Novel Reaction of Cycloheptatriene(tricarbonyl)iron: Nucleophilic Addition to and Breaking of the Cycloheptatriene Ring

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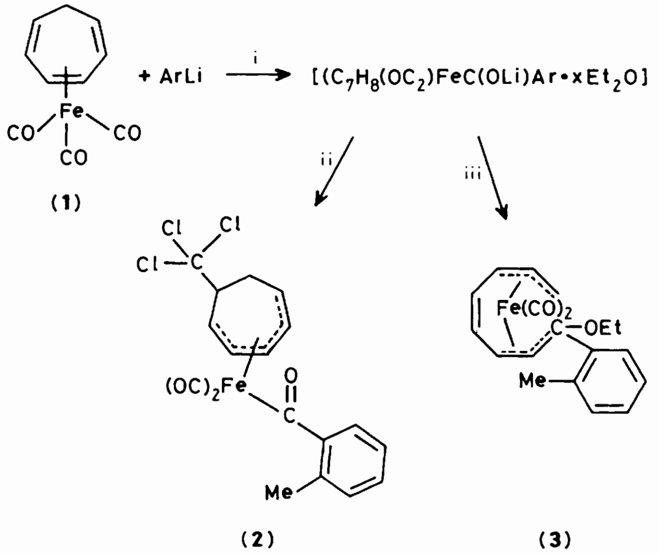
Reaction of cycloheptatriene(tricarbonyl)iron (**1**) with *o*-tolyl-lithium, followed by reaction of the intermediate acylmetallate with Et_3OBF_4, in CH_2Cl_2 at −60 °C and in aqueous solution at 0 °C, affords the novel compounds $(CCl_3\text{-cyclo-}C_7H_8)(OC)_2Fe(COC_6H_4Me\text{-}o)$ (**2**) and the ring-opened $(OC)_2Fe\{C(OEt)(C_6H_4Me\text{-}o)C_7H_8\}$ (**3**), respectively, the structures of which have been determined by *X*-ray crystallography.

Alkene–metal carbene complexes are interesting as important intermediates in various reactions of metal carbene complexes with alkenes.[1—3] Recently, we reported the synthesis and structure of a series of isomerized products of butadiene-, isopropene-, and cyclo-octatetraene-(dicarbonyl)[ethoxy-(aryl)carbene]iron complexes.[4—6] Herein we report the unprecedented reaction of cycloheptatriene(tricarbonyl)iron (**1**) with aryl-lithium reagents at low temperature which leads to addition to and cleavage of the cycloheptatriene ring.

Cycloheptatriene(tricarbonyl)iron (**1**) was treated with *o*-tolyl-lithium in ether at −60 °C for 3 h and the acylmetallate formed was treated with Et_3OBF_4, first in CH_2Cl_2 at −60 °C and second in aqueous solution at 0 °C, to give the yellow, crystalline $(CCl_3\text{-cyclo-}C_7H_8)(OC)_2Fe(COC_6H_4\text{-}Me\text{-}o)$ (**2**) in 30% yield, and the orange-red, crystalline $(OC)_2Fe\{C(OEt)(C_6H_4Me\text{-}o)C_7H_8\}$ (**3**) in 44% yield, respectively.

When phenyl-lithium and *p*-tolyl-lithium were used in place of *o*-tolyl-lithium, under the same conditions, no analogous



Scheme 1. Ar = *o*-MeC_6H_4; i, Et_2O, −60 °C; ii, Et_3OBF_4, CH_2Cl_2, −60 °C; iii, Et_3OBF_4, H_2O, 0 °C.

products were obtained. Both products (**2**) and (**3**) were highly sensitive to air and temperature. Their structures were determined by elemental analyses, spectral studies, and *X*-ray crystallography.†

The molecular structure of (**2**) is shown in Figure 2.‡ A trichloromethyl group is bonded to the cycloheptatriene ligand which causes the ligand to be transformed into a conjugated delocalized η^5–π bonded system composed of C(2), C(3), C(4), C(5), and C(6). Of the other three ligands bonded to Fe, each CO ligand contributes two electrons, and C(11) of the *o*-toluoyl group forms a σ bond with the Fe atom providing one σ electron to satisfy the 18 electron rule.

It is not yet clear how the trichloromethyl group is formed and how it becomes bonded to the cycloheptatriene ring during the reaction. However, we believe that it is formed by a metathetical reaction of solvent CH_2Cl_2 molecules aided by iron at Et_3OBF_4. No chloroform, carbon tetrachloride, or other chlorides were found in the solvents before reaction, but hexachloroethane and chloroform, evidence for the presence of trichloromethyl species, were detected by chromatography following the treatment with Et_3OBF_4.

