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π-Dihydropentalenylmanganese Tricarbonyl

BY T. H. COFFIELD, K. G. IHRMAN AND W. BURNS

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The reaction of acetylene with manganese carbonyl has been shown to give [1,2-(propenylene)-cyclopentadienyl]-manganese tricarbonyl, (π-dihydropentalenylmanganese tricarbonyl). An independent synthesis of a derivative of this compound conclusively proves its structure. The reaction of cycloöctatetraene with manganese carbonyl gives a tetrahydropentalenylmanganese tricarbonyl complex.

The reactions of acetylenes with metallocarbonyls to form π-bonded complexes have been the subject of a number of papers. Reppe[1] was the first to describe these reactions, but he did not elucidate the structures of the products. Complexes have been described in which the acetylene becomes part of a cyclopentadienone ring,[2,3] a duroquinone moiety,[4] or one in which the acetylene is complexed without the formation of any new carbon–carbon bonds.[5,6]

A recent paper describes a number of compounds formed by the reaction of substituted acetylenes with iron, cobalt, manganese and tungsten carbonyls.[3] These are described as being of the various types mentioned above and, in addition, cyclobutadiene and aromatic moieties are postulated.

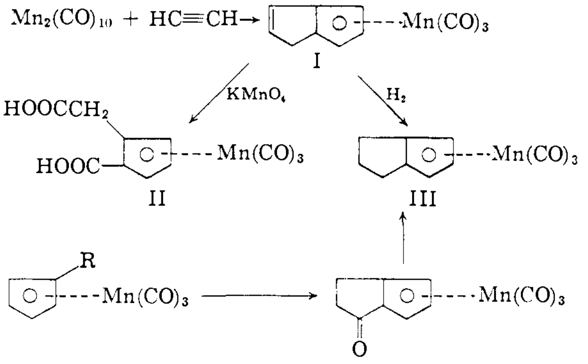
We now wish to report the first case of formation of a π-bonded cyclopentadienyl organometallic by treatment of a metallocarbonyl compound with acetylene.

Treatment of a THF[7] solution of manganese carbonyl with acetylene in an autoclave gave a volatile yellow oil which was subsequently shown to be [1,2 - (propenylene) - cyclopentadienyl] - manganese tricarbonyl (I). A smaller yield of I was obtained by treating methylmanganese pentacarbonyl with acetylene under similar conditions.

Analysis indicated formula $C_{11}H_7MnO_3$ for I and a molecular weight determination showed it to be monomeric. It was found to be diamagnetic[8] and the nuclear magnetic resonance spectrum showed three types of protons, the shifts being at 191, 277 and 382 c.p.s. from the tetramethylsilane reference. with the relative areas being 2:3:2. The 277 peak is in the region where hydrogens on a cyclopentadiene ring complexed to a manganese tricarbonyl moiety absorb.[9,10] Permanganate oxidation of I gave a diacid (II) and hydrogenation over Raney nickel gave a $C_{11}H_9MnO_3$ compound (III).

On the basis of the above results the structures of I, II and III were postulated to be those shown below.[11] Isolation and identification of the organic portion of the complex by removing it from the manganese tricarbonyl moiety was considered. A method regarded as ideal for doing this was the use of a lithium–triethylamine system which gave excellent results with ferrocene.[12] However, when this method was applied to cyclopentadienylmanganese tricarbonyl only decomposition resulted. Thus, it could not be applied to I. Therefore final structure proof of I and III demanded an independent synthesis. Since a hydrocarbon having the necessary ring system is not available, it was decided to build up the second ring on a cyclopentadiene ring already complexed to a manganese tricarbonyl moiety.

Accordingly [(chloroformyl)-cyclopentadienyl]-manganese tricarbonyl[13] (IV) was reduced to the aldehyde V with lithium tri-*t*-butoxyalumino hydride[14] and V was condensed with malonic acid to give [(2-carboxyvinyl)-cyclopentadienyl]-manganese tricarbonyl (VI). This was reduced over Raney nickel to [(2-carboxyethyl)-cyclopentadienyl]-manganese tricarbonyl (VII). The acid was



IV, R = COCl
V, R = CHO
VI, R = CH=CH—COOH
VII, R = CH_2CH_2COOH

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[1] W. Reppe, "Neue Entwicklungen auf dem Gebiet der Chemie des Acetylene und Kohlenoxyds," Springer-Verlag, 1949, p. 122; W. Reppe and H. Vetter, *Ann.*, **582**, 133 (1953).

[2] E. R. H. Jones, P. C. Wailes and M. C. Whiting, *J. Chem. Soc.*, 4021 (1955); G. N. Schrauzer, *Chemistry & Industry*, 1404 (1958); F. A. Cotton and J. R. Leto, *ibid.*, 1592 (1958); J. R. Leto and F. A. Cotton, THIS JOURNAL, **81**, 2970 (1959).

