3J_{6(8),7} = 2.7$	$^4J_{5(9),7} = 1.9$
	4.90	dd	6(8)-H	$^3J_{5(9),6(8)} = 5.3$	
	5.38	dd	5(9)-H		
	6.60	d	2(3)-H		
10[a]	3.35	m	7-H	$^3J_{7,10} = 7.5$ $^3J_{6,7} = 2.3$	$^3J_{7,8} = 2.4$ $^4J_{5,7} = 2.3$
	3.48	dd	3-H	$^3J_{2,3} = 3.0$	$^4J_{3,10} = 1.6$
	3.96	dm	10-H		
	5.38	d	2-H		
	5.52	dd	8-H	$^3J_{8,9} = 5.4$	
	5.87	dd	9-H	$^4J_{7,9} = 2.0$	
	6.13	dd	5-H	$^3J_{5,6} = 5.3$	
	6.22	dd	6-H		

[a] Determined from the spectrum of the 1 : 2 mixture of **9** and **10**.

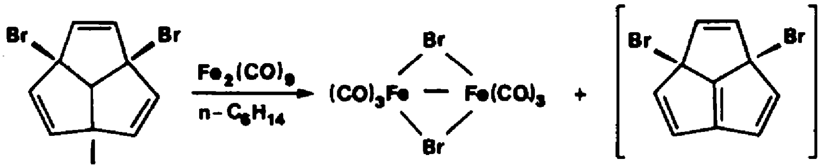
higher yield (20%). The trichloride **11a** under identical conditions also yielded **9** (7%), unequivocally identified by its ^{1}H-NMR spectrum.



11 a) X = Cl
b) X = Br

9

It can only be speculated that in this reaction **9** was formed either by reductive elimination of the third halogen atom after a 1,4-dehalogenation, or by a hydrogenation of the strained central double bond in an acepentalene complex, with the solvent THF acting as the hydrogen source. To avoid this possibility, **11b** was reacted with $Fe_2(CO)_9$ in n-hexane. The mixture turned deep red after 30 min, and after 18 h a red compound, extremely sensitive to air and heat, was isolated by column chromatography at −40°. The product showed no ^{1}H-NMR signal, but was identified by mass and IR[13] spectroscopy as di-μ-bromobis(tricarbonyliron)(Fe—Fe) (**12**). Compound **12** had previously been described by Koerner von Gustorf *et al.*[14] to be formed from t-butylbromide and $Fe(CO)_5$ or $Fe_2(CO)_9$ in pentane, along with hydrogen and isobutene, and it had been shown to be a reaction product of $Fe(CO)_4$ and HBr. This supports the conclusion that **11b** was first dehydrobrominated by $Fe_2(CO)_9$ in hexane and the hydrogen bromide subsequently yielded **12**. This is in line with earlier observations[8b,9] that **11b** can be dehydrobrominated with bases. Unfortunately, all attempts to isolate the elimination product, tetraene **13**, or any complexes thereof, were unsuccessful. Apparently, **13** is extremely reactive and decomposes prior to complexation, leading only to intractable materials.



11b

12

13

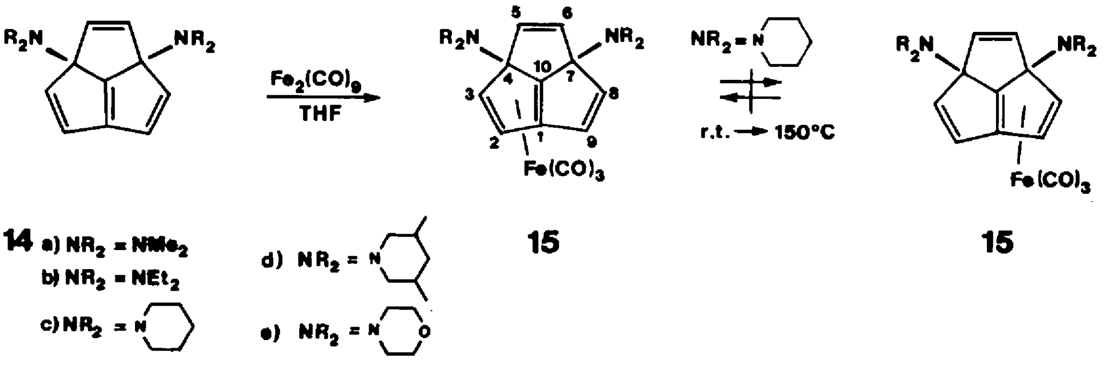
Tricarbonyliron complexes of bis(dialkylamino)tetraenes **14**

As the bis(dialkylamino)tetraenes **14** are readily accessible from trihalides **11** and secondary amines, complexation of their cross-conjugated triene unit and subsequent reductive elimination of the dialkylamino substituents was conceived as an alternative strategy to complexes **3**. In a first trial run, **14c** was reacted with (benzylideneacetone)tricarbonyliron[15] in refluxing benzene to avoid unselective formation of a variety of olefin complexes.[4b,16] The yellow complex **15c** was isolated by column chromatography, but the complete removal of benzylideneacetone was troublesome.

