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XXX*. REACTIONS OF TETRAALKYLHEXAPENTAENES WITH IRON CARBONYLS

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Summary

Tetra-t-butylhexapentaene reacts with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ to give a mixture of the yellow monoolefin complex $[(CH_3)_3C]_4C_6Fe(CO)_4$ and the red butatriene complex $[(CH_3)_3C]_4C_6Fe_2(CO)_6$. Carbon-13 NMR spectroscopy indicates that the center carbon—carbon double bond(s) of the hexapentaene chain are bonded to the iron carbonyl units in these complexes suggesting that the large size of the t-butyl substituents prevents access of the metal to the outer carbon—carbon double bonds. A tetramethylhexapentaene complex, red $(CH_3)_4C_6Fe_2(CO)_6$, is obtained in low yield by reaction of 2,7-dichloro-2,7-dimethyl-3,5-octadiyne with $Fe_3(CO)_{12}$ in the presence of zinc.

Introduction

During the past ten years several reports of reactions of iron carbonyls with allenes [2-4] and butatrienes [2, 5-7] have appeared. Thus allene has been reported to react with $Fe_3(CO)_{12}$ with dimerization to give the tetramethyleneethane complex $C_6H_8Fe_2(CO)_6$ (I) in which all six carbon atoms of the allene dimer are bonded to metal atoms [3]. However, tetramethylallene was reported [4] to react with $Fe_2(CO)_9$ to give an iron tetracarbonyl complex $[(CH_3)_2C{=}C{=}C(CH_3)_2]Fe(CO)_4$ (II) in which only one of the two double bonds of the allene unit is bonded to the iron atom. Reactions of butatrienes with iron carbonyls give complexes of the type $R_4C_4Fe_2(CO)_6$ (III: R = C_6H_5) in which the butatriene ligand is bonded to a pair of iron atoms as a bis(h^3-allyl) ligand.

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* For part XXIX of this series see ref. 1.

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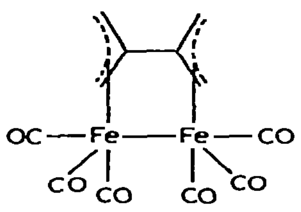
The unusual products obtained from reactions of allenes and butatrienes with iron carbonyls made of interest similar reactions of higher cumulenes with iron carbonyls in order to see whether the additional carbon—carbon double bonds would make possible unprecedented types of metal complexes. Since pentatetraenes are relatively difficult to make, we chose to work with the more accessible hexapentaene derivatives. A further complication in this cumulene chemistry is the need for relatively large alkyl groups such as t-butyl at the ends of the cumulene chain in order to have organic derivatives of acceptable stability for the synthetic procedures.

This paper describes our studies on the reaction of iron carbonyls with the tetraalkylhexapentaenes IV (R = t-butyl and methyl).



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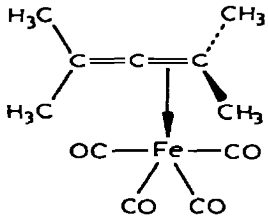

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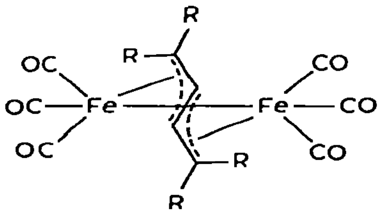

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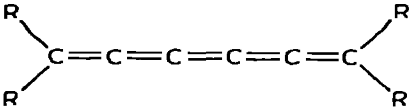


(IV)

Experimental

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia, and Schwarzkopf Microanalytical Laboratory, Woodside, New York. Molecular weights were determined by Schwarzkopf on benzene solutions using vapor pressure osmometry. Infrared spectra (Table 1) were taken in hexane solutions and recorded on a Perkin—Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601 cm^{-1} band of polystyrene film. Proton NMR spectra were taken in $CDCl_3$ or C_6D_6 solutions and recorded on a