[3] W. Hübel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

[4] H. W. Sternberg, R. Markby and I. Wender, THIS JOURNAL, **80**, 1009 (1958).

[5] J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[6] H. Greenfield, *et al.*, THIS JOURNAL, **78**, 120 (1956).

[7] Tetrahydrofuran.

[8] We wish to thank Dr. Stanley Kirschner of Wayne State University for making this measurement.

[9] The hydrogens on cyclopentadienylmanganese tricarbonyl absorb at 283 c.p.s. and the ring hydrogens on (methylcyclopentadienyl)-manganese tricarbonyl absorb at 275 c.p.s.

[10] We are indebted to Dr. James Shoolery and Mr. Roy Johnson of Varian Associates for these measurements, taken on a 60 mc. high resolution spectrometer.

[11] The authors are indebted to J. Kozikowski for first suggesting this structure for compound I.

[12] D. S. Trifan and L. Nicholas, THIS JOURNAL, **79**, 2746 (1957).

[13] Prepared by the method of J. Kozikowski and M. Cais, unpublished work.

[14] H. C. Brown and R. F. McFarlin, THIS JOURNAL **80**, 5372 (1958).

cyclized with polyphosphoric acid to yield [1,2-(1-oxo-trimethylene)-cyclopentadienyl]-manganese tricarbonyl (VIII). This ketone was reduced by a typical Clemmensen reaction to [1,2-(trimethylene)-cyclopentadienyl]-manganese tricarbonyl (III). Comparison of this product with that obtained *via* reduction of I, by mixed melting point, infrared, vapor phase chromatography and X-ray diffraction showed the materials to be identical in every respect.

It is of interest that cycloöctatetraene reacted with manganese carbonyl to give small yields of III. Cycloöctatetraene is known to behave as bicyclo[4.2.0]octa-2,4,5-triene in certain reactions,[15] but this is the first report of its forming a bicyclo-[3.3.0]octane derivative.

Experimental

Reaction of Acetylene and Manganese Carbonyl.—A solution of 20 g. (0.05 mole) of manganese carbonyl in 600 g. of THF was placed in a 2-liter autoclave and 60 g. (2.3 moles) of acetylene was introduced. The pressure was brought up to 600 p.s.i. with nitrogen. The autoclave was heated to 150° over 2 hours and this temperature maintained for 5 hours. The autoclave was discharged and the mixture filtered, leaving a red-brown residue. The solvent was removed from the filtrate *in vacuo* and the residual oil distilled through an 18-inch spinning band column. A yellow, somewhat viscous oil (I), b.p. 144° (18 mm.), weighing 9.9 g. (40% yield) was obtained. The infrared showed C–H absorption at 3.45 and 3.55 μ and strong metallocarbonyl absorption at 5.05 and 5.25 μ. The compound was found to be diamagnetic.

Anal. Calcd. for $C_{11}H_7MnO_3$: C, 55.5; H, 2.88; Mn, 22.7; mol. wt., 242. Found: C, 55.4; H, 3.2; Mn, 22.2; mol. wt., 231.

Reduction of I to 1,2-(Trimethylene)-cyclopentadienylmanganese Tricarbonyl (III).—A 0.242-g. sample of I dissolved in ethanol was hydrogenated over Raney nickel at atmospheric pressure. Hydrogenation started with stirring and proceeded rapidly until 22.3 ml. of hydrogen had been absorbed. The theoretical uptake is 25.0 ml. The solvent was removed *in vacuo* and the remaining oil cooled to induce crystallization. It then was sublimed to give yellow rhombs, m.p. 34.5–35.5°.

Anal. Calcd. for $C_{11}H_9MnO_3$: C, 54.2; H, 3.7; Mn, 22.5. Found: C, 54.3; H, 3.9; Mn, 22.4.

Oxidation of I to II.—To a solution of 8 g. (0.056 mole) of potassium permanganate dissolved in 2 liters of acetone was added 2.4 g. (0.01 mole) of I. Reaction started at once. The mixture was warmed slightly on a steam-bath. After 30 minutes the purple color had faded considerably and the mixture was filtered. The residue was slurried with aqueous potassium hydroxide, filtered, the filtrate acidified and extracted with ether. Removal of the ether left an oily solid. Recrystallization from ethyl acetate–isoöctane gave a yellow solid, m.p. 233–235°. The neutralization equivalent was determined to be 160. The infrared spectrum showed two metallocarbonyl bands at 5.0 and 5.2μ. A partially resolved doublet at 5.9 and 5.95μ indicated two carboxyl groups were present.

Although the yield was only about 7%, milder conditions led to incomplete oxidation and mixtures of products.

The neutralization equivalent, infrared and general behavior indicated the compound to be a cyclopentadiene ring, with two different types of carboxyl groups as substituents, complexed to a manganese tricarbonyl moiety. Structure II or its position isomer were the most likely possibilities for this compound and this also indicated a bicyclic structure for I.

