Reaction of Di-t-butoxyethyne with Fe₂(CO)₉: X-Ray Crystal Structure of (Tetra-t-butoxycyclopentadienone)tricarbonyliron(o) and an Improved Formal Synthesis of Hydrocroconic Acid and the Croconate Dianion

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Di-t-butoxyethyne (1a) reacts with [Fe₂(CO)₉] affording (tetra-t-butoxycyclopentadienone)-tricarbonyliron(o) (5a), the crystal structure of which has been determined by X-ray diffraction. Treatment of (5a) with trimethylamine oxide affords tetra-t-butoxycyclopentadienone (8), which had been previously converted into hydrocroconic acid (2) and the croconate dianion (3). On the other hand, (5a) with trifluoroacetic acid affords (tetrahydroxycyclopentadienone)tricarbonyliron(o) (5b), which is converted into the croconate dianion (3) by oxidation with molecular oxygen in basic medium.
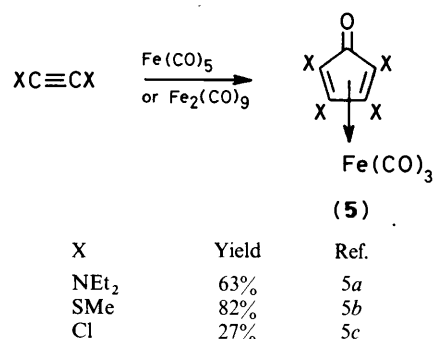
Acetylene diethers (1) possess a carbon-carbon triple bond flanked by two strongly electronegative, yet strongly π-donating, substituents, which exert a great influence on the thermal stability and reactivity of this kind of compound.

In fact, the simplest members of this series readily polymerise at room temperature or even below,[1] and only di-t-butoxyethyne (1a)[2] exhibits an important kinetic stabilisation due to the presence of the two bulky t-butoxy groups that preclude the intermolecular approach necessary for polymerisation to take place.

In recent years, we have studied the reaction of di-t-butoxyethyne with a variety of metal carbonyls, such as [Co₂(CO)₈], [Co(CO)₂(C₅H₅)], and [Ni(CO)₄], and the resulting cyclo-oligomers have found application as intermediates in rational and efficient syntheses of hydrocroconic acid (2),[3c] the croconate dianion (3),[3b,3c] and rhodizonic acid (4).[3a,3d]

ROC≡COR

(1)

a; R = Buᵗ
b; R = Me

(2)

(3)

(4)
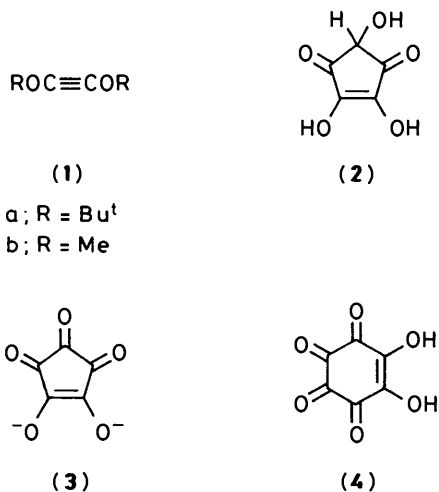
In this context, it seemed interesting to study the reaction of compound (1a) with [Fe₂(CO)₉]. It is known that alkynes react with iron carbonyls leading to a great variety of complexes;[4] however, disubstituted alkynes bearing electronegative π-donating substituents afford almost exclusively the tricarbonyl-iron(o) complexes (5) of the corresponding cyclopentadienones[5]

$$XC\equiv CX \xrightarrow[\text{or Fe}_2(CO)_9]{\text{Fe(CO)}_5}$$

Fe(CO)₃

(5)

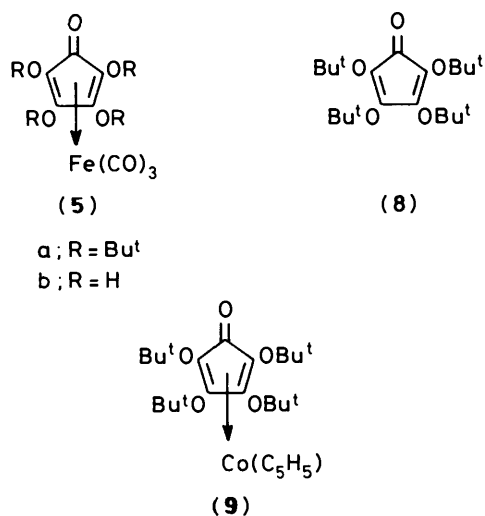| X	Yield	Ref.
NEt₂	63%	5a
SMe	82%	5b
Cl	27%	5c

Scheme 1.

