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## PRELIMINARY COMMUNICATION

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# A NOVEL TRANSANNULAR CYCLIZATION OF A MACROCYCLIC DIACETYLENE TO FORM A SUBSTITUTED π-CYCLOPENTADIENYLMETAL DERIVATIVE

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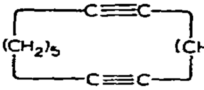
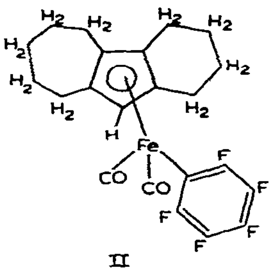
Iron carbonyls have been used for the oligomerization of acetylenes into various cyclic organic systems[1], for the isomerization of non-conjugated diolefins into conjugated diolefins[2], and for the isomerization of terminal olefins into internal olefins[3]. This communication reports a different type of interaction of iron carbonyls with unsaturated organic systems which results in the conversion of a macrocyclic diacetylene to a tricyclic system which functions as a tetrasubstituted π-cyclopentadienyl ligand in forming metal complexes.

Reaction of pentacarbonyliron with 1,8-cyclotetradecadiyne (I) in boiling toluene for ~24 h gives a complex mixture from which dark red crystalline $[C_{14}H_{19}Fe(CO)_2]_2$, m.p. 155–159° (Anal.: Calcd.: C, 64.0%, H, 6.7%; O, 10.7%; Fe, 18.6%; mol. wt., 598. Found: C, 63.3%; H, 6.5%; O, 11.7%; Fe, 18.8%; mol. wt., 591 (osmometer in benzene) was isolated in 23% yield after chromatography on alumina in benzene solution. The infrared spectrum of this complex (KBr pellet) exhibited a strong terminal metal ν(CO) frequency at 1935 $cm^{-1}$ and a strong bridging metal ν(CO) frequency at 1759 $cm^{-1}$. This spectrum is very similar to that of the π-cyclopentadienyl derivative $[C_5H_5Fe(CO)_2]_2$ (in KBr: ν(CO) (terminal), 1942 $cm^{-1}$; ν(CO) (bridging), 1757 $cm^{-1}$) thus suggesting $[C_{14}H_{19}Fe(CO)_2]_2$ to be a substituted π-cyclopentadienyl derivative of structure similar to that of $[C_5H_5Fe(CO)_2]_2$.



I



II

A characteristic reaction of $[C_5H_5Fe(CO)_2]_2$ is its reduction with sodium amalgam in tetrahydrofuran solution to give the very reactive sodium salt $NaFe(CO)_2C_5H_5$ which reacts with a variety of halides to form $RFe(CO)_2C_5H_5$ compounds[4]. The new

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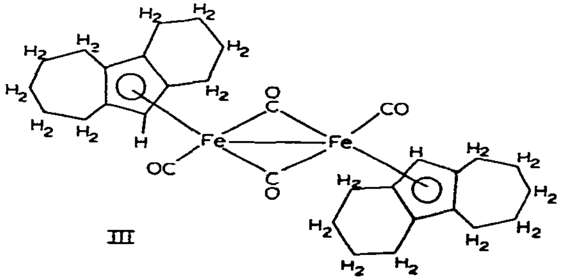
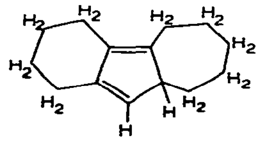
complex $[C_{14}H_{19}Fe(CO)_2]_2$ likewise reacts with sodium amalgam in tetrahydrofuran to give a solution which must contain the sodium salt $NaFe(CO)_2C_{14}H_{19}$ since it reacts with hexafluorobenzene to give the yellow mononuclear pentafluorophenyl derivative $C_6F_5Fe(CO)_2C_{14}H_{19}$, m.p. 128–129° (Anal.: Calcd.: C, 56.5%; H, 4.3%; F, 20.3%; Fe, 12.0%; mol. wt., 466 (monomer). Found: C, 56.8%; H, 4.1%; F, 19.0%; Fe, 11.8%; mol. wt., 466 (mass spect.))[5].

The proton NMR spectrum ($CS_2$ solution) of the pentafluorophenyl derivatives $C_6F_5Fe(CO)_2C_{14}H_{19}$ indicates its formulation as the tetrasubstituted $\pi$-cyclopentadienyl derivative II. A rather weak single at $\tau$ 5.66 may be assigned to the single proton bonded to the $\pi$-cyclopentadienyl ring. The remainder of the NMR spectrum consists of broad, strong, and rather complex resonances all in the range $\tau$ 7.6 to 8.4 appropriate for the nine methylene groups in structure II. Integration suggests that the resonances peaked at $\tau$ ~7.7 and ~7.85 arise from the four methylene groups bonded to the substituted $\pi$-cyclopentadienyl ring and the resonance peaked at $\tau$ 8.3 to arise from the five more remote methylene groups. This demonstration of structure II for the complex $C_6F_5Fe(CO)_2C_{14}H_{19}$ indicates that its precursor $[C_{14}H_{19}Fe(CO)_2]_2$ must have related structure III.

Formation of a complex of structure II from 1,8-cyclotetradecadiyne (I) and iron carbonyls is consistent with previous results in acetylene and metal carbonyl chemistry. Dale[6] has shown the favored conformation of 1,8-cyclotetradecadiyne to have the two carbon–carbon triple bonds in close proximity for transannular reactions. Formation of the tetrasubstituted cyclopentadiene IV from which complexes II and III are derived requires only a shift of one hydrogen atom from a propargylic methylene group to the adjacent *sp* carbon atom followed by transannular formation of carbon–carbon single bonds between two pairs of spatially proximate carbon atoms. The ability for iron carbonyls to cause hydrogen migration in unsaturated systems has already been demonstrated for reaction of iron carbonyls with both olefins[3] and diolefins[2]. The requirement of spatial proximity of the two carbon–carbon triple bonds for formation of the complex III from 1,8-cyclotetradecadiyne and $Fe(CO)_5$ is further suggested by the failure to isolate a complex analogous to III from 1,7-cyclotridecadiyne and $Fe(CO)_5$. Dale[6] has shown the two carbon–carbon triple bonds in 1,7-cyclotridecadiyne not to be spatially proximate like those in 1,8-cyclotetradecadiyne owing to the pressure of different numbers of methylene groups on each side of the carbon–carbon triple bonds. Whitlock and Sandvick[7] have reported some reactions of *o*-bis(phenylethynyl) benzene which also appear to depend on the spatial proximity of two carbon–carbon triple bonds.



III



IV

Further studies of reactions of various metal carbonyls with polyacetylenes are under investigation and will be reported in the future[8]. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1435-68.

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