TABLE 1

SOME ν(CO) FREQUENCIES IN CUMULENEIRON CARBONYL COMPLEXES

Compound	ν(CO) frequencies (cm^{-1})
$(Me_3C)_4C_6Fe(CO)_4$	2090m, 2028s, 1991s
$C_4H_4Fe_2(CO)_6$	2085m, 2043s, 2009vs, 1999vs, 1983m
$(Me_3C)_4C_6Fe_2(CO)_6$	2077m, 2038s, 2006vs, 1992vs, 1980m
$Me_4C_6Fe_2(CO)_6$	2078w, 2059m, 2031w, 2009m, 2005m, 1998s, 1992s, 1984m, 1981m

TABLE 2

CARBON-13 NMR SPECTRA OF CUMULENE DERIVATIVES

Compound	Cumulene carbons[a]			t-Butyl carbons		Carbonyl groups
	α	β	γ	Tertiary	CH_3	
$(Me_3C)_2C{=}C{=}C{=}C(CMe_3)_2$	158.4	134.6		38.8	32.7	
$C_4H_4Fe_2(CO)_6$	70.6	123.2				209.5
$(Me_3C)_4C_6$	156.6	140.1	131.9	38.9	31.9	
$(Me_3C)_4C_6Fe(CO)_4$	168.0	126.5	91.6	37.0	31.9[b]	208.0
$(Me_3C)_4C_6Fe_2(CO)_6$	161.7	83.1	139.7	37.8	33.0	211.8, 207.0

[a] The designations α, β, γ refer to the positions of the cumulene carbon atoms relative to the alkyl (or hydrogen in the case of $C_4H_4Fe_2(CO)_6$) substituents. [b] A less intense t-butyl methyl carbon resonance is observed at δ 32.3. The relative intensity of this methyl resonance at δ 32.3 is about 25% of that of the methyl resonance at δ 31.9.

Varian HA-100 spectrometer operating at 100 MHz. Carbon-13 NMR spectra (Table 2) were taken in $CDCl_3$ solutions and recorded on a Jeolco spectrometer operating at ~25 MHz in the Fourier transform mode with a deuterium lock and a 3 to 4 sec pulse repetition rate. Carbon-13 chemical shifts (δ) are given in ppm downfield from internal tetramethylsilane. Melting points were taken in capillaries and are uncorrected.

Materials

Commercial $Fe(CO)_5$ (GAF, Inc., New York, N.Y.) was converted to $Fe_2(CO)_9$ [8] and $Fe_3(CO)_{12}$ [9] by the cited published procedures. Tetra-t-butylhexapentaene [10], tetra-t-butylbutatriene [10], 2,7-dichloro-2,7-dimethyl-3,5-octadiyne [11] and butatrienediiron hexacarbonyl (designated in the tables as $C_4H_4Fe_2(CO)_6$) [2] were prepared by the cited published procedures.

Reaction of tetra-t-butylhexapentaene with $Fe_2(CO)_9$

A mixture of 3.0 g (10 mmol) of tetra-t-butylhexapentaene, 5.0 g (13.7 mmol) of $Fe_2(CO)_9$, and 100 ml of anhydrous diethyl ether was stirred for 20 h at room temperature. Solvent was removed from the filtered reaction mixture at ~25°/35 mm. Chromatography of the residue in hexane solution on a 2 × 80 cm alumina column gave a yellow band followed by an orange band. Each band was eluted with hexane, the hexane eluates were evaporated at ~25°/35 mm, and the residues were sublimed at ~100°/0.01 mm to give 0.924 g (20% yield) of yellow tetra-t-butylhexapentaeneiron tetracarbonyl, m.p. 102-104°, proton NMR in $CDCl_3$ τ 8.72 and 8.75 (CH_3), from the yellow band and 0.379 g (6.5% yield) of red tetra-t-butylhexapentaenediiron hexacarbonyl, m.p. 114-116°, proton NMR in C_6D_6 τ 8.66 (CH_3), from the orange band. The latter product solidified only after the sublimate was washed with cold hexane. Anal. (a) for $[(CH_3)_3C]_4C_6Fe(CO)_4$: Found: C, 67.2; H, 8.0; O, 13.4; mol. wt., 423. $C_{26}H_{36}FeO_4$ calcd.: C, 66.7; H, 8.0; O, 13.7%; mol. wt., 468. (b) For $[(CH_3)_3C]_4C_6Fe_2(CO)_6$: Found: C, 58.3; H, 6.3; O, 16.3; Fe, 20.0; mol. wt., 537. $C_{28}H_{36}Fe_2O_6$ calcd.: C, 58.0; H, 6.2; O, 16.5; Fe, 19.3%; mol. wt., 580.