This difficulty was circumvented by reacting tetraenes **14** with $Fe_2(CO)_9$ in THF at 25°, which gave, surprisingly, only (diene)tricarbonyliron complexes **15** as yellow oils in yields ranging from 4% (**15a**, large losses upon purification) to 64% (**15b**). The structures of **15** were unequivocally proven by their characteristic IR,[4c,17] ^{1}H-NMR, ^{13}C-NMR and mass spectra. As the plane of symmetry in **14** is lifted due to complexation, the ^{1}H-NMR signals for the olefinic protons change from a singlet and an AB system in **14** to three AB patterns in **15** (see Table 2). Although there is no experimental evidence, the tricarbonyliron units in **15** are, for steric reasons, most likely located on the side opposite to the amino substituents.

The ^{1}H-NMR signal assignments for **15** are in accord with those for other tricarbonyliron complexes of cross-conjugated trienes.[16,18] They take into account that the chemical shifts of protons bound to coordinated carbon atoms suffer a larger change than those of other protons. Such chemical shift changes ($\Delta\delta$) are smaller for the "inner" protons on a coordinated diene unit than for the "outer" protons.[19]

^{13}C-NMR signal assignments were made in a similar



14 a) NR_2 = NMe_2
b) NR_2 = NEt_2
c) NR_2 = N
d) NR_2 = N
e) NR_2 = N O

15

15

Table 2. ^{1}H-NMR data of 1,2,3,10η^4-(4,7-bis(dialkylamino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene)tricarbonyliron **15** (olefinic protons)[a]

Compound	Solvent	ν(MHz)	2-H	3-H	5-H	6-H	8-H	9-H	$^3J_{2,3}$	$^3J_{5,6}$	$^3J_{8,9}$	$^5J_{3,9}$ (Hz)
15a	$CDCl_3$	270	5.21	3.81	6.07	5.68	6.61	6.71	3.1	6.0	5.5	n.o.
15b	$CDCl_3$	270	5.23	3.70	5.93	5.76	6.51	6.56	3.1	6.0	5.5	n.o.
	[D_8]-THF	270	5.41	3.81	5.94	5.72	6.54	6.61	3.1	6.0	5.5	n.o.
	C_6D_6	270	4.73	3.33	5.66	5.52	6.14	6.26	3.1	6.0	5.5	n.o.
15c	$CDCl_3$	270	5.19	3.82	6.08	5.67	6.56	6.71	3.1	6.0	5.4	n.o.
	[D_8]-THF	80	5.35	3.95	6.14	5.67	6.59	6.77	3.4	6.1	5.2	n.o.
	C_6D_6	270	4.71	3.51	5.90	5.44	6.20	6.45	3.1	6.1	5.4	0.6
15d	C_6D_6	270	4.70	3.59	5.90	5.52	6.19	6.42	3.1	6.0	5.4	n.o.
15e	C_6D_6	80	4.66	3.38[b]	5.71	5.43	6.13	6.29	3.2	6.1	5.4	n.o.

[a] δ_{TMS} in ppm, signals of the amino groups see Experimental.

[b] Covered in part by the signal of the morpholino substituent.

way. They are all (Table 3) within the expected range,[19,20] and the $\Delta\delta$ values for the coordinated carbon atoms C-1(2,3,10) are by far larger than those for the non-coordinated carbon atoms. The carbonyl-ligands give rise to only one signal, as usual for tricarbonyliron complexes.[21]

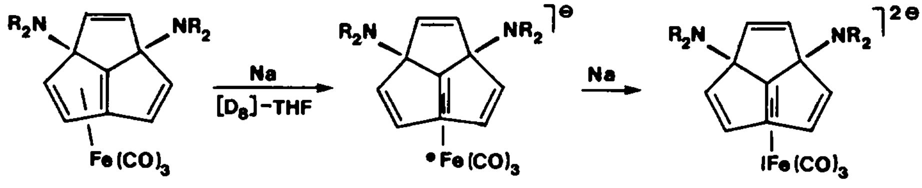
The conceivable degenerate metallotropic rearrangement in complexes **15**, which would make the pairs 2-H/9-H, 3-H/8-H, and 5-H/6-H equivalent, could not be observed in the ^{1}H-NMR spectra of the bis(1′-piperidinyl) derivative **15c** in [D_5]-bromobenzene at temperatures up to 150°. According to recent MO calculations on complexes of type **3**,[22] such a process might well have a reasonably high activation energy and therefore not be observable at 150°. At higher temperatures **15c** started to decompose.

Reduction of dihydroacepentalene complexes **15** *with sodium*

Following the above mentioned strategy, complexes **15b** and **c** were reacted with sodium in [D_8]-THF, under NMR monitoring.[23] In both cases the originally yellow solutions, upon contact with sodium wire, turned green within 3 h, and yellow again after another 15 h. The green intermediates appeared to be paramagnetic species as they gave no NMR signals. The intermediate from **15c** showed a broad singlet in the ESR spectrum, which confirmed its nature as a radical anion. Its g-value of 2.01593 indicated substantial unpaired electron spin density at the iron atom.[24] Without exposure to excess sodium, the green radical persisted for several weeks at room temperature (25°).