(Scheme 1). This would be perhaps also the case with the acetylene diether (1a).

A precedent for the reaction of acetylene diethers with [Fe₂(CO)₉] can be found in early work on dimethoxyethyne (1b) published by our own research group. As reported,[1c] attempts to trap this highly unstable compound [Fe₂(CO)₉] at low temperature resulted in isolation of the dinuclear complexes (6b) and (7b). No close parallels were, however, to be expected between the reactions of dimethoxyethyne and di-t-butoxy-ethyne with [Fe₂(CO)₉]. In the first place, the steric requirements of the two diethers are quite different, and it is known from our earlier work that even smaller changes in the steric characteristics of acetylene diethers are able to provoke substantial changes on the course of their reactions with metal carbonyls.[2a]

(6)

(7)

a; R = Buᵗ
b; R = Me
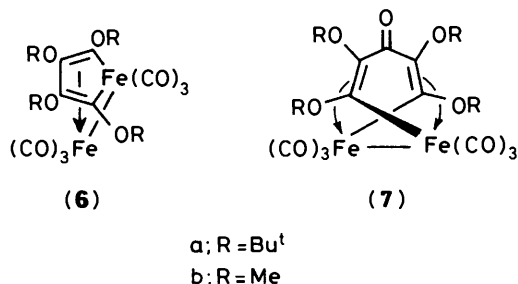
In the second place, the greater thermal stability of di-t-butoxyethyne, allows its manipulation at relatively higher temperatures without significant decomposition. Since it is well known[6] that complexes like (6) and (7) are thermal precursors of tricarbonyliron(0) cyclopentadienones (5), as well as plausible reaction intermediates leading to them, it was expected that the reaction of di-t-butoxyethyne (1a) with [Fe₂(CO)₉], either at room temperature or above, could directly lead to (tetra-t-butoxycyclopentadienone)tricarbonyliron(0) (5a).

On the other hand, if (5a) could be successfully obtained in this way, the possibility of a greatly improved synthesis of hydrocroconic acid (2) and of the croconate dianion (3) would be open, since it is known that the tricarbonyliron complexes of many diene systems can be readily and efficiently demetallated with trimethylamine oxide,[7] and the expected free ligand of (5a), tetra-t-butoxycyclopentadienone (8), has already been converted[3c] into (2) and (3).

(5)

(8)

a ; R = Buᵗ
b ; R = H

(9)

Results and Discussion

When di-t-butoxyethyne (1a) was treated with [Fe₂(CO)₉] in benzene solution at room temperature for 6—7 h (Scheme 2), a single compound was formed in high yield, which could be easily purified by column chromatography on alumina. The reaction product crystallised as yellow-orange crystals, fairly stable to air, and it was identified, on the basis of elemental analysis, and i.r. and ^{1}H and ^{13}C n.m.r. spectroscopy, as (tetra-t-butoxycyclopentadienone)tricarbonyliron(0) (5a). A single-crystal X-ray analysis of (5a) (see below) confirmed the assigned structure. The chemical yield for the synthesis of (5a) was optimised with respect to the di-t-butoxyethyne: [Fe₂(CO)₉] molar ratio, the best results being obtained when a 2.2:1 ratio was used. Under these conditions, the yield of (5a) was 77% relative to (1a) and 43% relative to the iron metal used. Moreover, in a series of experiments performed with [Fe₂(CO)₉] in stoicheiometric deficit, the yield relative to the iron metal was always less than 50%, a fact that suggests the intermediacy of dinuclear complexes like (6a) and/or (7a) in the formation of (5a). Strong steric interactions between t-butoxy groups and tricarbonyliron entities in the forementioned species would account for their easy conversion into the final product. As expected, treatment of (5a) with trimethylamine oxide in acetone under reflux for 18 h allowed the isolation of tetra-t-butoxycyclopentadienone (8) in essentially quantitative yield. It is worth noting that the corresponding cobalt complex, (η⁵-cyclopentadienyl)(η⁴-tetra-t-butoxycyclopentadienone)cobalt-(I) (9), formed in the photochemically induced reaction of (1a)