A similar reaction of 0.3 g (1.0 mmol) of tetra-t-butylhexapentaene and

1.0 g (2.0 mmol) of $Fe_3(CO)_{12}$ in 100 ml of boiling hexane for 20 h gave 0.075 g (16% yield) of $[(CH_3)_3C]_4C_6Fe(CO)_4$ and 0.24 g (41% yield) of $[(CH_3)_3C]_4C_6Fe_2(CO)_6$. However, neither of these tetra-t-butylhexapentaeneiron carbonyl complexes was obtained from the reaction of 0.3 g of tetra-t-butylhexapentaene with 2.0 g of $Fe(CO)_5$ in 100 ml of boiling octane for 20 h; instead complete decomposition was observed.

Reactions of tetra-t-butylhexapentaene with other transition metal derivatives

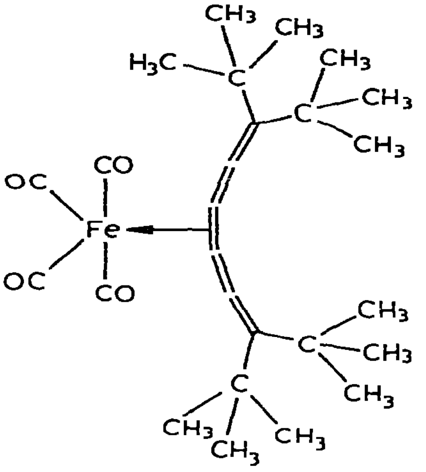
The following reactions failed to give any new tetra-t-butylhexapentaene-metal complexes after chromatography of the reaction mixture: (a) Reaction of 0.3 g of tetra-t-butylhexapentaene with 0.6 g of benzalacetoneiron tricarbonyl in boiling benzene for 24 h. (b) Reaction of 0.3 g of tetra-t-butylhexapentaene with 1 ml of $C_5H_5Co(CO)_2$ in boiling octane for 16 h. (c) Reaction of 0.3 g of the tetra-t-butylhexapentaene with 2.5 g of $Cr(CO)_6$ in boiling heptane containing 1% of 1,2-dimethoxyethane for 24 h.

Preparation of tetramethylhexapentaenediiron hexacarbonyl

A solution of 10.0 g (49 mmol) of 2,7-dichloro-2,7-dimethyl-3,5-octadiyne in 50 ml of redistilled tetrahydrofuran was added dropwise to a boiling mixture of 10.0 g (20 mmol) of $Fe_3(CO)_{12}$, 8.0 g (120 mmol) of zinc dust, and 150 ml of redistilled tetrahydrofuran. The reaction mixture became red-brown in a reaction sufficiently exothermic to boil the tetrahydrofuran without external heating. After the reaction was complete, the tetrahydrofuran was removed at ~25°/35 mm. The residue was extracted with 500 ml of hot hexane in five portions. The hexane was evaporated from the filtered extracts at ~25°/35 mm. The residue was chromatographed on a 2 × 150 cm alumina column in hexane solution. The major red band was eluted with hexane. Evaporation of the hexane from the eluate at ~25°/35 mm gave a red oil which was allowed to stand at −10° until it solidified. Further purification by low temperature crystallization from pentane followed by rechromatography on alumina in hexane solution gave 0.2 g (1.6% yield) of red solid $(CH_3)_4C_6Fe_2(CO)_6$, m.p. 117-119°, proton NMR in $CDCl_3$ τ 7.78. Anal. Found: C, 46.5; H, 2.9. $C_{16}H_{12}Fe_2O_6$ calcd.: C, 46.6; H, 2.9%.