The ^{1}H-NMR spectra (Table 4) of the final reduction product showed only two doublets and a singlet (intensity ratio 1 : 1 : 1) in the olefinic region. This implies a plane of symmetry in the reduced complexes. The coupling constants (4.9 and 4.8 Hz) are larger than expected for protons bound to a coordinated double bond. The dialkylamino groups apparently did not leave the parent molecule upon reduction, since the methylene protons of the product from **15b** showed up as two multiplets at 2.73 and 3.38 ppm with a geminal coupling constant $^2J = -14.2$ Hz, indicating diastereotopicity impossible in diethylamide anions.

The ^{13}C-NMR data (Table 5) of the reduction product from **15b** confirmed its C_s-symmetry. Three signals at 122.3, 136.8, and 142.8 ppm, with $^1J_{C,H}$ values around 160 Hz are typical for olefinic carbon atoms not coordinated to iron. The quaternary carbons C-4(7), bearing the amino substituents, show up at 86.6 ppm, similar to the corresponding ones in **14** and **15**. C-1 and C-10 give rise to resonances at 78.7 and 68.7 ppm, respectively, the signal of C-1 being broadened due to small couplings to the neighbouring olefinic protons. The unusually small chemical shifts of the quaternary olefinic C-1(10) show these atoms to be coordinated to the iron, which is consistent with the postulated C_s-symmetry. The resonances of the carbonyl ligands appear at 237.6 ppm, which is an unusual value for an olefin iron carbonyl complex.[19,20,25] The additional signal at 225.8 ppm, 12.5 times less intensive than the other one, most likely stemmed from a very minor side product.



15 **16** **17**

The ^{1}H- and ^{13}C-NMR data strongly corroborate the structure **17** for the reduced complexes from **15**. These η^2-(olefin)tricarbonylferrates(−2) **17** apparently are formed, because the added electrons are predominantly located on the iron atom rather than the tetraene ligand. Some excess electron density is donated back to the tetraene ligand as evidenced by the considerable upfield shift, especially of C-1(10) in **17b** by 83.5 and 96.5 ppm (see Table 6) compared to those in

Table 3. Selected ^{13}C-NMR data (100.63 MHz) of tricarbonyliron complexes **15b** and **c**

Compound	Observ.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CO
15b[b]	δ_{TMS} (ppm)	116.1	77.0	78.4	78.3	137.0	125.5	83.5	141.2	147.3	88.6	212.3
	Multipl.	bs	dd	dd	s	dd	dd	s	d	d	s	s
	$^1J_{CH}$ (Hz)	—	177.7	168.7	—	167.1	170.9	—	164.2	164.9	—	—
	$^2J_{CH}$ (Hz)	—	4.1	6.5	—	2.6	2.8	—	—	—	—	—
	$\Delta\delta$[c]	−46.1	−59.2	−70.1	−3.7	+8.2	−3.3	+1.5	+5.0	−1.2	−76.6	—
	Δ^1J_{CH}[d]	—	+11.5	+3.2	—	+2.9	+6.7	—	−2.0	−0.6	—	—
15c[e]	δ_{TMS} (ppm)	115.6	77.1	79.5	76.3	137.8	126.6	83.1	138.3	144.3	87.8	212.8
	Multipl.	s	d	dd	s	d	d	s	d	d	s	s
	$^1J_{CH}$ (Hz)	—	178.1	169.9	—	165.5	165.2	—	162.8	169.7	—	—
	$^2J_{CH}$ (Hz)	—	—	6.2	—	—	—	—	—	—	—	—
	$\Delta\delta$[c]	−47.3	−58.8	−68.3	−5.8	+8.2	−3.0	+1.0	+2.4	−3.5	−75.6	—
	Δ^1J_{CH}[d]	—	+12.7	+4.5	—	+0.1	−0.2	—	−2.6	−2.7	—	—

[a] Signals of the dialkylamino groups see Experimental.
[b] Solvent $CDCl_3$.
[c] $\Delta\delta = \delta_{15} - \delta_{14}$ in ppm.
[d] $\Delta^1J_{CH} = {}^1J_{CH}(15) - {}^1J_{CH}(14)$ in Hz.
[e] Solvent C_6D_6.

14b. In contrast, the ^{13}C-resonances of the CO ligands are shifted downfield by 25.3 ppm on going from **15b** to **17b**. In accord with the ESR spectrum, the green radical anion most likely possesses structure **16**.

The formation of **17** from **15** occurs in analogy to the well-known reduction of $Fe(CO)_5$ with sodium to afford disodium tetracarbonylferrate(−2) ($Na_2[Fe(CO)_4]$),[26a] which can be accelerated by benzophenone as an electron transfer catalyst.[26b,c] In **15**, the tetraenic ligand may act as the electron transfer catalyst. The ionic complexes **17** are extremely sensitive towards oxygen and water. An attempted chromatographic purification failed. Because of the extreme sensitivity of **17**, several attempts to record its CO stretching frequencies in the IR spectrum were unsuccessful. IR and mass spectra only showed signals of precursor **15**. This, however, appears to be the result of a reoxidation of **17**, as the NMR spectra did not show any signals of **15**.

