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IRON CARBONYL COMPLEXES OF THE HOMOPENTALENE SYSTEM

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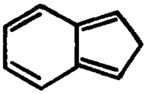
In recent years a number of examples have been reported in which coordination to an iron tricarbonyl moiety allowed the isolation of highly reactive polyolefins which are not normally stable at room temperature as their metal complexes. These types of coordination compounds are important from both experimental and theoretical points of view. Among the prominent examples of this phenomena are cyclobutadieneiron tricarbonyl[1], cyclopentadienone iron tricarbonyl[2] nonbornadienone iron tricarbonyl[3], heptafulveneiron tricarbonyl[4], and cis-cyclononatetraeneiron-tricarbonyl[5a,b]. The isomeric bicyclo[4.3.0] nonatrienes, isoindene (1) and homopentalene (2), are examples of elusive compounds which undergo rapid aromatization to indene but which should be stabilized by binding at least one of the carbocyclic rings to a transition metal. The iron tricarbonyl complex of an isoindene, 3 has indeed been reported by Meier[6].



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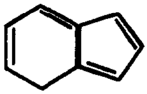

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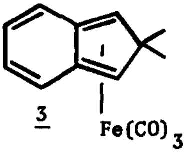

3

(1)

The initial goal was the synthesis of a 1-substituted 8,9-dihydroindeneiron tricarbonyl derivative which could potentially serve as a precursor for an iron complex of 2*. Four exo-1-substituted 8,9-dihydroindene derivatives have been prepared by us**, where 6c, the exo-1-hydroxy derivative, was chosen as our initial synthetic goal. Important synthetic transformations are summarized below in scheme 2.

Reaction of 9-anti-methoxy-cis-bicyclo-[6.1.0]nonatriene, 4[7], with $Fe_2(CO)_9$ at 45°C yielded a dark red mixture of two complexes, 6a[11], 1-exo-methoxy-cis-8,9-dihydroindene-$Fe(CO)_3$ along with binuclear complex, 9-anti-methoxy-bicyclo[6.1.0]nonatrienediiron hexacarbonyl 5[8,11], as a red-orange crystalline compound, m.p. 130-132°decomp., mass spectrum m/e 428(M^+), 400(M^+-28), 372 (M^+-2CO), 344(M^+-3CO), 260($L.Fe_2^+$), 148(260-Fe_2^+); pmr signals ($CDCl_3$, TMS standard) τ:6.4(m,$H_{3,4}$) 5.8(m,$H_{2,5}$), 7.28(d,$H_{1,6}$, $J_{1,2}$=10 Hz), 8.7(d,$H_{7,8}$$J_{8,9}$=1.0 Hz), 6.16(t,$H_9$), 6.58(s,$OCH_3$); carbonyl stretching frequencies (hexane) 2066,2022,2004,1988 and 1970 cm^{-1}.

A stable $Mo(CO)_3$ complex of 4 has been prepared also in our laboratory, as a red-orange compound m.p. 107-108°, ir(hexane) 2000,1937,1919 (C≡O)cm^{-1} PMR signals: τ3.98(m,$H_{3,4}$), 4.55 (m,$H_{2,5}$), 5.14(d,$H_{1,6}$, $J_{1,2}$=10.5 Hz), 8.61(d,$H_{7,8}$, $J_{8,9}$=1.0 Hz), 6.80(t,H_9, $J_{8,9}$=2.5 Hz) 6.52

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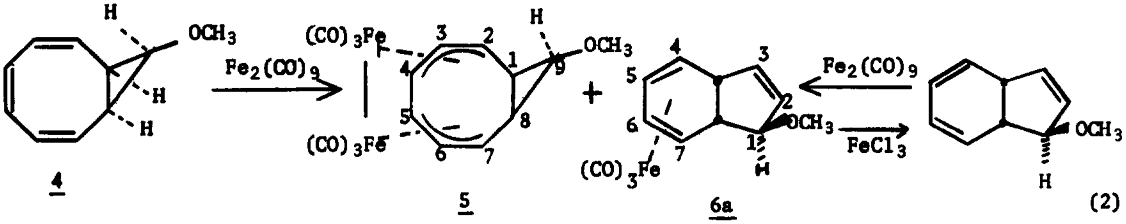
* Preliminary observations on this subject were made while enjoying the kind hospitality of the late Professor S. Winstein at U.C.L.A. California.

** trifluoroacetoxy, methoxy and endo-hydroxy derivatives.

(s,OCH$_3$): The chemical shifts of the two compounds, show that the olefinic protons in 5 are much more shielded than in 4'[11], and the reverse relation exist for H$_9$.