Discussion

The reaction of tetra-t-butylhexapentaene (IV: $R = C(CH_3)_3$) with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gives two different products which can be separated by chromatography and which can be sublimed in vacuum without decomposition. The yellow product $[(CH_3)_3C]_4C_6Fe(CO)_4$ appears to be an (olefin)$Fe(CO)_4$ derivative in which one of the five carbon—carbon double bonds of the hexapentaene is bonded to the $Fe(CO)_4$ group. Its infrared spectrum in the $\nu(CO)$ region (Table 1) is similar to those of equatorially substituted (olefin)$Fe(CO)_4$ derivatives [12] except for difficulties in resolving the $A_1{}^1$ and B_2 modes which appear as a single band at 2028 cm^{-1}. Grevels and Koerner von Gustorf [13] had similar difficulties in resolving the $A_1{}^1$ and B_2 $\nu(CO)$ frequencies in certain 1,2-dihaloethyleneiron tetracarbonyl complexes. The red product $[(CH_3)_3C]_4C_6Fe_2(CO)_6$ appears to be a butatrienediiron hexacarbonyl derivative with three adjacent carbon—carbon double bonds of the hexapentaene system involved in the bonding to the two iron atoms. The infrared spectrum of $[(CH_3)_3C]_4C_6Fe_2(CO)_6$ in the ν(CO) region (Table 1) is very similar to that of the unsubstituted butatrieneiron hexacarbonyl (III: R = H).



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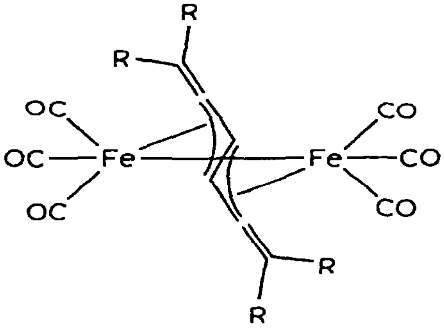

(VI)

Carbon-13 NMR spectroscopy (Table 2) is useful for determining which carbon—carbon double bonds of the tetra-t-butylhexapentaene system are bonded to the iron atoms in $[(CH_3)_3C]_4C_6Fe(CO)_4$ and $[(CH_3)_3C]_4C_6Fe_2(CO)_6$. In both compounds only three carbon resonances assignable to the six cumulene carbons of the hexapentaene chain are observed indicating that the $Fe(CO)_4$ unit is bonded to the center carbon—carbon double bond in $[(CH_3)_3C]_4C_6Fe(CO)_4$ (V) and that the $Fe_2(CO)_6$ unit is bonded to the center three carbon—carbon double bonds in $[(CH_3)_3C]_4C_6Fe_2(CO)_6$ (VI: R = $C(CH_3)_3$). These observations suggest that the t-butyl groups block access of the iron carbonyl groups to the end carbon—carbon double bonds of the tetra-t-butylhexapentaene, in accord with the large steric requirements of the t-butyl group.