Compared to Collman's reagent, **17** contains an η^2-olefin ligand instead of a CO ligand. Reports about reductions of (diene)tricarbonyliron complexes are very scarce. With sodium–potassium alloy, radical anions and/or products of two-electron reductions were observed, but not fully characterized by spectroscopic methods except ESR.[27] Through cyclic voltammetry and polarography indirect evidence for the formation of ferrate(−2) complexes was obtained.[27,28] The cyclic voltammogram of **15c** shows the reduction to take place, but in two irreversible wave steps at −2.19 and −2.63 V vs SCE. The irreversibility is not completely understood, but may be due to a primary reduction of the tetraenic ligand immediately followed by an electron transfer from the ligand to the iron atom, with the tetraenic ligand acting as an electron carrier.

It certainly deserves special comment that apparently only the 1,10-η^2-complexes **17** are formed from **15**, and not the less symmetric 2,3η^2-compounds. This selectivity can be rationalized with a kinetic and a thermodynamic argument. In contrast to the 2,3-double bond, the 1,10-double bond is conjugated to *two* neighbouring double bonds. This may lower the transition state leading to **16** with respect to the one leading to the unsymmetric complex. In addition, complexation at the highly strained double bond (C-1)═(C-10) should be thermodynamically more favourable because of the possible strain relief upon complexation.[29]

DISCUSSION

Although the original goal was not reached, there was a reward for this investigation. The present results show that by proper choice of conditions reactions of 1,4,7-trihalo- and other 1,4,7-trisubstituted triquinacenes with metal carbonyls may eventually lead to acepentalene complexes of type **3** or **4**. Indeed, **9** is the first complex containing the yet unknown dihydroacepentalene ligand tricyclo[5.2.1.0^{4,10}]deca-1,3,5,8-tetraene. Crystalline complexes of this type may be used to study structural implications in their strained skeleton. The new complexes **15** contain the tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene ligand, an isomeric dihydroacepentalene, albeit in 4,7-disubstituted form. With better leaving groups in these positions, e.g. quaternized amino substituents, complexes of type **15** might well prove the feasibility of the

Table 4. ^{1}H-NMR data (δ_{TMS}, [D_8]-THF) of the olefinic protons of disodium-1,10η^2-(4,7-bis(dialkylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10),2,5,8-tetracarbonylferrates(−2) **17**[a]

Compound	Observ.	2-H	3-H	5-H	6-H	8-H	9-H
17b	δ^b	6.11[c]	4.70[c]	5.97[d]	5.97[d]	4.70[c]	6.11[c]
	$\Delta\delta$(**14b**)[e]	−0.56	−1.58	+0.40	+0.40	−1.58	−0.56
	$\Delta\delta$(**15b**)[e]	+0.70	+0.89	+0.03	+0.25	−1.84	−0.50
17c	δ^f	6.16[g]	4.72[g]	5.90[d]	5.90[d]	4.72[h]	6.16[h]
	$\Delta\delta$(**14c**)[e]	−0.54	−1.56	+0.31	+0.31	−1.56	−0.54
	$\Delta\delta$(**15c**)[e]	+0.76	+0.75	−0.17	+0.30	−1.89	−0.66

[a] Signals of the amino groups see Experimental.
[b] 270 MHz.
[c] Doublet, $^3J_{2(9),3(8)} = 4.9$ Hz.
[d] Singlet.
[e] $\Delta\delta(X) = \delta_{17} - \delta_X$.
[f] 80 MHz.
[g] Doublet, $^3J_{2(9),3(8)} = 4.8$ Hz.

envisaged route to the acepentalene complex **3**, i.e. reductive 1,4-elimination of the 4,7-substituents.

To our knowledge complexes **17b,c** are the first representatives of this class and have been fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy. Recently, we generated the corresponding ionic complex from simple (cyclohexadiene)tricarbonyliron with sodium, sodium–potassium alloy or even $LiBEt_3H$, and spectroscopically assigned the same type of η^2-(monoene)tricarbonylferrate(−2) structure.[30] In contrast to $Na_2[Fe(CO)_4]$ (so-called Collman's reagent),[26] (olefin)tricarbonylferrates(−2) like **17** are very soluble in THF, due to their organic ligand. These new η^2-(olefin)iron complexes may well prove to have a similar synthetic potential as $Na_2[Fe(CO)_4]$. In particular, useful reactions of such η^2-(olefin)ferrates (−2) with electrophiles (e.g. alkylating RX) can be conceived.[30] In addition, they might offer the advantages of reactions which can be done under homogeneous conditions.

EXPERIMENTAL

General remarks. All operations were carried out under Ar, all solvents were degassed and subsequently saturated with Ar three times. Column chromatography was performed with silica gel 60 of E. Merck, which had been degassed (0.1 Torr) and then put under Ar (5 cycles of degassing and Ar addition). UV (nm): Perkin–Elmer–Hitachi 200; IR (cm^{-1}): Perkin-Elmer 297, 399, Beckman Acculab 4; MS: Varian MAT 311, MAT 311A, CH7; HRMS: Varian MAT 311, MAT 731; ^{1}H-NMR: Bruker WP 80 (80 MHz), WH 270 (270 MHz), WM 400 (400 MHz); ^{13}C-NMR: Bruker WH 270 (67.91–67.93 MHz), WM 400 (100.62 MHz). s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet; mc, multiplet centred at . . .; ESR: Bruker 420S; cyclic voltammetry: Princeton Applied Research 170.

