

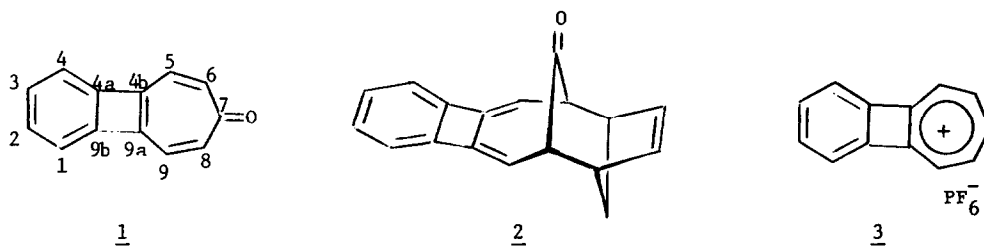
TRICARBONYL(1,2,2a,7a- η -CYCLOBUTA[d]TROPONE) IRON AND TRICARBONYL(1,2,2a,7a- η -CYCLOBUTATROPYL-
IUM) IRON HEXAFLUOROPHOSPHATE

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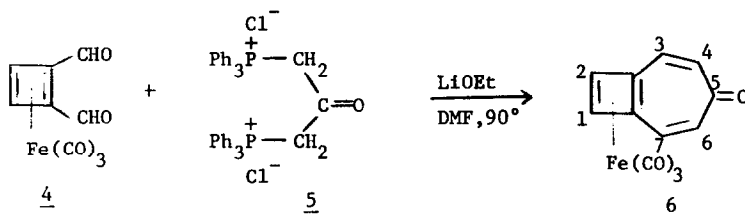
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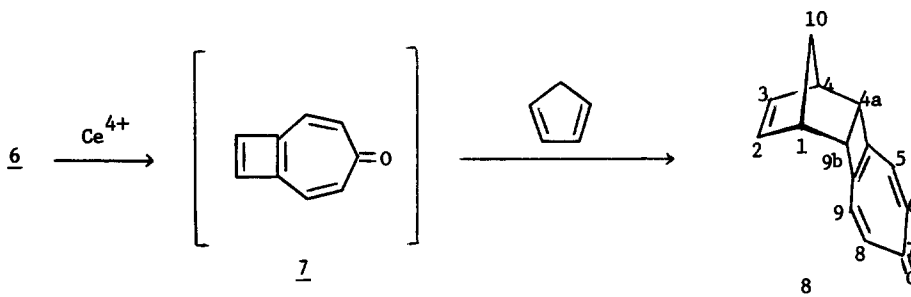
We have recently described the generation of benzo[3,4]cyclobuta[1,2-d]tropone 1 and its trapping with cyclopentadiene to give the (6+4)-adduct 2.¹ This work forms part of a study of novel aromatic systems possessing 4-membered rings,^{1,2,3} which has included the tropylium salt 3.³



In view of the high reactivity 1,¹ and the propensity of 3 to undergo skeletal rearrangement on nucleophilic capture,³ it seems attractive to prepare 4a,4b,9a,9b- η iron tricarbonyl complexes of 1 and 3, in order to stabilise these systems, and further study their chemistry. The analogous iron tricarbonyl complexes of benzocyclobutadiene and cyclobutadiene are known to be stable, and the free olefinic ligands can readily be generated oxidatively from such complexes.⁴ In this note we report the preparation of the title iron tricarbonyl complexes 6 and 12, which lack the annellated benzene ring of 1 and 3, and which were chosen for initial study because a suitable precursor, tricarbonyl(1,2,3,4- η -cyclobutadiene-1,2-dicarboxaldehyde) iron 4, has recently become available.⁵