Scheme 2.

with [Co(CO)₂(C₅H₅)] was highly reluctant to demetallation by this method.[8] Since compound (8) has already been converted into hydrocroconic acid (2) and the croconate dianion (3),[3c] the present synthesis of tetra-t-butoxycyclopentadienone (8) represents a formal synthesis of both compounds (2) and (3) in which not only the overall yield is almost two-fold increased with respect to the early procedure, but also the experimental manipulations are greatly simplified.

On the other hand, looking for an alternative route to compound (3), the trifluoroacetolysis of (5a) was attempted. Thus, treatment of (5a) with trifluoroacetic acid at room temperature resulted in the total cleavage of the t-butoxy groups, the tricarbonyliron complex (5b) being obtained in high yield. Compound (5b) crystallised as a monohydrate, a fact that can be related to the known tendency of tricarbonyl-iron(0)cyclopentadienones (5) to form adducts with proton donors.[9]

It is to be noted that the tricarbonyliron complex (5b) is a stabilised bis-enediol form of hydrocroconic acid (2).[10]

Finally, compound (5b) could be directly converted into croconate dianion (3) by treatment of an alkaline aqueous solution with molecular oxygen, the demetallation/oxidation process being easily monitored by ^{13}C n.m.r. spectroscopy, on the basis of the croconate single peak at 189.30 p.p.m.[11] The yield, estimated by quantitative u.v. spectroscopy,[12] was 63%.

Crystal Structure of (Tetra-t-butoxycyclopentadienone)tri-carbonyliron(0), (5a).—A computer generated plot of the structure (5a) is shown in Figure 1. The Table lists the final fractional co-ordinates; interatomic distances, bond angles, and thermal parameters have been deposited with the Cambridge Crystallographic data centre and are available on request.*

Some structural features of (5a) deserve a little comment. First, the cyclopentadienone skeleton consists of two planes, one defined by C(2), C(3), C(4), and C(5), and the other one by C(2), C(1), and C(5). The dihedral angle between these two planes is 17.7°. On the other hand, O(1) lies 4.4° out of the

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Table. Final atomic co-ordinates for compound (5a)

	x/a	y/b	z/c
Fe	24 803(6)	17 133(2)	4 113(6)
C(1)	2 107(4)	862(2)	−648(4)
C(2)	3 053(4)	914(2)	721(4)
C(3)	4 116(4)	1 241(2)	630(4)
C(4)	3 763(4)	1 479(2)	−657(4)
C(5)	2 461(4)	1 304(2)	−1 400(4)
O(1)	1 190(3)	553(1)	−1 054(3)
O(2)	3 253(3)	606(1)	1 827(3)
C(21)	2 267(5)	278(2)	2 176(5)
C(22)	1 006(5)	560(2)	1 986(6)
C(23)	2 083(6)	−228(2)	1 344(7)
C(24)	2 941(6)	163(3)	3 660(6)
O(3)	5 268(3)	1 326(1)	1 593(3)
C(31)	6 272(4)	925(2)	2 075(5)
C(32)	5 963(5)	425(2)	1 246(7)
C(33)	7 507(5)	1 178(3)	1 905(9)
C(34)	6 412(8)	838(3)	3 501(7)
O(4)	4 593(4)	1 805(2)	−1 017(4)
C(41)	4 970(5)	1 778(2)	−2 234(5)
C(42)	4 747(6)	1 235(3)	−2 883(8)
C(43)	6 388(7)	1 925(4)	−1 773(9)
C(44)	4 201(9)	2 201(3)	−3 142(8)
O(5)	1 977(3)	1 453(2)	−2 705(3)
C(51)	682(5)	1 334(3)	−3 643(5)
C(52)	−384(5)	1 456(3)	−2 994(7)
C(53)	605(6)	1 694(3)	−4 791(6)
C(54)	636(7)	763(3)	−4 088(6)
C(6)	788(5)	1 677(2)	333(6)
O(6)	−276(4)	1 664(2)	299(6)
C(7)	2 392(5)	2 363(2)	−280(6)
O(7)	2 315(5)	2 771(2)	−731(6)
C(8)	3 150(7)	1 912(3)	2 132(6)
O(8)	3 605(7)	2 028(3)	3 225(5)