General procedure for reactions of halotriquinacenes with $Fe_2(CO)_9$ *in THF.* Halotriquinacene and diironenneacarbonyl† were placed in a 50 ml round bottom flask equipped with a gas inlet. The flask was evacuated (0.1 Torr) and filled with Ar; 30 ml anhyd, freshly distilled THF were added. The mixture was again degassed three times, and then stirred at 25°. $Fe_2(CO)_9$ dissolved within 2 h, and the mixture turned dark purple. After 1 d the soln was red. TLC (toluene) showed one red spot ($R_f = 0.64$). After 2 d the mixture was filtered through a sintered glass filter, the solvent and $Fe(CO)_5$ were evaporated *in vacuo*. The residue was chromatographed with benzene (70 g silica gel, column 40 × 3 cm).

1,8,9η^3; 4 - 6η^3 - *(Tricyclo*[5.2.1.$0^{4,10}$]*deca* - 1,3,5,8 - *tetraene)hexacarbonyldiiron*(Fe—Fe) (**9**)

(a) Compound **8**[8] (159 mg, 0.55 mmol) was reacted with 1502 mg (4.13 mmol, 1 : 7.5) $Fe_2(CO)_9$, as described above. Yield 34 mg (0.08 mmol, 15%) **9**; red, air-sensitive oil.

(b) Compound **11b**[8] (240 mg, 0.65 mmol) was reacted with 1785 mg (4.90 mmol, 1 : 7.5) $Fe_2(CO)_9$. The mixture turned green–yellow after 30 min, dark yellow after 2 h, and red after 15 h. Yield 53 mg (0.07 mmol, 20%) **9**.

(c) Compound **11a**[31] (165 mg, 0.71 mmol) was reacted with 1292 mg (3.55 mmol, 1 : 5) $Fe_2(CO)_9$. Yield 20 mg (0.05 mmol, 7%) **9**. IR (film, C_6D_6) 2057, 2040, 2020, 1990, 1957. ^{1}H-NMR see Table 1. MS (70 eV) *m/e* (rel. int.) 408 (M^+, 30), 380 ($M^+ - CO$, 28), 352 ($M^+ - 2CO$, 24), 324 ($M^+ - 3CO$, 32), 296 ($M^+ - 4CO$, 37), 268 ($M^+ - 5CO$, 72), 240 ($M^+ - 6CO$, 100), 184 ($M^+ - 6CO - Fe$, 73), 131 (76), 129 ($M^+ + 1 - Fe_2(CO)_6$, 56), 128 ($M^+ - Fe_2(CO)_6$, 56), 115 (14), 112 (Fe_2, 30). HRMS: calc ($C_{16}H_8Fe_2O_6$) 407.90186; found 407.90121.

1,8,9η^3; 4 - 6η^3 - (*Tricyclo*[5.2.1.$0^{4,10}$]*deca* - 1,3,5,8 - *tetraene)hexacarbonyldiiron* (**9**) *and* 1,8,9η^3; 2 - 4η^3 - (tricyclo-[5.2.1.$0^{4,10}$]*deca* - 1,3,5,8 - *tetraene)hexacarbonyldiiron* (**10**)

Compound **8** (150 mg, 0.52 mmol) was reacted with 948 mg (2.60 mmol, 1 : 5) $Fe_2(CO)_9$, as described above. Yield 32 mg (0.08 mmol, 15%) mixture (1 : 2, determined by ^{1}H-NMR) of **9** and **10**; red, air-sensitive oil. IR (film, C_6D_6, mixture) as for **9**. ^{1}H-NMR see Table 1. MS (70 eV, mixture) as for **9**.

Reaction of 1,4,7-*tribromotriquinacene* (**11b**) *with* $Fe_2(CO)_9$ *in* n-*hexane*

Compound **11b** (210 mg, 0.57 mmol) and 1562 mg (4.29 mmol, 1 : 7.5) $Fe_2(CO)_9$ were placed in a 50 ml round bottom flask equipped with a gas inlet, the flask was evacuated (0.1 Torr) for 30 min, and filled with Ar. Freshly distilled anhyd n-hexane (35 ml) was added, and the mixture was stirred at 25°. After 30 min it turned deep red and after 18 h it was filtered through a sintered glass filter. The solvent and $Fe(CO)_5$ were removed *in vacuo* and the residue was chromatographed at −40° with toluene (70 g silica gel, column 40 × 3 cm). Yield 20 mg (0.05 mmol, 6%) di-μ-bromobis(tricarbonyliron)(Fe—Fe) (**12**); red, extremely air- and heat-sensitive oil, identified by IR, MS.[13,14a]

1,2,3,10η^4 - 4,7 - (*Bis(dialkylamino)tricyclo*[5.2.1.$0^{4,10}$]*deca* - 1(10),2,5,8 - *tetraene)tricarbonyliron* (**15**)

General procedure. Tetraene **14**[8b,9] and $Fe_2(CO)_9$ were placed in a round bottom flask equipped with a gas inlet. The

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† Diironenneacarbonyl was obtained by photolysis of pentacarbonyliron in glacial acetic acid.[11]

Table 5. Selected ^{13}C-NMR data of disodium(1,10η^2-(4,7-bis(diethylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10),2,5,8-tetraene)tricarbonylferrate(−2) (**17b**)^a

