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CYCLOADDITION REACTIONS OF TRIENONEIRON TRICARBONYL COMPLEXES.
THE OXIDATIVE REARRANGEMENT OF σ,π-ALLYLIRON TRICARBONYL COMPLEXES.

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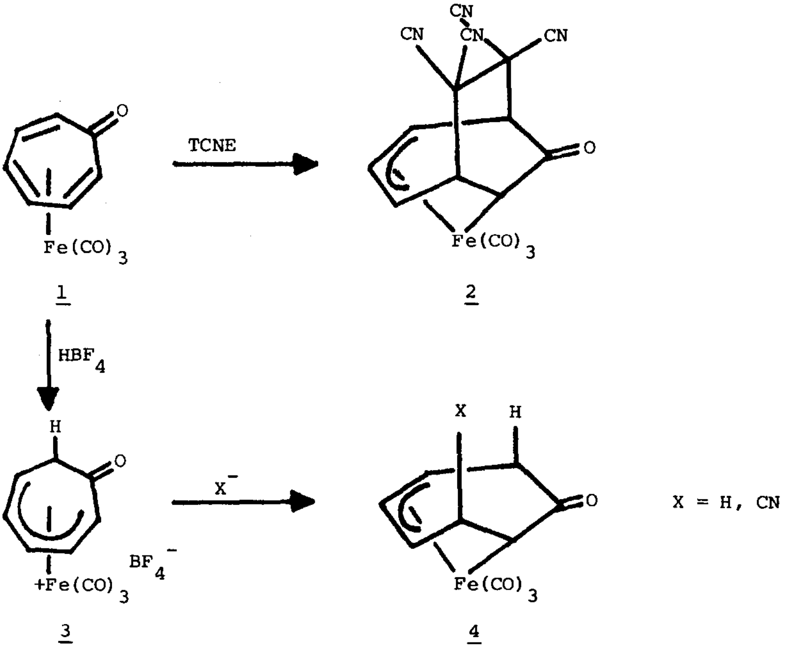
The reactions of uni- and biparticulate electrophiles[1] with cyclic trieneiron tricarbonyl complexes can lead to a variety of cycloaddition products,[2] the nature of which depends upon factors which are not yet completely understood. Recently, we have recognized and explored a novel 1,5-cycloaddition of tetracyanoethylene (TCNE) to troponeiron tricarbonyl (1) forming the σ,π-allyliron tricarbonyl complex 2. Selective deuterium labeling suggested the involvement of the uncomplexed double bond in the initial electrophilic attack.[3] Concurrently, Eisenstadt reported[4] an analogous formal 1,5-addition of biparticulate electrophiles, to give 4, on treating troponiumiron tricarbonly fluoroborate 3 with either CN^- or H^- .



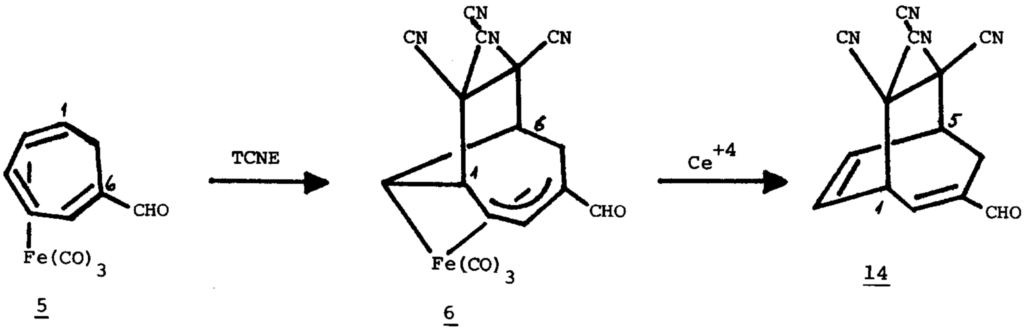
We have extended our studies to other cyclic carbonyl conjugated triene complexes and now wish to report the first example of an initial electrophilic attack on a coordinated double bond by TCNE. We also wish to describe a general oxidative rearrangement of σ,π-allyliron tricarbonyl cycloadducts which provides a new synthetic route to bridged homoconjugated dienones.

