CYCLOPENTADIENYL-AROMATIC SANDWICH COMPLEXES OF MANGANESE AND IRON

Sir:

The isolation of ferrocene[1,2] initiated extensive research effort on the chemistry of cyclopentadienyl-metal complexes. More recently, a second series of remarkable complexes has been reported in which aromatic molecules, such as benzene, are coördinated with transition metals *via* the π-electrons of the ring. This chemistry came to light with the elucidation of the structure of Hein's[3] enigmatic polyphenylchromium compounds by Zeiss,[4] and the elegant synthesis and characterization of dibenzene chromium by Fischer.[5]

We now wish to report the first synthesis of sandwich complexes of transition metals in which both a cyclopentadiene and an aromatic ring are coordinated to the central metal atom. We also wish to report the first synthesis of an aromatic complex of a Group VIIB metal, specifically, manganese.

Methylcyclopentadienyl manganese benzene has been prepared by allowing phenylmagnesium bromide to react with methylcyclopentadienyl manganese chloride or bis-methylcyclopentadienyl manganese in tetrahydrofuran and under an inert atmosphere. The latter compounds were obtained by allowing one or two equivalents, respectively, of sodium methylcyclopentadienide to react with manganous chloride. Following hydrolysis and evaporation of the Grignard reaction mixture, the product was isolated as ruby-red crystals, m.p. 116–118°, from the residues which were chromatographed and sublimed several times. (*Anal.* calcd. for $C_{12}H_{13}Mn$: C, 67.9; H, 6.2; Mn, 25.9. Found: C, 67.9; H, 6.2; Mn, 25.9.) The pure crystalline material was relatively stable to air and showed no signs of thermal decomposition up to the melting point. However, thermal degradation at higher temperatures gave benzene and methylcyclopentadiene in good yield.

Treatment of cyclopentadienyl iron dicarbonyl chloride, prepared by the method of Piper,[6] with aluminum chloride in refluxing mesitylene resulted in the smooth evolution of two equivalents of carbon monoxide. Hydrolysis, followed by saturation of the water layer with potassium iodide gave ionic cyclopentadienyl iron mesitylene iodide as stable ivory needles in 40% yield (*Anal.* calcd. for $C_{14}H_{17}IFe$: C, 45.7; H, 4.7; I, 34.5; Fe, 15.2. Found: C, 45 3; H, 4.84; I, 34.6; Fe, 14.6). The infrared spectrum supports the assigned structure.

The mesitylene manganese tricarbonyl cation resulted from the reaction of bromomanganese pentacarbonyl[7] with refluxing mesitylene in the presence of aluminum chloride. After hydrolysis, the cation was isolated as the iodide from the water layer in 90% yield as cream-colored crystals (*Anal.* calcd. for $C_{12}H_{12}O_3IMn$: C, 37.3; H, 3.1; I, 32.9; Mn, 14.2. Found: C, 37.1; H, 3.0; I, 33.3; Mn, 14.3.) The infrared spectrum showed carbon-hydrogen stretching bands at 3.35, 4.05 and 4.10 μ and bands at 4.80 and 5.00 μ in the metallo-carbonyl region. The toluene and benzene analogs also were prepared.

All of the products described above are diamagnetic[8] and thus exhibit the inert gas configuration. A complete discussion of the above work will be the subject of a forthcoming publication.

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[2] S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1852).

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[4] H. H. Zeiss and M. Tsutsui, Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, p. 29-O; H. H. Zeiss and W. Herwig, THIS JOURNAL, **78**, 5959 (1956).

[5] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955).

[6] T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[7] T. H. Coffield, J. Kozikowski and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

[8] We are indebted to Dr. Stanley Kirschner of Wayne State University for carrying out these measurements.

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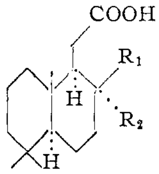
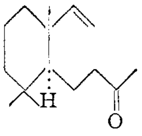
C_β-C_γ CLEAVAGE OF A γ-HYDROXY ACID BY ELECTROLYTIC OXIDATION[1]

Sir:

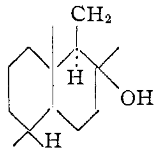
We recently reported the conversion of salts of I and II to tetracyclic triterpenes of the onocerane series by electrolytic oxidation.[2] The present communication concerns a novel elimination process which occurs concurrently with the previously described coupling during the electrolysis of I and leads to the unsaturated ketone IV ($C_{15}H_{26}O$).



I, $R_1 = CH_3$, $R_2 = OH$
II, $R_1 = OH$, $R_2 = CH_3$
III, $R_1 = CH_3$, $R_2 = OCOCH_3$



IV



V

The ketone (b.p. 95–96° (0.4 mm), $n^{21}D$ 1.4857, $[\alpha]^{26}D$ −10.4° ($CHCl_3$); found: C, 80.88; H, 10.80) was obtained in 34–38% yield from I and usually was contaminated with a small amount (*ca.* 3%) of a closely similar ketonic impurity (probably isomeric) as determined by vapor chromatography. The presence of a ketone function was shown by conversion to a semicarbazone (m.p. 175.5–178.5°; found: C, 68.71; H, 10.33) and unsaturation was demonstrated by the formation of a dihydroketone (semicarbazone, m.p. 156.5–158.5°; found: C, 68.56; H, 10.91) by hydrogenation with palladium-charcoal in methanol. The infrared spectrum of the unsaturated ketone (in CCl_4) lacked hydroxyl absorption and manifested bands at 1722 cm.$^{-1}$ (C=O), 1637 cm.$^{-1}$ (C=C), 1008 and 917 cm.$^{-1}$ (-CH=CH$_2$), the last three bands

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[1] This investigation was supported by a fellowship (AF-6570) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

[2] E. J. Corey and R. R. Sauers, THIS JOURNAL, **79**, 3925 (1957).