Journal of Organometallic Chemistry, 86 (1975) 239–242
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

INTRAMOLECULAR TRANSANNULAR CYCLIZATION OF MACROCYCLIC DIALLENES WITH IRON CARBONYLS TO FORM TETRAMETHYLENEETHANE DERIVATIVES

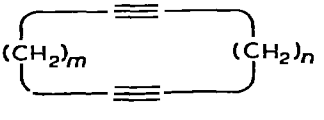
R.B. KING* and C.A. HARMON*
Department of Chemistry, University of Georgia, Athens, Ga. 30602 (U.S.A.)

(Received July 3rd, 1974)

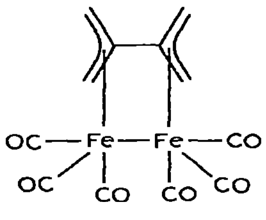
The macrocyclic diallenes 1,2,6,7-cyclodecatetraene and 1,2,9,10-cyclohexadecatetraene undergo intramolecular transannular cyclizations upon reaction with $Fe_3(CO)_{12}$ in boiling hexane to give the red-orange bicyclic tetramethyleneethane—diiron hexacarbonyl derivatives $C_{10}H_{12}Fe_2(CO)_6$ and $C_{16}H_{24}Fe_2(CO)_6$, respectively. Cerium(IV) degradation of $C_{10}H_{12}Fe_2(CO)_6$ gives 1,2,3,4-tetrahydronaphthalene in accordance with the proposed structure of $C_{10}H_{12}Fe_2(CO)_6$ with two fused six-membered rings.

Recent papers from our laboratory have described transannular cyclizations of macrocyclic alkadiynes of the type I (m = 4, n = 4, 5 and 6; m = 5, n = 5 and 6) with iron carbonyls [1-4] or $C_5H_5M(CO)_2$ (M = Co [5,6] and Rh [7]) to give cyclobutadiene [2,3,5-7], metallacyclopentadiene [2-4] or cyclopentadienyl [1,3] derivatives. In all of these reactions the two carbon—carbon triple bonds unite to form an organic ligand which then complexes with transition metals in various ways.

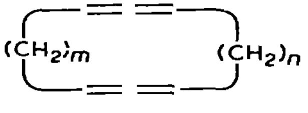
The allene unit is another type of unsaturated organic moiety which can dimerize to give ligands which form stable transition metal complexes. For example, allene reacts with $Fe_3(CO)_{12}$ to form the complex [8] $C_6H_8Fe_2(CO)_6$



(I)



(II)



(III)

---

* Post-doctoral research associate, 1973-1975.

(II) in which two allene units unite to form a tetramethyleneethane (also called diallylene [9]) ligand. This paper describes reactions of the macrocyclic diallenes III (m = 2 and 5) with $Fe_3(CO)_{12}$ to form bicyclic tetramethyleneethane complexes in which the tetramethyleneethane ligand is formed by intramolecular transannular cyclization of the two allene units in the macrocyclic ring.

Experimental

Microanalyses and molecular weight determinations by vapor pressure osmometry were performed by Atlantic Microlab, Inc., Atlanta, Georgia, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Infrared spectra were taken in hexane solutions and recorded on a Perkin—Elmer Model 621 spectrometer with grating optics. Proton NMR spectra were taken in $CDCl_3$ solutions and recorded on a Varian T-60 spectrometer. Carbon-13 NMR spectra were taken in $CDCl_3$ solutions using a Jeolco PFT-100 spectrometer operating at 25.0336 MHz in the Fourier transform mode with proton decoupling and deuterium lock. A pulse angle of 45° and a pulse interval of 3 sec were used. Carbon-13 chemical shifts are reported in ppm downfield from internal tetramethylsilane. Melting points were taken in capillaries and are uncorrected.