Reaction of Cycloöctatetraene and Manganese Carbonyl to Give III.—A solution of 12 g. (0.03 mole) of manganese carbonyl, 26 g. (0.25 mole) of cycloöctatetraene and 750 ml. of THF was placed in an autoclave and pressured to 500 p.s.i. with nitrogen. It was heated to 150° and 790 p.s.i. and these conditions maintained for 7 hours. The reaction mixture was discharged from the autoclave and the solvent removed *in vacuo*. The viscous residue was distilled to give 10 g. of cycloöctatetraene and a mixture of yellow solid and oil. The mixture was chromatographed on alumina. The first fraction was manganese carbonyl. The second was an oil whose infrared spectrum was identical to that of III.

Reaction of Methylmanganese Pentacarbonyl and Acetylene to Give I.—A solution of 20 g. (0.1 mole) of methylmanganese pentacarbonyl and 700 ml. of THF was placed in an autoclave and saturated with acetylene at 17° and 70 p.s.i. The solution was heated to 150° and this temperature maintained for 7 hours. The reaction mixture was filtered, the solvent removed *in vacuo* and the remaining oil distilled to give 6.5 g. (27% yield) of a yellow oil. The infrared spectrum was identical to that of I and reduction to III over Raney nickel confirmed its identity.

Synthesis of III. [(Formyl)-cyclopentadienyl]-manganese Tricarbonyl (V).—A solution of 21.4 g. (0.084 mole) of $LiAlH(OBu\text{-}t)_3$ in 49 ml. of DMC (diethylene glycol dimethyl ether) was added to a stirred solution of 16.5 g. (0.062 mole) of [(chloroformyl)-cyclopentadienyl]-manganese tricarbonyl in 215 ml. of DMC at −78° over a 1.5-hour period. After addition was complete the reaction mass was allowed to warm to room temperature. It was poured on ice and acidified to congo red with hydrochloric acid. The mixture was extracted with ether, the ether dried and the solvent removed to yield an oil. This was distilled to give 11.6 g. (81% yield) of V, a low melting solid.

The [(2-Carboxyvinyl)-cyclopentadienyl]-manganese Tricarbonyl (VI).—A mixture of 11.6 g. (0.05 mole) of V, 5.3 g. (0.05 mole) of malonic acid and 4.66 g. (0.05 mole) of α-picoline was heated on a steam-bath for 2 hours. Evolution of 800 ml., out of a theoretical 1100 ml., of gas was observed. The reaction mixture was poured into water, this extracted with ether and the ether extracts extracted with carbonate solution. Acidification of the carbonate extracts gave 8.3 g. (61% yield) of a yellow solid, m.p. 156–157° after recrystallization from chloroform–benzene.

The [(2-Carboxyethyl)-cyclopentadienyl]-manganese Tricarbonyl (VII).—A solution of 0.5 g. of VI in 20 ml. of ethanol was hydrogenated over Raney nickel at atmospheric pressure. After 1 hour the hydrogen uptake ceased, the mixture was filtered and the solvent removed. Recrystallization of the remaining oil from chloroform–petroleum ether gave 0.3 g. (60% yield) of a yellow solid, m.p. 136–138°.

The [1,2-(1-Oxo-trimethyl)-cyclopentadienyl]-manganese Tricarbonyl (VIII).—To 40 g. of polyphosphoric acid was added 4.67 g. (0.017 mole) of VII. The mixture was stirred and heated at 70–90° for 3 hours. After pouring on ice the mixture was extracted with ether. The ether extracts were extracted with carbonate solution, then dried and the solvent removed to yield 2.8 g. (65% yield) of the ketone.

The [1,2-(Trimethylene)-cyclopentadienyl]-manganese Tricarbonyl (III).—To a mixture of 5 g. of amalgamated zinc, 30 ml. of water, 30 ml. of hydrochloric acid, 10 ml. of toluene and 3 ml. of dioxane was added 1 g. (0.004 mole) of VIII. The mixture was stirred and refluxed for 24 hours. At the 3-hour mark 30 ml. of hydrochloric acid and 5 g. of amalgamated zinc were added and at the 18-hour mark 10 ml. of hydrochloric acid was added. After the reaction mixture was cooled the liquid was decanted and extracted with ether. The ether extracts were extracted several times with 10% hydrochloric acid, then dried and the solvent removed. The residual oil was chromatographed on alumina with benzene. The first fraction was taken and distilled, after removal of the solvent, to give 0.3 g. (32% yield) of a yellow solid, m.p. 34.5–35.5°. This was shown to be identical to III by infrared, mixed melting point, vapor phase chromatography and X-ray diffraction patterns.

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(15) J. W. Reppe, "Acetylene Chemistry," Charles A. Meyer and Co., Inc., New York, N. Y., 1949, p. 135.