Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

An unusual trimetallic product from 2,4-hexadiyne and dodecacarbonyltriiron

R.B. KING and C.W. EAVENSON

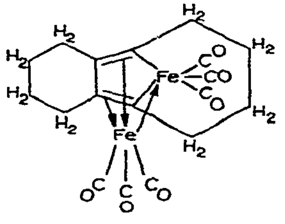
Department of Chemistry, University of Georgia, Athens, Georgia 30601 (U.S.A.)

(Received May 31st, 1972)

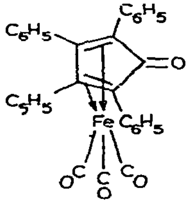
Recent work from our laboratory[1,2] has demonstrated the intramolecular transannular cyclization of macrocyclic alkadiynes (*e.g.*, 1,7-cyclododecadiyne and 1,7- and 1,8-cyclotetradecadiyne) with iron carbonyls to give substituted cyclobutadiene[2], cyclopentadienyl[1], and tricarbonylferrole[2] derivatives. These results make of interest the reactions of acyclic alkadiynes with iron carbonyls under similar conditions. This communication describes a novel trimetallic product obtained from the reaction of 2,4-hexadiyne with $Fe_3(CO)_{12}$. A previous paper by Hübel and Merényi[3] described some monometallic and bimetallic products from diphenylbutadiyne and various iron carbonyls.

A boiling solution of 5.04 g (10 mmoles) of $Fe_3(CO)_{12}$ in 75 ml of toluene was treated dropwise with a solution of 1.60 g (20.5 mmoles) of 2,4-hexadiyne in 75 ml of toluene. After continuing the boiling under reflux for ~ 16 h, the reaction mixture was filtered. The residue from evaporation of the filtrate appeared to be a complex mixture of iron carbonyl derivatives. Chromatography of this material on an alumina column in benzene or dichloromethane/pentane solution gave a yellow band followed by a brown or dark red band followed by an orange band. Evaporation of the eluate from the orange band followed by purification using repeated chromatography and crystallization from mixtures of dichloromethane and hexane gave up to a ~7% yield of yellow crystals, m.p. 200–205° (Analysis found: C, 49.2; H, 2.6; Fe, 24.3; O, 23.5; mol. wt., 670 (vapor pressure osmometer in benzene). $(C_6H_6)_3Fe_3(CO)_{10}$ calcd.: C, 49.3; H, 2.6; Fe, 24.6; O, 23.5; mol. wt., 682).

The infrared spectrum of this $(C_6H_6)_3Fe_3(CO)_{10}$ in cyclohexane solution exhibited terminal metal ν(CO) frequencies at 2076 m, 2065 s, 2041 s, 2014 s, 2005 s, 1990 m, and 1944 w cm^{-1} and a ketonic ν(CO) frequency at 1626 w cm^{-1}. This spectrum indicates that six of the ten carbonyl groups in $(C_6H_6)_3Fe_3(CO)_{10}$ arise from a tricarbonylferrole–iron tricarbonyl moiety of the type $(alkyne)_2Fe_2(CO)_6$ and that the remaining four carbonyl groups in $(C_6H_6)_3Fe_3(CO)_{10}$ arise from a cyclopentadienone–iron tricarbonyl moiety of the type $(alkyne)_2COFe(CO)_3$. Thus the ν(CO) frequencies at 2076, 2041, 2014, 2005, and 1944 cm^{-1} in $(C_6H_6)_3Fe_3(CO)_{10}$ may be assigned to the tricarbonylferrole–iron tricarbonyl moiety on the basis of their similarities in positions and relative intensities to the ν(CO) frequencies (2063, 2023, 1985, 1979, and 1917 cm^{-1}) in the tricarbonylferrole–iron tricarbonyl derivative $C_{12}H_{16}Fe_2(CO)_6$ (I) recently[2] obtained from 1,7-cyclododecadiyne and $Fe_3(CO)_{12}$, The remaining ν(CO) frequencies in $(C_6H_6)_3Fe_3(CO)_{10}$ (2065, 1990, and 1625 cm^{-1}) may be assigned to the cyclopentadienoneiron tricarbonyl moiety on the basis of their similarities in positions and relative intensities to the ν(CO) frequencies (2063, 2013, 1989, and 1642 cm^{-1}) reported[4] for tetraphenylcyclopentadienone–iron tricarbonyl $(C_6H_5)_4C_4COFe(CO)_3$ (II). The infrared spectrum of $(C_6H_6)_3Fe_3(CO)_{10}$ (KBr pellet) also exhibits a weak band at 2243 cm^{-1} assigned to an uncomplexed carbon–carbon triple bond. The proton NMR spectrum of $(C_6H_6)_3Fe_3(CO)_{10}$ exhibits five methyl resonances at τ 7.39, 7.65, 7.94, 8.30, and 8.34 ppm of relative intensities 1/2/1/1/1, respectively, and no resonances in other regions. This indicates a structure of rather low symmetry and also the absence of hydrogen shifts in the conversion of 2,4-hexadiyne to $(C_6H_6)_3Fe_3(CO)_{10}$. The mass spectrum of $(C_6H_6)_3Fe_3(CO)_{10}$ exhibits a weak but detectable molecular ion at m/e 682 as well as the families of ions $(C_6H_6)_3Fe_3(CO)_n^+$ (n = 9, 8, 7, 6, 5, 4, 3, 2, 1, and 0) and $(C_6H_6)_3Fe_3(CO)_n^{2+}$ (n = 6, 4, 3, 2, 1, and 0).