The 1,2,6,7-cyclodecatetraene (III, m = 2) was prepared from commercial 1,5-cyclooctadiene by addition of dibromocarbene followed by methyllithium debromination [10]. The 1,2,9,10-cyclohexadecatetraene (III, m = 5) was prepared by partial hydrogenation of commercial 1,8-cyclotetradecadiyne (Farchan Chemical Company, Willoughby, Ohio) over a Lindlar $Pd/CaCO_3/PbO$ catalyst to give 1,8-cyclotetradecadiene [11] followed by addition of dibromocarbene and methyllithium debromination [10]. The $Fe_3(CO)_{12}$ was prepared from commercial $Fe(CO)_5$ (GAF Corp., New York, N.Y.) by a standard procedure [12]. All solutions of organometallic compounds were handled under nitrogen using a nitrogen-filled glove box where necessary.

Reaction of 1,2,6,7-cyclodecatetraene with $Fe_3(CO)_{12}$

A solution of 3.0 g (6.0 mmol) of $Fe_3(CO)_{12}$, 1.0 g (7.6 mmol) of 1,2,6,7-cyclodecatetraene, and 100 ml of hexane was boiled under reflux for 23 h. Solvent was removed at 25°/35 torr. A concentrated solution of the residue in dichloromethane was chromatographed on a 2 × 80 cm alumina column. The single red band of product was eluted with 1/10 dichloromethane/hexane to give 0.875 g (28% yield) of red-orange solid $C_{10}H_{12}Fe_2(CO)_6$, m.p. ~150° (dec.). The analytical sample was purified by crystallization from hexane in a nitrogen-filled glove box.

Analysis Found: C, 46.9; H, 2.9; O, 23.3; mol. wt., 466 (in 2-butanone). $C_{16}H_{12}Fe_2O_6$calcd.: C, 46.6; H, 2.9; O, 23.4; mol. wt., 412.

Infrared ν(CO) frequencies: 2053 m, 2013 (sh), 2009 s, 1975 s and 1955 (sh) cm^{-1}.

Proton NMR Spectrum: Complex multiplets at τ 7.27, τ ~7.8 and τ 8.5 of approximate relative intensities 1/1/1, respectively.

Carbon-13 NMR Spectrum: Singlet resonances at 215.0, 211.5, 83.0, 53.4, and 22.9 ppm assigned to two types of metal carbonyl groups, the two equivalent carbons bearing no hydrogens, and the two non-equivalent sets of four methylene carbons each, respectively.

Degradation of $C_{10}H_{12}Fe_2(CO)_6$ with ammonium hexanitratocerate(IV)

A solution of 0.255 g (0.54 mmol) of $C_{10}H_{12}Fe_2(CO)_6$ in 50 ml of 95% ethanol was treated with solid ammonium hexanitratocerate(IV) at room temperature until no further gas evolution was observed. After addition of 100 ml of water, the resulting mixture was extracted with 100 ml of diethyl ether in two portions. The ether extracts were washed with a total of 100 ml of water in two portions and then dried over solid sodium carbonate. Removal of the diethyl ether at 25°/35 torr gave a small quantity of a liquid shown to be 1,2,3,4-tetrahydronaphthalene by comparison of its proton NMR spectrum in carbon tetrachloride with that of an authentic sample.

Reaction of 1,2,9,10-cyclohexadecatetraene with $Fe_3(CO)_{12}$

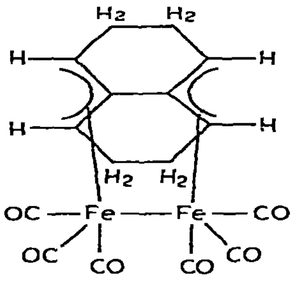
Reaction of 3.0 g (6.0 mmol) of $Fe_3(CO)_{12}$ with 1.0 g (4.6 mmol) of 1,2,9,10-cyclohexadecatetraene in 100 ml of boiling hexane for 24 h gave 0.32 g (14% yield) of red-orange $C_{16}H_{24}Fe_2(CO)_6$, m.p. > 160° (dec.), after isolation by chromatography and crystallization similar to that described above for the preparation of $C_{10}H_{12}Fe_2(CO)_6$.

Analysis Found: C, 53.6; H, 4.7; O, 19.1. $C_{22}H_{24}Fe_2O_6$ calcd.: C, 53.2; H, 4.9; O, 19.3.

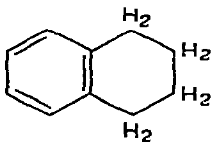
Infrared ν(CO) frequencies: 2052 m, 2012 s, 2008 s, 1974 s and 1952 (sh) cm^{-1}.