Figure 2.

that of 14.1° reported for (3,4-bisprop-1-ynyl-2,5-dimethyl-cyclopentadienone)tricarbonyliron(o).[15] The observed value does not support the hypothesis that electron-donating substituents on the ring favour a resonance interaction with the carbonyl group and force that group to approach to the ring plane.

Another salient structural feature of (5a) is the relative values of the C–C distances of the cyclopentadienone ring, observing that the C(3)–C(4) distance [1.406(6) Å] is significantly shorter than C(2)–C(3) or C(4)–C(5) [average value 1.446(5) Å]. The values of these distances have been normally used to discuss the contributions of the canonical forms I and II (Figure 2) in the description of the electronic structure of (cyclo-pentadienone)tricarbonyliron(o) complexes,[13,15,16] so that the shorter the C(3)–C(4) distance the greater the contribution of form (II).

To the best of our knowledge, this is the first reported example in which the more localised form (II) would have a greater contribution than form (I). In accord with this interpretation is also the fact that C(2) and C(5) are somewhat pyramidalised, since O(2) and O(5) lie out of the plane defined by C(2), C(3), C(4), and C(5).
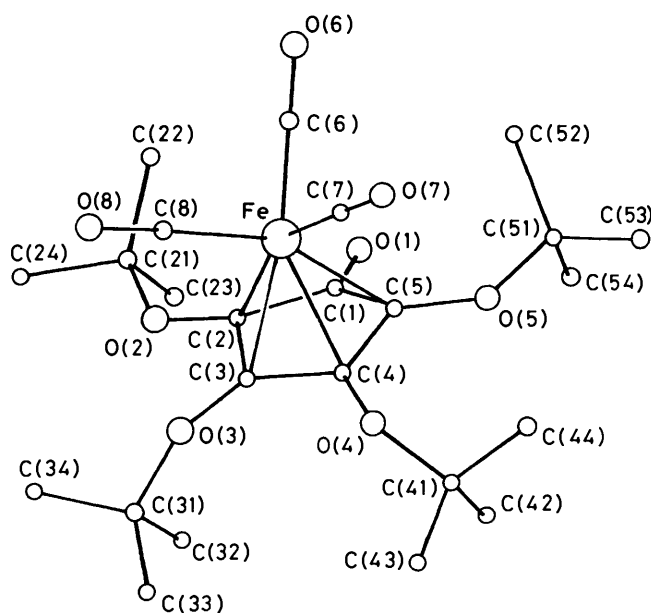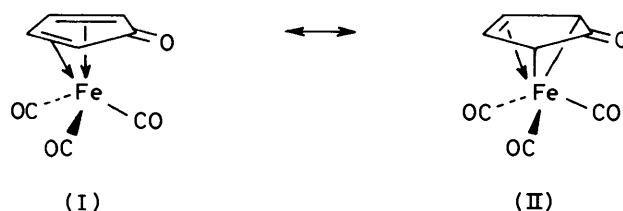

Figure 1.