When 6-formyl-cycloheptatrieneiron tricarbonyl (5)[5] was treated with TCNE in CH_2Cl_2 solution, a slow reaction took place affording a 1:1 crystalline adduct[6] (44% from acetone-pentane, mp. 165° dec.). The structural assignment as the 1,3-cycloadduct 6 was based on the nmr spectrum in acetone-d_6 which displayed signals at δ 3.71 (H_{5n},dd,J=16.5, 13); 4.20 (H_6,ddd,13,6,2); 4.70 (H_1,dd,9.5,7); 5.52 (H_2,t,7); 5.78 (H_3,d,7); 9.36 (formyl-H,s). The additional C-5x and C-9 protons which are covered by the acetone signal form a two proton complex (in DMSO-d_6) at δ 1.80 with the H_{5x} doublet (J=16.5) covering the H_9 signal. The relatively high field signal of H_9 together with the close resemblance of the spectrum to that of the parent hydrocarbon 7 [7] confirm this structural assignment. The reaction clearly involves the unprecedented initial electrophilic attack of TCNE at the C-1 position of the coordinated double bond, which is followed by a ring closure at C-3.

This reversed regiospecificty is not shared by cyclooctatrienone complex 8,[8,9] which reacts rapidly with TCNE under similar conditions to give cycloadduct 9 (68%, mp. 142° dec., CH_2Cl_2-pentane).[6] This complex while stable in its crystalline form, decomposes rapidly in polar solvents, making the nmr measurements difficult. Nevertheless, the nmr spectrum in acetone-d_6 confirms the structural assignments (Cf. 6) displaying signals at δ 3.64 (1H_6,m); 4.2 (H_7,m); 4.31 (H_4,d,10); 4.88 (H_1,dd,7,9.5); 5.4 (H_2,t,9.5); 5.8 (H_3, bt, 9.5,10); with the two missing protons hidden under the acetone signals. Evidently, cyclooctatrienone complex 8 like tropone complex 1, reacts through the free double bond. However, only 1 prefers the 1,5-cycloaddition, while both 5 and 8 take the 1,3-cycloaddition route exclusively. This exceptional behavior of 1 in entering 1,5-cycloaddition reactions was further exemplified by the reaction with the powerful uniparticulate electrophile N-phenyl-triazolinedione (NPTD) in benzene solution to give the cycloadduct 10 [6] (90%, mp. 153° dec., CH_2Cl_2-pentane), characterized by its nmr signals ($CDCl_3$) at δ 2.54 (H_7,dd,9,2); 4.3 (H_1,ddd,7,6,2); 4.88 (H_2dd,9,7); 5.0-5.2 (H_3,H_4,H_5,m).

Examining the structures of the intermediate transient zwitterions, 11, 12 and 13, in the reaction of the three trienone complexes, we note that they all have a carbonyl group conjugated to the pentadienyl moeity. This group seems to stabilize the intermediate and thus control the initial site of electrophilic attack. On the other hand the factors which control the site of the subsequent nucleophilic attack on the pentadienyl moiety are much more difficult to assess at this point. Whether steric or electronic factors play a role must await more detailed structural investigations.

No less interesting was our attempt to release the organic ligand of the cycloaddition products from its metal complex, by oxidation. Usually, the oxidative degradation



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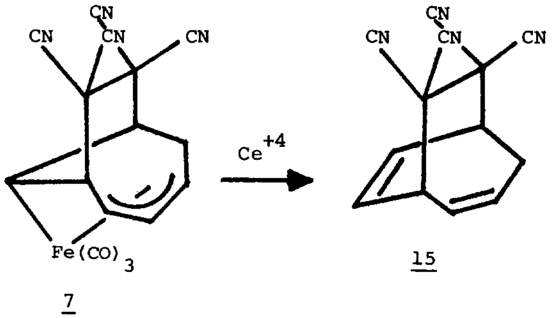

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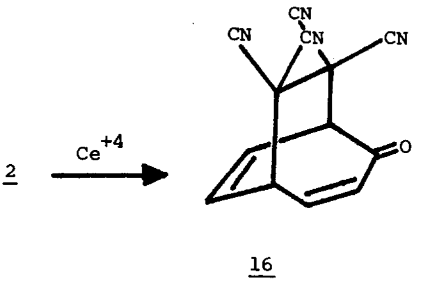