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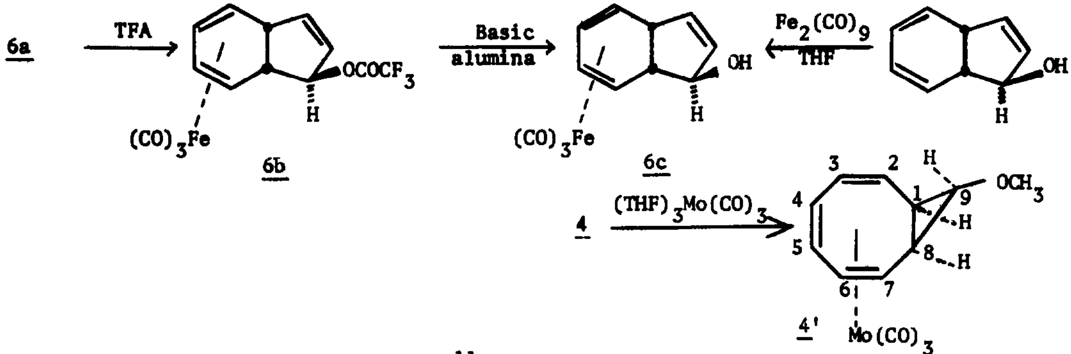
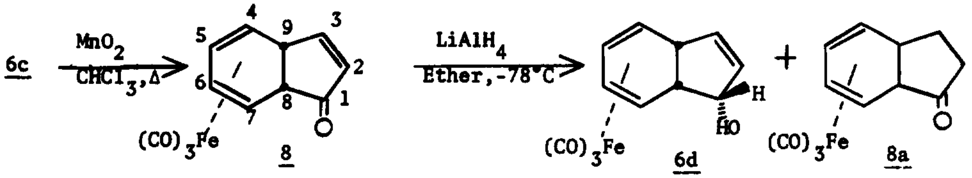
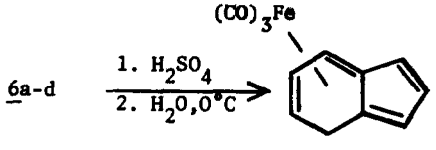


The methoxy dihydroindene complex 6a[11] was isolated as yellow needles, m.p. 66-68° (after sublimation), exhibiting carbonyl bands in the ir (hexane) at 2055, 1988 and 1982 cm^{-1}, and rather complex pmr signals (CDCl$_3$, 100 MHz, TMS) at τ4.29(dq, H$_7$, $J_{3,9}$=1.5 Hz), 4.53(dt, H$_2$), 4.68(q, H$_{5,6}$) 6.11(q, H$_1$J$_{1,7}$=1.0 Hz), 6.73(s,OCH$_3$), 6.55-6.95(m,H$_8$, H$_4$, H$_7$) 7.31 (8 lines, H$_9$). The mass spectrum showed the parent peak at m/e 288 and peaks for successive loss of CO's, 204(M$^+$-360), 174(204-HOCH$_3$), 116(174-Fe). Further structural proof was derived when 6a was oxidatively degraded with ferric chloride in ethanol/NaOAc solution to yield the free triene ligand, identical with an authentic sample of 1-exo-methoxy-8,9-cis-dihydroindene[9a]; the latter produced 6a in high yield on reaction with Fe$_2$(CO)$_9$ in a hexane-benzene solution.

The 1-exo-hydroxy-cis-8,9-dihydroindene iron tricarbonyl, 6c[11], could be prepared either directly from reaction of Fe$_2$(CO)$_9$ with ligand 7[9b] in THF or by elution of the 1-exo-trifluoroacetate derivative 6b on a basic alumina column. Compound 6c[(m.p.95-97°; ir(CHCl$_3$) 3586 cm^{-1} (OH) 2040, 1970 cm^{-1}(C≡O)]exhibits a very similar pmr spectrum as well as mass spectrum in comparison with the methoxy derivative. Oxidation of 6c with freshly-prepared manganese dioxide in boiling chloroform afforded cis-8,9-dihydroinden-1-one iron tricarbonyl 8, with some decomposition.Dihydroindenone itself has been shown rapidly to tautomerize after a few hours to the more stable indanone molecule.[10a,b]



Compound 8[11] was isolated as yellow needles, m.p. 104-105° (stable in air), ir (hexane) 2058, 1990(C≡0)1730(C=0)cm^{-1}, pmr signals ($CDCl_3$, TMS standard) τ2.65(dd,H_3,$J_{3,2}$6.0 Hz; $J_{3,9}$=3.0 Hz). 7.15 (q,H_8,$J_{8,7}$=4.0 Hz) 6.8(dt,H_7), 6.9(m,H_4), mass spectrum m/e 272(M^+) etc. Reduction of 8 with $LiAlH_4$ in ether at -78°C yielded 1-endo-hydroxy-cis-8,9 dihydroindeneiron tricarbonyl, 6d, (an epimer of 6c) together with an 1,4 hydride-addition product of 8, the ketone 8a. The endo-alcohol, 6d, (yellow needles, m.p. 93-94°C) exhibited similar mass and ir spectra as for 6a, and pmr signals ($CDCl_3$, TMS) at τ4.3-4.75 (m,$H_{2,3,5,6}$), 5.57(bs,H_1), 6.85(m,$H_{4,7}$,H_9) 7.1(2x4 lines, H_8) and 8.45(s,OH); when any of the 1-substituted cis-8,9 dihydroindene complexes, 6a-d, were extracted from CH_2Cl_2 into conc. H_2SO_4 and then quenched in Na_2CO_3-H_2O, the tetraene complex,9, >50% yield) together with polymeric compounds were obtained.