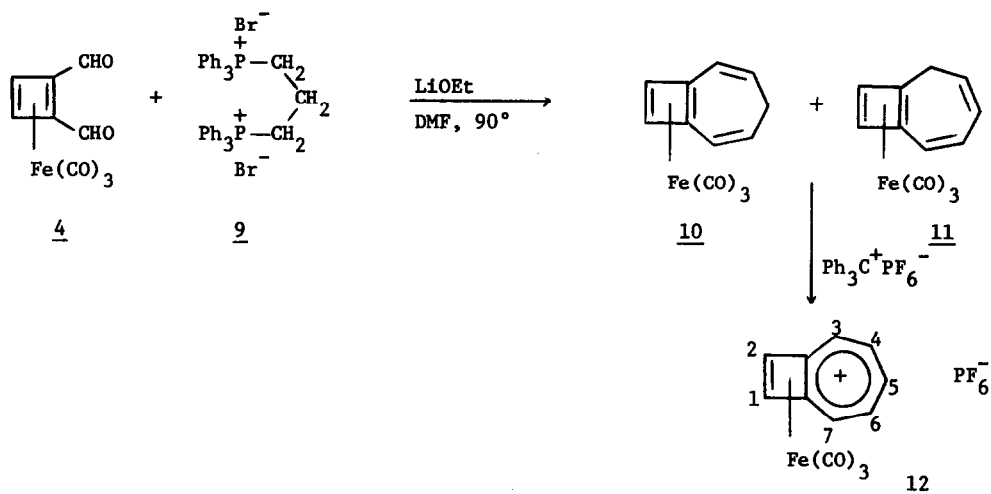


A bis-Wittig reaction⁶ between dialdehyde 4 and the ylid derived from 5⁷ (in situ generation⁸) gave, after chromatography and sublimation, tricarbonyl(1,2,2a,7a-η-cyclobuta[d]-tropone)iron 6⁹ (8%) as yellow-orange crystals, m.p. 150.5-151°; ν_{\max} (CCl₄) 2056 (s) and 1995 (s) (metal CO), 1622 (w) (Tropone CO), 1607 (m) cm⁻¹; m/e 270 (M⁺, 30%), 242 (M⁺-CO, 37%), 214 (M⁺-2CO, 37%), 186 (M⁺-3CO, 74%), 158 (M⁺-4CO, 33%), 132 (M⁺-4CO-C₂H₂, 100%); ¹H nmr $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 6.66 and 6.24 (ABq, J = 11.5Hz, 4H, H₃, H₇ and H₄, H₆ respectively), 4.57 (s, 2H, H₁, H₃). On expansion each line of the ABq shows some fine structure, indicating that the tropone protons really constitute an AA'BB' system, but the cross-ring couplings appear to be less than 1Hz.