C(1),C(2),C(5) plane. The dihedral angle of 17.7°, which defines the puckering of the ring has an intermediate value between those reported for [tetrakis(trifluoromethyl)cyclopenta-dienone]tricarbonyliron(o)[13] or the parent (cyclopentadi-enone)tricarbonyliron(o),[14] of 20.1 and 19.9° respectively, and

Experimental

Mass spectra were run with an electron-impact Hewlett-Packard 5930A spectrometer. U.v. and i.r. spectra were recorded with Perkin-Elmer spectrophotometers (Lambda 5 and 681, respectively). [1]H N.m.r. spectra were obtained with a Hitachi Perkin-Elmer R-24B spectrometer or with a Varian XL-200 spectrometer. [13]C N.m.r. spectra were recorded with the Varian XL-200 instrument. Di-t-butoxyethyne (1a) was prepared by a previously described procedure.[2]

(*Tetra-t-butoxycyclopentadienone*)*tricarbonyliron*(o) (5a).— Under an atmosphere of argon, a solution of di-t-butoxyethyne (0.3 g, 1.8 mmol) in benzene (12 mol) was added to [Fe$_2$(CO)$_9$] (0.29 g, 0.8 mmol) and the mixture stirred at room temperature until no starting material was detected in the n.m.r. (6—7 h). The crude reaction mixture was evaporated under reduced pressure and the residue chromatographed on alumina, using hexane–ethyl acetate as eluant, to give the title compound (5g) (0.345 g, 77%) as orange-yellow crystals, m.p. 130 °C (Found: C, 56.9; H, 7.3. C$_{24}$H$_{36}$FeO$_8$ requires C, 56.70; H, 7.14%); m/z 508 (M^+, 0.3%), 480 (0.8), 452 (0.7), 424 (0.9), 390 (1.8), 368 (3.6), 340 (6.0), 312 (12.4), 284 (15.1), 256 (48.5), 255 (18.2), 254 (15.1), 238 (5.4), 228 (15.1), 200 (15.1), 199 (54.3), 198 (51.5), 182 (7.6), 181 (7.6), 170 (4.5), 169 (8.5), 154 (27), 153 (1.5), 144 (10), 142 (4.5), 125 (7), 115 (3), 114 (12.4), 112 (6.6), 98 (3.3), 97 (4.5), 96 (3.9), 85 (3.9), 84 (11.2), 73 (3.3), 70 (7), 58 (5.2), 57 (100), 56 (10.9), and 55 (6.4); $\bar{\nu}_{max.}$(CCl$_4$) 2 980, 2 940, 2 025, 1 980, 1 630, 1 460, 1 430, 1 400, 1 370, 1 260, 1 170, 1 100, 1 070, 1 040, 1 020, 880, and 610 cm^{-1}; δ$_H$ (200 MHz; CDCl$_3$; Me$_4$Si) 1.60 (s, 18 H), and 1.51 (s, 18 H). Crystals of (5a), suitable for X-ray crystallographic study, were grown by slow evaporation of a concentrated solution in hexane.

Tetra-t-butoxycyclopentadienone (**8**).—Trimethylamine oxide (0.61 g, 8.8 mmol) was added to a solution of (tetra-t-butoxy-cyclopentadienone)tricarbonyliron(o) (**5a**) (0.30 g, 0.59 mmol) in acetone (20 ml) and the mixture heated under reflux for 18 h. The mixture was evaporated under reduced pressure and chromatographic purification on alumina of the resulting residue afforded, after elution with hexane, the title compound (**8**) (0.217 g, 99%) as a red crystalline solid, m.p. 44 °C, identical in all respects with an authentic sample;[2c] $\lambda_{max.}$(hexane) 460 and 234.1 nm (ε 193 and 5 000 dm^3 mol^{-1} cm^{-1}); $\bar{\nu}_{max.}$(CCl$_4$) 2 980, 2 920, 2 860, 1 730, 1 660, 1 630, 1 470, 1 390, 1 370, 1 310, 1 260, 1 150, 1 110, 1 040, 1 000, and 840 cm^{-1}; δ_H (60 MHz; CCl$_4$; Me$_4$Si) 1.25 (s, 18 H) and 1.40 (s, 18 H).