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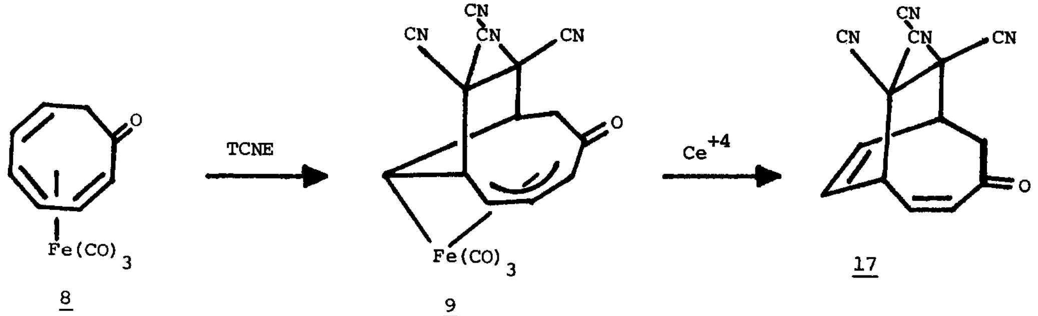

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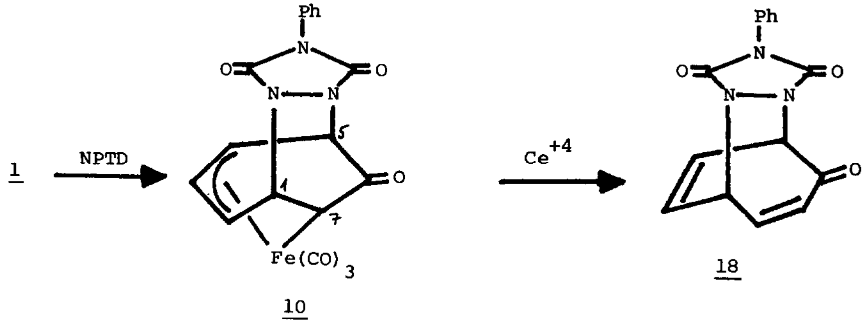

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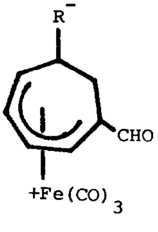

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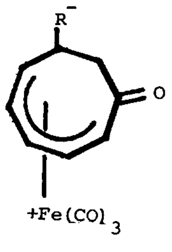

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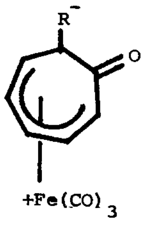

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R = $(CN)_2C-C(CN)_2$

of σ,π-allyl complexes leads to the formation of the unrearranged organic ligands.[7,10] However, Entholt and Kerber were first to show[7] a single example of an oxidative rearrangement of the σ,π-allyl complex 7 to the bicyclic diene 15. We have observed a similar rearrangement on Ce^{+4} oxidation of the TCNE and NPTD σ,π-allyl complexes regardless of whether they were 1,3- or 1,5- cycloadducts. Thus, a careful Ce^{+4} oxidation of the tropone complexes 2 and 10 gave the corresponding TCNE and NPTD bridged cycloheptadienones 16 [6] [71%, methanol, m.p. 165° dec., nmr (acetone-d_6) δ 4.72 (H_1,dd,8,2); 4.93 (H_5,t,8); 6.24 (H_3,dd,11,2); 6.78 (H_7,t,8); 7.14 (H_6,t,8); 7.38 (H_4,dd,11,8)] and 18 [11] (25% yield). Similarly, oxidation of aldehyde 6 gave 14 [6] [40%, methanol, mp. 169° dec., nmr (acetone-d_6) δ 2.74 (H_{4n},ddd, 20,4,2); 3.21 (H_{4x},ddd,20,3,1.5); 4.08 (H_5,m); 4.58 (H_1,dt,8,1.5); 6.83 (H_6,H_7,m); 7.18 (H_2,dt,8,2,1.5); 9.6 (formyl-H,s)]. Finally, oxidation of trienone adduct 9 afforded the rearranged dienone 17 [6] [18%, methanol, mp. 148° dec., nmr (acetone-d_6) δ 2.92 (H_{5n},dd,12,2); 3.44 (H_{5x},t,12); 4.32 (H_1,H_6,m); 5.94 (H_3,d,12); 6.56 (H_2,H_7, H_8,m)]. No other products could be isolated from the reaction mixtures.

References and Footnotes

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