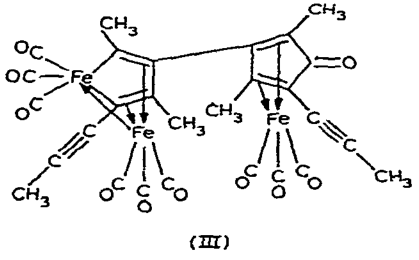


(I)

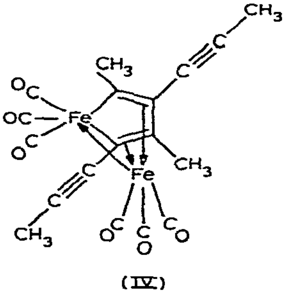


(II)

These data are in accord with any one of 16 (=2^4) possible structures for $(C_6H_6)_3Fe_3(CO)_{10}$ exemplified by structure (III). The remaining 15 alternatives to (III) differ only in the position of the two non-equivalent substituents in each of the two non-equivalent halves of the two non-equivalent five-membered rings (dividing each ring in half by a plane passing thru the CO or $Fe(CO)_3$ group). Differentiation between these 16 alternatives for $(C_6H_6)_3Fe_3(CO)_{10}$ is impossible by any available spectroscopic technique but will only be possible when X-ray crystal structure data become available on $(C_6H_6)_3Fe_3(CO)_{10}$.



(III)



(IV)

A likely intermediate in the formation of $(C_6H_6)_3Fe_3(CO)_{10}$ (*e.g.* (III)) from 2,4-hexadiyne and $Fe_3(CO)_{12}$ is the tricarbonylferrole–iron tricarbonyl complex $(C_6H_6)_2Fe_2(CO)_6$ ((IV) or isomers with reversed methyl and 1-propynyl groups). In one experiment the eluate from the brown band preceding the orange band containing the $(C_6H_6)_3Fe_3(CO)_{10}$ gave a small quantity of a solid, m.p. 66–68°, identified by its mass and infrared spectra to be this $(C_6H_6)_2Fe_2(CO)_6$ (*e.g.* (IV)). Thus the mass spectrum of this solid exhibited the families of ions $(C_6H_6)_2Fe_2(CO)_n^+$ (n = 6, 5, 4, 3, 2, 1, and 0) and $(C_6H_6)_2Fe_2(CO)_n^{2+}$ (n = 4, 3, 2, 1, and 0) in accord with this formulation. The infrared spectrum of this solid in cyclohexane solution exhibited terminal metal ν(CO) frequencies at 2076 m, 2060 m, 2040 s, 1998 vs (br), and 1943 m cm^{-1} but no bridging or ketonic ν(CO) frequencies similar to the infrared spectra of other tricarbonylferrole–iron tricarbonyl complexes prepared in this and previous[2,4] work.

In most cases the reactions of alkynes with iron carbonyls[1,2,4,5] involve the combination of two alkyne units with one iron carbonyl unit to form (cyclobutadiene)-$Fe(CO)_3$ derivatives of the stoichiometry $(alkyne)_2Fe(CO)_3$, (cyclopentadienone)-$Fe(CO)_3$ derivatives of the stoichiometry $(alkyne)_2COFe(CO)_3$, (tricarbonylferrole)-$Fe(CO)_3$ derivatives of the stoichiometry $(alkyne)_2Fe_2(CO)_6$, etc. In this context the iron carbonyl moiety can be regarded as a difunctional reagent towards alkynes since it bonds to two alkyne units in such complexes. The combination of an acyclic 1,3-alkadiyne and an iron carbonyl moiety thus involves two bifunctional reagents which potentially can lead to polymer formation. The compound $(C_6H_6)_3Fe_3(CO)_{10}$ (*e.g.* (III)) prepared and characterized in this work is significant in illustrating the first step of polymerization of a mononuclear★ derivative from an alkadiyne and an iron carbonyl by interactions of the free carbon–carbon triple bonds with additional iron carbonyl moieties to form a binuclear derivative (in this case a trimetallic compound). An interesting feature of the polymer chemistry derived from acyclic 1,3-diynes and iron carbonyls is the fact that the same alkadiyne unit can give different building blocks with iron carbonyls depending on whether cyclization occurs to give a (cyclopentadienone)$Fe(CO)_3$, (tricarbonylferrole)$Fe(CO)_3$, or any of the other types of units[4,5] found by combination of two alkynes with iron carbonyls.

We have also carried out some preliminary investigations on the reactions of the acyclic 1,5-alkadiyne 2,6-octadiyne with iron carbonyls. Reaction between 2,6-octadiyne and $Fe(CO)_5$ in boiling xylene was found to give a trace (< 1% yield) of a yellow solid, m.p. > 300°, exhibiting a mass spectrum corresponding to the stoichiometry $C_{24}H_{36}Fe_2(CO)_7$ apparently involving hydrogenation of the 2,6-octadiyne moieties as well as their trimerization. The nature of this product remains obscure because of the minute quantities which have been available up to the present time.

★ Such a mononuclear system can be bimetallic if it is a (tricarbonylferrole)$Fe(CO)_3$ unit or other system containing two metal atoms.

ACKNOWLEDGEMENT

We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF–AFOSR–1435–68. We are also indebted to Dr. James W. Howard, Jr., for assistance with some of the infrared spectra.

REFERENCES

1 R.B. King and C.W. Eavenson, *J. Organometal. Chem.*, 16 (1969) P75.
2 R.B. King and I. Haiduc, *J. Amer. Chem. Soc.*, 94 (1972) 4044.
3 W. Hübel and R. Merényi, *Chem. Ber.*, 96 (1963) 930
4 W. Hübel and E.H. Braye, *J. Inorg. Nucl. Chem.*, 10 (1959) 250.
5 F.L. Bowden and A.B.P. Lever, *Organometal. Chem. Rev.*, 3 (1968) 227.