The assignments in Table 2 for the cumulene carbon-13 resonances of tetra-t-butylhexapentaene and its two iron carbonyl complexes depend on chemical shift comparisons with similar cumulene carbon atoms in the butatriene derivatives $[(CH_3)_3C]_2C{=}C{=}C{=}C[C(CH_3)_3]_2$ and $C_4H_4Fe_2(CO)_6$ (III: R = H). The assignment of the carbon-13 resonance at δ 70.6 in $C_4H_4Fe_2(CO)_6$ to the end CH_2 carbons depends on the observed enhancement of this resonance relative to the other cumulene resonance at δ 123.2 from the nuclear Overhauser effect arising from decoupling of the protons of the end CH_2 groups. The assignments of the cumulene carbons in $C_4H_4Fe_2(CO)_6$ can then be used to make the assignments of the β and γ carbon atoms in the related butatriene-type complex $[(CH_3)_3C]_4C_6Fe_2(CO)_6$ (VI: R = $C(CH_3)_3$) leaving the cumulene resonance at δ 161.7 for the α-carbons of the hexapentaene chain (i.e. those bonded directly to the t-butyl groups). The assignment of the lowest of the three cumulene resonances in all of the tetra-t-butylhexapentaene derivatives to the two α-carbon atoms bearing the t-butyl groups is consistent with the relatively narrow range of this resonance (δ 156.6 to 168.0), since the tetra-t-butylhexapentaene is bonded to iron carbonyl units in complexes V and VI (R = $C(CH_3)_3$) without using these two carbon atoms.

In butatrienediiron hexacarbonyl complexes such as III (R = H) and VI (R = $C(CH_3)_3$) one carbonyl of each $Fe(CO)_3$ unit is *trans* to the iron—iron bond and the two remaining carbonyls of each $Fe(CO)_3$ unit are *trans* to iron—carbon bonds. This non-equivalence of the carbonyl groups in each $Fe(CO)_3$ unit of the tetra-t-butylhexapentaene complex VI (R = $C(CH_3)_3$) is indicated by the carbonyl region of the carbon-13 NMR spectrum (Table 2) which exhibits resonances at δ 211.8 and 207.0 which can be assigned to the carbonyl groups *trans* to the iron—carbon bond and those *trans* to the iron—iron bond, respectively, on the basis of their relative intensities. However, the carbonyl region of the carbon-13 NMR spectrum of the unsubstituted butatriene complex III (R = H) exhibits only a single resonance at the intermediate value of δ 209.5 indicating the presence of some process which averages the two different types of carbonyl groups on the carbon-13 NMR time scale. Presumably the large size of the t-butyl groups inhibits the necessary motions for a similar carbonyl averaging process in the tetra-t-butylhexapentaene complex VI (R = $C(CH_3)_3$). A detailed temperature dependence study of the carbon-13 NMR spectra of the carbonyl groups is needed to clarify this phenomenon.

The proton NMR spectrum of the diiron hexacarbonyl complex $[(CH_3)_3C]_4C_6Fe_2(CO)_6$ exhibited a single sharp methyl resonance at τ 8.66 suggesting equivalence of all four t-butyl groups, at least on the NMR time scale. However, the proton NMR spectrum of the iron tetracarbonyl complex $[(CH_3)_3C]_4C_6Fe(CO)_4$ (V) exhibited two very closely spaced t-butyl methyl resonances at τ 8.72 and 8.75. The resonance at τ 8.75 was appreciably weaker than that at τ 8.72. A similar effect was noted for the methyl carbon-13 resonances in V with the weak resonance at δ 32.3 being of about 25% of the intensity of the strong resonance at δ 31.9. Since the two different types of methyl groups in V are present in unequal quantities in both the proton and carbon-13 NMR spectra, this methyl group non-equivalence cannot arise from splitting of the four t-butyl groups into two non-equivalent pairs by twisting the hexapentaene chain. Equivalence of all four t-butyl groups in $[(CH_3)_3C]_4C_6Fe(CO)_4$ (V) but restricted rotation of the methyl groups within each of the equivalent t-butyl groups could account for these observations, but their more detailed explanation remains obscure.

