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REACTION OF DIBENZOSEMIBULLVALENE WITH $Fe_2(CO)_9$

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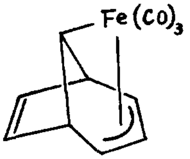
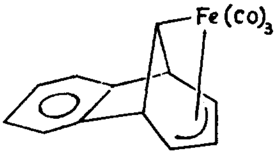
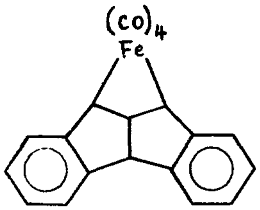
SEMIBULLVALENE and benzosemibullvalene reacted with $Fe_2(CO)_9$ in the manner typical of vinylcyclopropane systems to form σ-π-allyl complexes.[1,2] For example, (I) was obtained in 70% yield[1] on treatment of semibullvalene with $Fe_2(CO)_9$ whereas its benzo-analogue (II) was obtained in 75% yield from benzosemibullvalene in a similar reaction.[2]



(I)



(II)



(III)

Dibenzosemibullvalene, however, behaved as an isolated cyclopropane under similar conditions and gave ferretane (III) in 25% yield.[3] In spite of the dramatic differences between these products, it was believed[3] that the σ-π-allyl complexes were formed via intermediates, analogous to that leading to ferretane formation, prior to skeletal rearrangements. This assumption was supported by the reactions of semibullvalene and its benzo-derivative with potassium tetrachloropalladate yielding complexes with a bicyclo [3.3.0] octadiene skeleton as the organic ligand.[4] However, the comparatively low yield of ferretane from dibenzosemibullvalene would make this postulate unattractive since ferretane itself showed remarkable chemical stability.[3]

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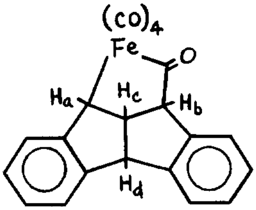
In order to gain further insight into the validity of the above assumption we undertook a more detailed investigation of the reaction of dibenzosemibullvalene with $Fe_2(CO)_9$ and isolated a new product (IV) in addition to ferretane.



(IV)

When dibenzosemibullvalene was treated with $Fe_2(CO)_9$ in 1:2 molar ratio in benzene at 55° for 2 hr., a mixture, which was separated into three fractions by column chromatography (silica gel; benzene-pet. ether (1:4)), was obtained. Fraction 1 gave ferretane[3] (yellow crystals, 18.3%) and fraction 2 yielded unreacted dibenzosemibullvalene[5] (colourless needles, 35%). Fraction 3, which separated very well from the previous two, gave off-cream needles (31%; m.p. 124 - 5° (dec.)). Found : C, 62.93; H, 3.14%; $C_{21}H_{12}FeO_5$ requires C, 63.03; H, 3.02%. IR (hexane) showed $C\equiv O$ absorption at 2102, 2053, 2030 (vs), 2000 cm^{-1} and $>C=O$ absorption at 1685 cm^{-1}. Its NMR (C_6D_6) is in complete accord with the assigned structure (IV) : τ, 5.05 (H_a or H_b, d, J = 10 Hz, 1 H); 5.42 (H_a or H_b, d, J = 9 Hz, 1 H); 5.81 (H_d, d, J = 10 Hz, 1 H); 6.50 (H_c, m, 1 H) and 2.5 - 3.2 (aromatic protons, m, 8 H). MS (source temp. at 55°) showed molecular ion at *m/e* 400; and the lower part of the spectrum is virtually identical with that of ferretane (III). On the basis of elemental analysis, spectral data and chemical reactions, structure (IV) was assigned. This new Fe(II)-containing heterocyclic ring system, 1-ferrocyclopent-2-one, is analogous to the Rh(III)-analogue reported by Wilkinson.[6]

Although compound IV is stable in the solid form, it slowly decomposes in solution as evidenced by the gradual development of yellow colour on standing even at room temp. Recrystallization from warm pentane gave a mixture of III and IV. Quantitative measurements showed that 0.65 mole of carbon monoxide gas was obtained per mole of IV from a benzene solution heated at 55° for 15 hr.

Facile loss of CO gas from metal acyl carbonyl is a common process.

When carbon monoxide gas was bubbled into the benzene solution of III at atmospheric pressure, the yellow colour gradually faded and eventually became colourless in about 15 hr. Compound IV was isolated as the sole product. This established the reversibility of compounds III and IV which again is typical of the "CO-insertion" in transition metal complexes.

$$\mathrm{III} \quad \underset{\text{CO, atm. pressure}}{\overset{\text{in solution, }\Delta}{\rightleftharpoons}} \quad \mathrm{IV}$$

Attempts to insert a further mole of CO into the second carbon-metal σ-bond has, so far, not been successful. A solution of IV in benzene had been subjected to CO gas under various conditions, including 60 atm. pressure for 60 hr. at room temp., but each time only starting material was recovered. Methanolic solution of IV under 100 atm. of CO at 50^{0} for 60 hr. led to some decomposition to III as revealed by TLC but the amount of starting material recovered was $>80\%$.

Taking into account the unreacted dibenzosemibullvalene, the yields of ferretane and compound IV from the initial reaction were 28% and 48%, respectively. Combination of these two figures gave a total yield comparable to that of semibullvalene and benzosemibullvalene.

The question of whether IV was initially formed which then decomposed to III through "CO-extrusion", or vice versa by means of a "CO-insertion" process, or both III and IV were formed at the same time, has not been ascertained. Analogy may be drawn from reactions of cyclopropanes with $Rh_2(CO)_4Cl_2$ or vinylcyclopropane systems with $Fe_2(CO)_9$ where the metal acyl derivatives were established [6,7] to be the initial products.

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