Observ.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CO
$\delta_{TMS}{}^c$	78.7(bs)	136.8(d)	142.8(d)	86.6(bs)	122.3(dd)	122.3(dd)	86.6(bs)	142.8(d)	136.8(d)	68.7(s)	237.7(s)
$^1J_{C,H}{}^d$	—	160.2	160.1	—	158.8	158.8	—	160.1	160.2	—	—
$^2J_{C,H}{}^d$	—	—	—	—	4.4	4.4	—	—	—	—	—
$\Delta\delta$(**14b**)^b	−83.5	+0.6	−5.7	+3.6	−6.5	−6.5	+3.6	−5.7	+0.6	−96.5	—
$\Delta\delta$(**15b**)^b	−37.3	+59.8	+64.4	+8.3	−14.7	−3.2	+3.1	+1.6	−10.6	−19.9	+25.3

^{a}Spectrometer frequency 67.93 MHz, solvent [D_8]-THF, signals of the amino groups see Experimental.

$^b\Delta\delta(X) = \delta_{17b} - \delta_X$.

^{c}In ppm.

^{d}In Hz.

flask was evacuated (0.1 Torr) for 15 min, and then filled with Ar. Freshly distilled anhyd THF (50 ml) was added, the mixture was degassed three times and then stirred at 25°. The solvent and $Fe(CO)_5$ were removed *in vacuo*. The residue was chromatographed with t-butylmethyl ether (MTBE) on 70 g silica gel (column 40 x 3 cm). The orange or yellow complexes **15** were obtained together with some green $Fe_3(CO)_{12}$. When the separation of $Fe_3(CO)_{12}$ was unsatisfactory, the solvent was removed *in vacuo* from the impure fractions, and the residue kept at −30° for 3 h. Then *ca* 3 ml MTBE was added to dissolve mainly **15**, the soln decanted, and this procedure repeated if necessary. The combined solns, containing only small amounts of $Fe_3(CO)_{12}$, were chromatographed with n-hexane–MTBE–trimethylamine 100:20:1 (70 g silica gel, column 40 x 3 cm) to yield **15** as orange or yellow oils, crystallizing in part.

1,2,3,10η^4-(4,7-*Bis(dimethylamino)tricyclo*[5.2.1.$0^{4,10}$]*deca*-1(10),2,5,8-*tetraene)tricarbonyliron* (**15a**)

Compound **14a** (120 mg, 0.56 mmol) containing 80 mg (0.31 mmol) 1,4,7-tris(dimethylamino)triquinacene (unseparated mixture from the reaction of **11b** with dimethylamine) was reacted with 1020 mg (2.80 mmol, 1:5) $Fe_2(CO)_9$ for 3 d, as described above. Yield 7 mg (0.02 mmol, 4%) **15a**, bright yellow, moderately air-sensitive oil; losses by chromatography. IR (film) 3060, 3045, 2930, 2860, 2770, 2045, 1985, 1960, 1460, 1260, 1050, 765. ^{1}H-NMR (270 MHz, $CDCl_3$) olefinic protons see Table 2, δ 2.21 (s, 6H, $N(CH_3)_2$), 2.24 (s, 6H, $N(CH_3)_2$). MS (70 eV) *m/e* (rel. int.) 326 ($M^+ - CO$, 13), 298 ($M^+ - 2CO$, 73), 270 ($M^+ - 3CO$, 23), 227 ($M^+ - 3CO - N(CH_3)_2 + H$, 100), 184 ($M^+ - 3CO - 2N(CH_3)_2 + 2H$, 66), 131 ($M^+ - Fe(CO)_3 - 2N(CH_3)_2 + 3H$, 25), 128 ($M^+ - Fe(CO)_3 - 2N(CH_3)_2 + 2H$, 40), 126 ($M^+ - Fe(CO)_3 - 2N(CH_3)_2$, 12). HRMS: calc ($C_{15}H_{18}FeN_2O$, $M^+ - 2CO$) 298.07683; found 298.07828.

1,2,3,10η^4-(4,7-*Bis(diethylamino)tricyclo*[5.2.1.$0^{4,10}$]*deca*-1(10),2,5,8-*tetraene)tricarbonyliron* (**15b**).

Compound **14b** (164 mg, 0.61 mmol) was reacted with 1658 mg (4.55 mmol, 1:7.5) $Fe_2(CO)_9$ for 3 d, as described above. Yield 160 mg (0.39 mmol, 64%) **15b**, bright yellow, air-sensitive oil. IR (film) 3050, 2975, 2045, 1985, 1955, 1205, 1070, 760. UV (THF) λ_{max} (log ε) 238 (shoulder, 3.982), 313 (4.011), 361 (3.807). ^{1}H-NMR (270 MHz, $CDCl_3$) olefinic protons see Table 2, δ 0.97 (t, 6H, 3′-H, $^3J_{2',3'}$ = 6.8 Hz), 1.05 (t, 6H, 3″-H, $^3J_{2'',3''}$ = 7.2 Hz), 2.40–2.75 (m, 8H, 2′-H, 2″-H). ^{13}C-NMR (100.63 MHz, $CDCl_3$): C-1—C-10 and CO see Table 3, δ 14.0 (q, C-3′, $^1J_{C,H}$ = 125.3 Hz), 14.8 (q, C-3″, $^1J_{C,H}$ = 125.3 Hz), 44.2 (t, C-2′, $^1J_{C,H}$ = 131.0 Hz), 45.4 (t, C-2″, $^1J_{C,H}$ = 131.0 Hz). MS (70 eV) *m/e* (rel. int.) 410 (M^+, 2), 354 ($M^+ - 2CO$, 43), 326 ($M^+ - 3CO$, 15), 255 ($M^+ - 3CO - N(C_2H_5)_2 + H$, 100), 183 ($M^+ - 3CO - 2N(C_2H_5)_2$, 25), 128 ($M^+ - Fe(CO)_3 - 2N(C_2H_5)_2 + 2H$, 33), 126 ($M^+ - Fe(CO)_3 - 2N(C_2H_5)_2$, 12), 115 (8). HRMS: calc ($C_{19}H_{26}FeN_2O$, $M^+ - 2CO$) 354.13943; found 354.1403.