The large size of the four t-butyl groups in tetra-t-butylhexapentaene (I: R = t-butyl) is undoubtedly a major factor in the tendency for iron carbonyl fragments to bond to center double bonds in the cumulene chain of this hexapentaene. For this reason the preparation of iron carbonyl complexes of a tetraalkylhexapentaene with less sterically demanding alkyl groups was investigated in order to see whether complexes with the terminal carbon—carbon double bonds also bonded to iron carbonyl groups could be obtained. Since tetraalkylhexapentaenes with small alkyl groups are unstable with respect to polymerization, a less direct synthesis avoiding the use of the free cumulene was used completely analogous to the reported [2] synthesis of butatrienediiron hexacarbonyl. The reaction of the dichloride $(CH_3)_2C(Cl)C{\equiv}CC{\equiv}C(Cl)(CH_3)_2$ with $Fe_3(CO)_{12}$ in the presence of zinc dust gave a low yield of a red solid of stoichiometry $C_{10}H_{12}Fe_2(CO)_6$ indicated to be a tetramethylhexapentaene complex by the observation of only methyl resonances in its proton NMR spectrum. The infrared spectrum of this tetramethylhexapentaene complex in the $\nu(CO)$ region (Table 1) was considerably more complex than that of either $C_4H_4Fe_2(CO)_6$ or tetra-t-butylhexapentaenediiron hexacarbonyl (IV: R = $C(CH_3)_3$) suggesting that the $C_{10}H_{12}Fe_2(CO)_6$ was not simply the pure methyl analogue IV (R = CH_3) but contained other isomers such as one with the butatriene unit at one end of the hexapentaene chain bonded to the $Fe_2(CO)_6$ group or possibly more complex $(CH_3)_4C_6Fe_2(CO)_6$ isomers in which the three carbons of the cumulene chain bonded to each $Fe(CO)_3$ unit are not adjacent carbons. Insufficient compound was available to study this system in greater detail.

This work suggests that the additional *sp* carbon atoms in the cumulene chain in going from a butatriene to a hexapentaene system introduce no new features into the metal carbonyl chemistry of these systems since the products V and VI (R = t-butyl) from reactions of tetra-t-butylhexapentaene with iron carbonyls contain only structural features found already in the tetramethylallene complex II and the butatriene complexes III (R = H, C_6H_5, etc.), respectively. Restrictions of the maximum diameter of a network of unsaturated carbon atoms which can bond entirely to a single metal atom to ~2.1 carbon—carbon bond lengths [14] means that a maximum of three carbons of a linear cumulene system can interact with a single metal atom. This is consistent with the observation that two metal atoms are required to bond entirely to a butatriene system (diameter: 3.0 carbon—carbon bond lengths) as in the butatrienediiron hexacarbonyl complexes III. Since the diameter of a linear hexapentaene chain is 5.0 carbon—carbon lengths, three metal atoms would appear to be necessary to bond to all six carbon atoms of a hexapentaene chain. Furthermore, the angle formed by three metal atoms bonding to all six carbon atoms of a linear hexapentaene chain would have to be obtuse in order for both end carbons of the chain to be near enough to bond to metal atoms. A maximum of only two rather than three metal—metal bonds is thus possible in a trio of metal atoms bonding entirely to a hexapentaene chain thereby excluding the more favorable metal triangles. A further disadvantage in preparing metal complexes of hexapentaene systems in which all six carbons of the hexapentaene chain are bonded to metal atoms is the need for large substituents on the end carbons of the hexapentaene chain in order for the free hexapentaene or even its highly unsaturated precursor to be stable enough for the synthetic conditions. Such large substituents block access of the metal atoms to the end sp^2 carbons of the hexapentaene chain. The synthesis of complexes with metals bonded to all six carbons of a hexapentaene chain may therefore be impossible since substituents large enough to protect the hexapentaene system and its precursors from self-destruction through polymerization, etc., during some of the necessary synthetic steps also prevent access of the metal atoms to the end carbon atoms of the hexapentaene chain for complex formation.

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