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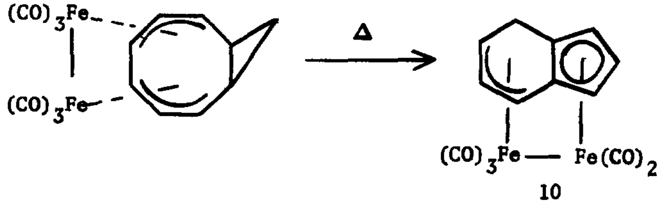
(4)

In the bicyclonona[4.3.0]tetraene complex, 9[11], the $Fe(CO)_3$ is bound to an organic ligand which is very sensitive to thermal rearrangement relative to the complexed organic system. The complex 9 was isolated as a red oil which solidifies at 15°C (sublimes at 50°, 0.1 mm) and shows strong ir carbonyl bands at 2062, 2004 and 1988 cm^{-1} (similar to those of cyclooctatetraene irontricarbonyl[12]). The 100 MHz pmr spectrum ($CDCl_3$) and signal assignments are shown in Fig. 1. PMR signals assignments were deduced from double irradiation experiments. The mass spectrum showed m/e 256, (M^+) and successive loss of 3 CO's (228,200,172) 116(172-Fe), and 115(116-1)=$C_9H_7^+$. The nmr of 9 is rather similar to the unsymmetrical binuclear complex 10 obtained as a byproduct[13] on thermolysis of cyclononatriendiironhexacarbonyl.



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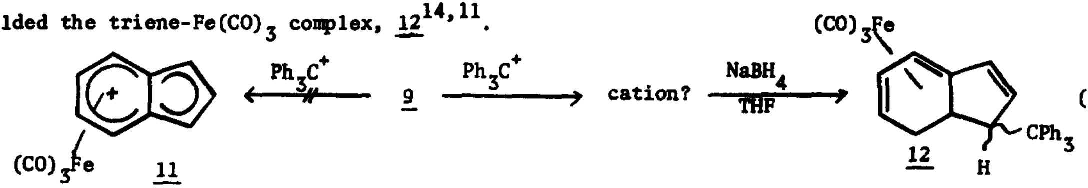
(5)

Treatment of tetraene complex 9 with $Ph_3C^+BF_4^-$ with the intent to abstract hydride from C_7 and produce an indenyl cation species 11 resulted instead in addition of trityl ion to 9 to produce a cation of undetermined structure. Reduction of this cation by borohydride in THF yielded the triene-$Fe(CO)_3$ complex, 12[14,11].



(6)

This yellow-orange triene complex (m.p.151-153°C) exhibited peaks in the mass spectrum at m/e 500 (M^+) and three peaks corresponding to successive loss of CO's. Compounds 8 and 9 represent further examples in which unstable organic molecules (under normal conditions) can form stable complexes with transition metals.

Acknowledgements

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9.a. A pure sample of this ligand was kindly donated by J. Grutzner from Purdue University,USA.
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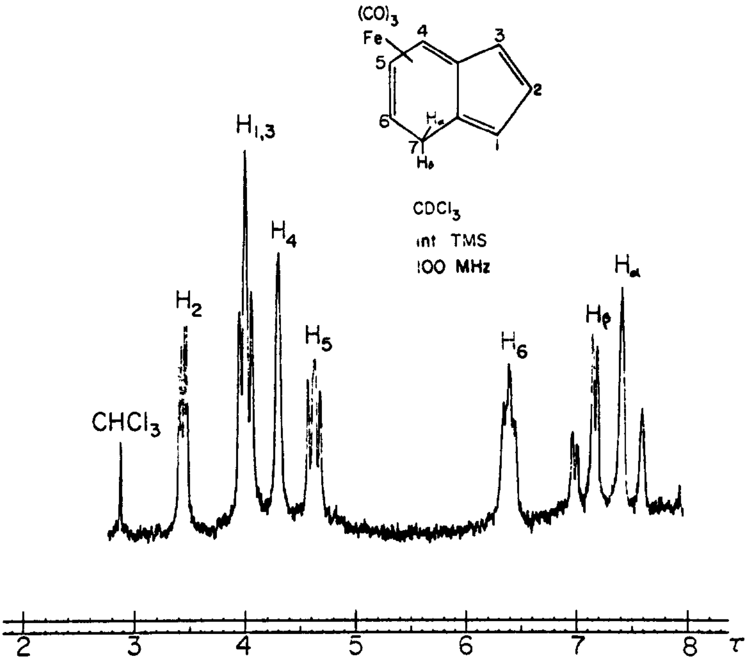

Fig. 1