1,2,3,10η^4-(4,7-*Bis(1′-piperidino)tricyclo*[5.2.1.$0^{4,10}$]*deca*-1(10),2,5,8-*tetraene)tricarbonyliron* (**15c**).

Compound **14c** (207 mg, 0.70 mmol) was reacted with 1281 mg (3.50 mmol, 1:5) $Fe_2(CO)_9$ for 24 h, as described above. Yield 91 mg (0.21 mmol, 30%) **15c**, yellow, moderately air-sensitive oil, crystallizing at the flask wall, m.p. 103°. IR (film, $CDCl_3$) 3045, 2930, 2850, 2790, 2035, 1980, 1955, 1255, 905, 730. ^{1}H-NMR (270 MHz, C_6D_6) olefinic protons see Table 2, δ 1.13–1.87 (m, 12H, CH_2), 2.32–2.81 (m, 8H, NCH_2). ^{13}C-NMR (100.63 MHz, C_6D_6): C-1—C-10 and CO see Table 3, δ 25.4 (t, C-4′, C-4″, $^1J_{C,H}$ = 131.8 Hz), 26.8 (t, C-2′, C-2″, $^1J_{C,H}$ = 130.7 Hz), 49.2 (t, C-1′, $^1J_{C,H}$ = 130.2 Hz), 50.9 (t, C-1″, $^1J_{C,H}$ = 130.2 Hz). MS (70 eV) *m/e* (rel. int.) 434 (M^+, 1), 378 ($M^+ - 2CO$, 65), 350 ($M^+ - 3CO$, 57), 267 ($M^+ - 3CO - C_5H_{10}N + H$, 100), 222 (30), 184 ($M^+ - 3CO - 2C_5H_{10}N + 2H$, 22), 128 ($M^+ - Fe(CO)_3 - 2C_5H_{10}N + 2H$, 14), 126 ($M^+ - Fe(CO)_3 - 2C_5H_{10}N$, 3). MS (isobutane CI) *m/e* (rel. int.) 436 ($M^+ + 2H$, 50), 435 ($M^+ + H$, 100), 433 ($M^+ - H$, 31), 379 ($M^+ + H - 2CO$, 97), 351 ($M^+ + H - 3CO$, 15), 350 ($M^+ - 3CO$, 42), 296

($M^+ + 2H - Fe(CO)_3$, 4). HRMS calc ($C_{23}H_{26}FeN_2O_3$) 434.1292635; found 434.129 ± 0.002.

1,2,3,10η^4 - 4,7 - *Bis*[1'(3',5' - *dimethylpiperidino*)]*tricyclo*-[5.2.1.$0^{4,10}$]*deca* - 1(10),2,5,8 - *tetraene*)*tricarbonyliron* (**15d**)

Compound **14d** (238 mg, 0.68 mmol) was reacted with 1859 mg (5.12 mmol, 1 : 7.5) $Fe_2(CO)_9$ for 24 h as described above. Yield 80 mg (0.16 mmol, 24%) not totally pure **15d**, orange, air-sensitive oil. IR (film) 3060, 2965, 2920, 2810, 2040, 1980, 1960, 1460, 1140, 1080, 860, 810, 765. ^{1}H-NMR (270 MHz, C_6D_6) olefinic protons see Table 2, δ 0.8–2.0 (m, 28H, substituents). MS (70 eV) *m/e* (rel. int.) 490 (M^+, 2), 462 ($M^+ - CO$, 1), 434 ($M^+ - 2CO$, 51), 406 ($M^+ - 3CO$, 58), 351 ($M^+ - Fe(CO)_3 + H$, 14), 350 ($M^+ - Fe(CO)_3$, 7), 319 (11), 295 ($M^+ - 3CO - C_7H_{14}N + H$, 14), 240 ($M^+ - Fe(CO)_3 - C_7H_{14}N + 2H$, 22), 183 ($M^+ - 3CO - 2C_7H_{14}N + 2H$, 14), 181 ($M^+ - 3CO - 2C_7H_{14}N$, 11), 128 ($M^+ - Fe(CO)_3 - 2C_7H_{14}N + 2H$, 20), 71 (100). HRMS: calc ($C_{27}H_{34}FeN_2O_3$) 490.191862; found 490.192 ± 0.002.