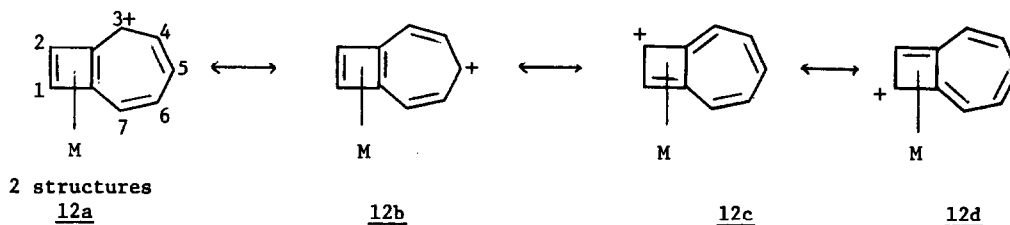


Oxidation of the complex 6 with ceric ammonium nitrate in the presence of cyclopentadiene gave a single product, endo-1,4,4a,9b-tetrahydro-1,4-methanobenzo[3,4]cyclobuta[1,2-d]tropone 8⁹ (63%), m.p. 90-91.5°, the structure of which follows from spectroscopic data: ν_{\max} (CCl₄) 1625 (s) cm⁻¹ (tropone CO); m/e 196 (M⁺, 30%), 168 (M⁺-CO, 68%), 102 (M⁺-CO-C₅H₆, 100%); ¹H nmr $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 6.92 and 6.79 (ABq, J = 12Hz, 4H, H₅, H₉ and H₆, H₈ respectively), 5.76 (apparent t, "J" = 2Hz, 2H, H₂, H₃), 3.44 (d, J = 4Hz, 2H, H_{4a}, H_{9b}), 2.95 (m, 2H, H₁, H₄), 1.97 and 1.68 (broadened ABq, J = 8 Hz, 2H, H₁₀). The endo-stereochemistry shown is assigned on the basis of the observed coupling constant, J = 4Hz, between the norbornene bridgehead and cyclobutenyl methine protons, which indicates an exo orientation of the latter. Thus cyclobuta[d]tropone 7 behaves as a π^2 component towards cyclopentadiene, while benzo[3,4]cyclobuta[1,2-d]tropone 1 reacts as a π^6 component.

Reaction of dialdehyde 4 with the ylid derived from 9 gave a mixture of hydrocarbon complexes⁹ 10 and 11 (23%) as a low-melting solid in variable ratio from reaction to reaction. These complexes were not separated preparatively, but could be resolved analytically by glc-ms. The ¹H nmr spectrum of the mixture showed, inter alia, two singlets at δ 4.16 and 3.97 for the cyclobutadiene protons of the unsymmetrical complex 11,¹⁰ and one singlet at δ 4.09 for



the corresponding protons of 10. This mixture, on treatment with trityl hexafluorophosphate in dichloromethane gave tricarboxyl(1,2,2a,7a-n-cyclobutatripylium)iron hexafluorophosphate 12⁹ as purple-black needles (63%), of indefinite m.p.; ν_{max} (Nujol mull) 2095 (s), 2049 (s), 2032 (s) cm^{-1} (metal CO); ^1H nmr (liquid SO_2 , 250K, relative to CH_3NO_2 at δ 4.33) δ 8.29 (d, $J = 9.5\text{Hz}$, 2H, H_3, H_7), 7.74 (t, $J = 10\text{Hz}$, 1H, H_5), 7.12 (d of d, $J \sim 9.5, 10\text{Hz}$, 2H, H_4, H_6), 5.73 (s, 2H, H_1, H_2). From these chemical shifts, the order of deshielding of the protons is $\text{H}_3 = \text{H}_7 > \text{H}_5 > \text{H}_4 = \text{H}_6 > \text{H}_1 = \text{H}_2$, which reflects the positive charge density at the corresponding carbon atoms; *i.e.* positive charge at $\text{C}_3 = \text{C}_7 > \text{C}_5 > \text{C}_4 = \text{C}_6 > \text{C}_1 = \text{C}_2$. In resonance terminology,



canonical form 12a makes the most important contribution, followed by 12b. The ability of a metal carbonyl residue to stabilise positive charge α to a complexed diene system, as in 12a, is well known for other systems.¹¹ Preliminary indications are that nucleophilic attack on 12 does occur chiefly at C_3 (C_7). Structures 12c and 12d appear to make an appreciable contribution, since the H_1, H_2 signal at δ 5.73 is significantly downfield from the

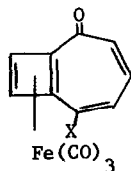
corresponding signals in 10 and 11 (ca. δ 4.0), or the four-membered ring proton signal in tricarbonyl(benzocyclobutadiene)iron (δ 4.02).¹²

The preparation of 6 and 12 thus represent further examples of the use of 1,2-disubstituted tricarbonyl(cyclobutadiene)iron derivatives in the synthesis of novel ring systems.¹³ Aspects of the chemistry of 6 and 12 are under investigation.

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References and Footnotes.

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13. For examples see (a) B.W. Roberts and A. Wissner, J. Amer. Chem. Soc., 92, 6382 (1970).
Included in this work is the preparation of complexes 13 and 14.



13 X = OC₂H₅

14 X = OH

- (b) B.W. Roberts and A. Wissner, J. Amer. Chem. Soc., 94, 7168 (1972).