Tetrahydroxycyclopentadienone)tricarbonyliron(o) (**5b**).—A solution of (tetra-t-butoxycyclopentadienone)tricarbonyliron-(o) (0.122 g, 0.2 mmol) in TFA (7 ml) was stirred at room temperature for 15 h. Evaporation of the acid under vacuum afforded the tetrahydroxy derivative (**10**) (0.058 g) in the form of a monohydrate (80% yield), m.p. >200 °C (Found: C, 31.75; H, 2.15. C$_8$H$_4$O$_8$Fe·H$_2$O requires C, 31.83; H, 2.00%); m/z 284 (M^+, 0.2), 257 (0.4), 256 (0.5), 243 (0.3), 242 (0.3), 236 (0.7), 229 (0.4), 228 (0.4), 213 (0.6), 208 (0.5), 199 (0.5), 194 (0.7), 185 (1), 171 (1), 129 (3.9), 111 (5.9), 109 (4.6), 98 (6.5), 97 (11.4), 96 (7.2), 95 (9.1), 85 (11.5), 83 (17.6), 81 (15.4), 73 (16.3), 71 (15.4), 69 (26.9), 67 (15.4), 60 (16.9), 57 (25), 55 (30.8), 45 (21.2), and 44 (100); $\bar{\nu}_{max.}$(KBr) 3 640, 3 520, 3 040, 2 680, 2 090, 2 020, 1 650, 1 590, 1 540, 1 450, 1 330, 1 190, 1 160, 1 000, 800, 790, 720, and 640 cm^{-1}; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 2.17 (s) and 2.25 (s).

Demetallation/Oxidation of Compound (**5b**): *the Croconate Dianion* (**3**).—Oxygen was bubbled through a solution of (tetrahydroxycyclopentadienone)tricarbonyliron(o) mono-hydrate (0.074 g, 0.245 mmol) in aqueous KOH (pH 10—11; 10 ml) for 5 h. The resulting suspension was filtered through sintered glass, evaporated under reduced pressure in the cold and studied by ^{13}C n.m.r. spectroscopy; it showed the exclusive presence of the croconate single peak at 189.30 p.p.m.[11] along with some CO$_3^{2-}$ (168.50 p.p.m.), a contaminant of the KOH used. The chemical yield of the demetallation/oxidation process, estimated by quantitative u.v. spectroscopy at $\lambda_{max.}$(KOH/H$_2$O) 362.8 nm [reported,[12] $\lambda_{max.}$ 365 nm (ε 39 800 dm^3 mol^{-1} cm^{-1})] was 63%.

Crystal Data for Compound (**5a**).—C$_{24}$H$_{36}$FeO$_8$, $M = 508.4$, Monoclinic, $a = 10.771(2)$, $b = 25.273(5)$, $c = 10.347(2)$ Å, $\beta = 107.34(2)°$, $V = 2\,689(2)$ Å^3 (by least squares refinement on diffractometer angles for 25 independent reflections (4 $\leqslant$ θ $\leqslant$ 12°), λ(Mo-K_α = 0.710 69 Å), space group $P2_1/n$, $Z = 4$, $D_x = 1.256$ g cm^{-3}, $F(000) = 1\,080$, orange-yellow tablets, μ(Mo-K_α) = 6.20 cm^{-1}.

Data Collection and Processing.—A tabular crystal (0.15 × 0.15 × 0.10 mm) was mounted on a Phillips PW-1100 four-circle diffractometer. Intensities were collected with Mo-K_α radiation, monochromatised by reflection from a graphite crystal using the ω-scan technique (scan width 1°, scan speed 0.03° s^{-1}). Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay not being observed. The intensity data were corrected for Lorentz and Polarisation but not absorption factors. 3 842 Independent reflections were measured in the range 2 $\leqslant$ θ $\leqslant$ 25°, of which 3 728 were considered observed with $I > 2.5$ $\sigma(I)$.

Structure Analysis and Refinement.—The Fe atom was located from a Patterson synthesis, and the remaining non-hydrogen atoms from a subsequent weighted Fourier synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares method, using the SHELX76 computer program.[17] The function minimised was $\Sigma w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.006|F_o|^2)^{-1}$.

The f, f', and f'' values were taken from International Tables of X-Ray Crystallography.[18] The positions of hydrogen atoms were computed and refined with an overall isotropic tempera-ture factor, and anisotropically the remaining atoms. The final R factor was 0.075 ($R_w = 0.087$) for all observed reflections.

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