1,2,3,10η^4 - (4,7 - *Bis*(4' - *morpholino*)*tricyclo*[5.2.1.$0^{4,10}$]*deca* - 1(10),2,5,8 - *tetraene*)*tricarbonyliron* (**15e**)

Compound **14e** (85 mg, 0.29 mmol) was reacted with 779 mg (2.14 mmol, 1 : 7.5) $Fe_2(CO)_9$ for 3 d, as described above. Yield 33 mg (0.08 mmol, 26%) **15e**, yellow, air-sensitive oil. IR (film, C_6D_6) 2965, 2860, 2050, 1990, 1970, 1455, 1265, 1115. ^{1}H-NMR (80 MHz, C_6D_6) olefinic protons see Table 2, δ 2.33 (m, 8H, 3'-H, 3''-H, $^3J_{2',3'} = {}^3J_{2'',3''} = 8.0$ Hz), 3.38 (m, 7H, 2'-H, 2''-H, 3-H). MS (70 eV) *m/e* (rel. int.) 410 ($M^+ - CO$, 0.1), 382 ($M^+ - 2CO$, 20), 354 ($M^+ - 3CO$, 11), 269 ($M^+ - 3CO - C_4H_8NO + H$, 20), 184 ($M^+ - 3CO - 2C_4H_8NO + 2H$, 15), 128 ($M^+ - Fe(CO)_3 - 2C_4H_8NO + 2H$, 17), 84 (FeCO, 100). MS (isobutane CI) *m/e* (rel. int.) 440 ($M^+ + 2H$, 90), 439 ($M^+ + H$, 100), 438 ($M^+ + H - 2CO$, 10), 352 ($M^+ + H - C_4H_9NO$, 21), 301 ($M^+ + H - Fe(CO)_3 + 2H$, 30), 299 ($M^+ + H - Fe(CO)_3$, 13), 214 ($M^+ + H - Fe(CO)_3 - C_4H_8NO + H$, 9), 127 ($M^+ + H - 2C_4H_8NO - Fe(CO)_3$, 17), 125 ($M^+ + H - 2C_4H_9NO - Fe(CO)_3$, 15), 113 ($Fe_2 + H$, 35). HRMS: calc ($C_{19}H_{22}FeN_2O_3$, $M^+ - 2CO$) 382.09732; found 382.09652.

Disodium(1,10η^2 - 4,7 - *bis*(*diethylamino*)*tricyclo*[5.2.1.$0^{4,10}$] - *deca* - 1(10),2,5,8 - *tetraene*)*tricarbonylferrate*(−2) (**17b**)

Compound **15b** (80 mg, 0.20 mmol) in 0.8 ml [D_8]-THF was reacted with sodium under NMR control[23] at 25°. The soln turned green within 2 d, and no NMR signals were observable. After 4 d the soln turned yellow again, and after 10 d the reaction was complete, the soln being dark yellow. The NMR spectra showed signals of one product only, estimated yield 90% **17b**, yellow, extremely sensitive towards air and moisture. ^{1}H-NMR (270 MHz, [D_8]-THF) olefinic protons see Table 4, δ 0.99 (t, 12H, 3'-H, $^3J_{2',3'} = 7.0$ Hz), 2.73 (mc, 4H, 2'-H, $^2J_{2',2'} = -14.2$ Hz), 3.38 (mc, 4H, 2'-H). ^{13}C-NMR (67.92 MHz, [D_8]-THF): C-1—C-10 and CO see Table 5, δ 14.2 (q, C-3', $^1J_{C,H} = 124.1$ Hz), 43.7 (t, C-2', $^1J_{C,H} = 133.7$ Hz).

Disodium(1,10η^2 - 4,7 - *bis*(1' - *piperidino*)*tricyclo*[5.2.1.$0^{4,10}$] - *deca*-1(10),2,5,8 - *tetraene*)*tricarbonylferrate*(−2) (**17c**)

Compound **17c** (25 mg, 0.06 mmol) in 0.8 ml [D_8]-THF was reacted with sodium under NMR control at 25°. The soln had turned green after 3 h, no NMR signals were observable. ESR (9.236 GHz, [D_8]-THF) $g = 2.01598$ (bs). The soln had turned yellow again after 12 h, and the sodium wire showed dark spots. After 2 d an NMR spectrum was observable, showing the signals of one product, **17c**, estimated yield 90% yellow, extremely sensitive towards air and moisture. ^{1}H-NMR (80 MHz, [D_8]-THF) olefinic protons see Table 4, δ 1.20–1.60 (m, 3'-H, 4'-H), 2.10–3.20 (m, 2'-H).

Cyclic voltammograms of **15c** (20 mg, 0.05 mmol) were recorded under N_2 in 50 ml freshly distilled, anhyd acetonitrile with 0.1 M tetra-n-butylammoniumperchlorate at 25° with an $Ag/AgNO_3$ electrode, calibrated with ferrocene (reduction potential 350 mV vs SCE). At speeds of 50, 100, and 200 mV s^{-1} two irreversible reduction waves were recorded at −2.19 and −2.63 V vs SCE, and an oxidation wave at −0.52 V vs SCE. The reduction remained irreversible, when the potential was reversed after the first reduction step.

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