Discussion

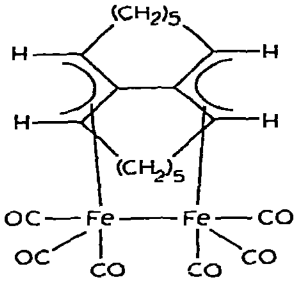
The available data on the complex $C_{10}H_{12}Fe_2(CO)_6$ from 1,2,6,7-cyclodecatetraene (III, $m = 2$) and $Fe_3(CO)_{12}$ support its formulation as the bicyclic tetramethyleneethane complex IV. The infrared spectrum of $C_{10}H_{12}Fe_2(CO)_6$ in the ν(CO) region exhibits bands at 2053, 2013, 2009, 1975 and 1955 cm^{-1} which are close to the reported [13] ν(CO) bands at 2068, 2030, 2003 and 1990 cm^{-1} for the unsubstituted tetramethyleneethane complex II, thereby suggesting the presence of a tetramethyleneethanediiron hexacarbonyl unit in $C_{10}H_{12}Fe_2(CO)_6$. The molecular weight of $C_{10}H_{12}Fe_2(CO)_6$ in 2-butanone is consistent with the simple formulation rather than an oligomer thereof, indicating that the tetramethyleneethane unit is formed by intramolecular rather than intermolecular cyclization of the two allene units in 1,2,6,7-cyclodecatetraene. The carbon-13 NMR spectrum shows only three different types of carbons in the $C_{10}H_{12}$ unit of $C_{10}H_{12}Fe_2(CO)_6$, in accord with structure IV but inconsistent with possible other structures of lower symmetry with more than three types of carbon atoms in the $C_{10}H_{12}$ unit. The carbon-13 NMR spectrum also indicates that one of the carbonyl groups in each $Fe(CO)_3$ unit is different from the remaining two carbonyl groups, consistent with the fact that one of the three carbonyl groups is *trans* to an iron—iron bond and the other two carbonyl groups are *trans* to tetramethyleneethane ligands. Degradation of $C_{10}H_{12}Fe_2(CO)_6$ with cerium(IV) gave 1,2,3,4-tetrahydronaphthalene (V) in accord with the presence of two fused six-membered rings as in structure IV. This tetrahydronaphthalene V is the only possible bicyclic $C_{10}H_{12}$ isomer with two fused six-membered rings with one of them being benzenoid.



(IV)



(V)



(VI)

The available spectroscopic and other data on the complex $C_{16}H_{24}Fe_2(CO)_6$ from 1,2,9,10-cyclohexadecatetraene (III, *m* = 5) and $Fe_3(CO)_{12}$ are similar to those of the complex $C_{10}H_{12}Fe_2(CO)_6$ (IV), suggesting the analogous structure VI for $C_{16}H_{24}Fe_2(CO)_6$.

Acknowledgement

We are indebted to the National Science Foundation for partial support of this work under Grant GP-31347-X and for a grant to the University of Georgia Chemistry Department towards the purchase of the Fourier transform NMR spectrometer.

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 R.B. King, I. Haiduc, and C.W. Eavenson, J. Amer. Chem. Soc., 95 (1973) 2508.
4 H.B. Chin and R. Bau, J. Amer. Chem. Soc., 95 (1973) 5068.
5 R.B. King and A. Efraty, J. Amer. Chem. Soc., 92 (1970) 6071.
6 R.B. King and A. Efraty, J. Amer. Chem. Soc., 94 (1972) 3021.
7 R.B. King and M.N. Ackermann, J. Organometal. Chem., 67 (1974) 431.
8 A. Nakamura, P.J. Kim, and N. Hagihara, J. Organometal. Chem., 3 (1965) 480.
9 R.B. King, J. Amer. Chem. Soc., 91 (1969) 7217.
10 L. Skattebøl, Acta. Chem. Scand., 17 (1963) 1683.
11 J. Dale, A.J. Hubert, and G.S.D. King, J. Chem. Soc., (1963) 73.
12 R.B. King, Organometal. Syn., 1 (1965) 95.
13 A. Nakamura and N. Hagihara, J. Organometal. Chem., 3 (1965) 480.