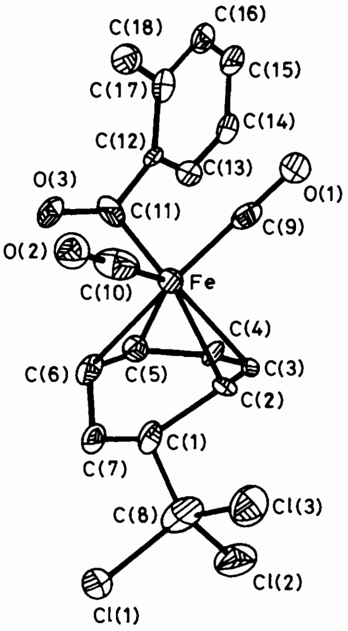


Figure 1. Molecular structure and labelling diagram for (**2**). Fe–C(2), 2.318(26); Fe–C(3), 2.070(24); Fe–C(4), 2.079(24); Fe–C(5), 2.059(29); Fe–C(6), 2.142(26); Fe–C(9), 1.715(27); Fe–C(10), 1.619(35); Fe–C(11), 2.005(28); O(3)–C(11), 1.181(31); C(1)–C(2), 1.543(34); C(2)–C(3), 1.420(37); C(3)–C(4), 1.441(37); C(4)–C(5), 1.409(36); C(5)–C(6), 1.380(39); C(6)–C(7), 1.465(39); C(7)–C(1), 1.491(39) Å.

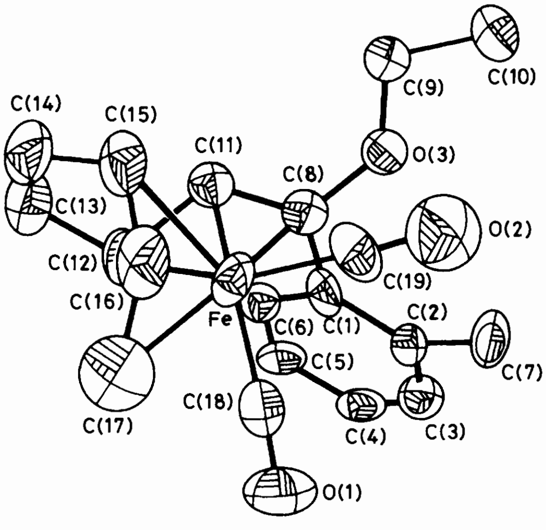


Figure 2. Molecular structure and labelling diagram for (**3**) Fe–C(8), 2.443(6); Fe–C(11), 2.065(6); Fe–C(12), 2.114(7); Fe–C(15), 2.236(5); Fe–C(16), 2.093(6); Fe–C(17), 2.129(7); Fe–C(18), 1.794(6); Fe–C(19), 1.779(6); O(3)–C(8), 1.367(6); C(8)–C(11), 1.395(7); C(11)–C(12), 1.467(8); C(12)–C(13), 1.475(8); C(13)–C(14), 1.328(11); C(14)–C(15), 1.491(11); C(15)–C(16), 1.405(10); C(16)–C(17), 1.450(11) Å. ∠ C(1)–C(8)–C(11), 126.7(5); O(3)–C(8)–C(1), 109.2(4); O(3)–C(8)–C(11), 121.1(5)°.

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† *Spectral data*: (**2**), m.p. 120 °C (decomp.); i.r. (ν_{CO} cm^{-1}) 2016vs, 1967vs (CH_2Cl_2); 2023vs, 1977vs (pentane); 1998vs, 1958vs; Ar–CO 1615vs (KCl); ^1H n.m.r. (CD_3COCD_3) δ 7.58, 7.32 (m, 4H, C_6H_4Me), 7.28 (m, 1H, $C_7H_8CCl_3$), 5.55 (m, 2H, $C_7H_8CCl_3$), 5.20 (m, 1H, $C_7H_8CCl_3$), 2.32 (s, 3H, MeC_6H_4), 2.20 (m, 2H, $C_7H_8CCl_3$), 1.96 (m, 2H, $C_7H_8CCl_3$); *m/z* 440 (M^+).

(**3**), M.p. 72—73 °C (decomp.); i.r. (ν_{CO} cm^{-1}) 1973vs, 1912vs (CH_2Cl_2); 1980vs, 1925vs (pentane); 1975vs, 1915vs (KCl); ^1H n.m.r. (CH_3COCD_3) δ 7.60—7.05 (m, 4H, C_6H_4Me), 6.10 (m, 1H, C_7H_8), 5.50 (m, 1H, C_7H_8), 4.70 (q, 2H, OCH_2Me), 3.80—3.20 (m, 6H, C_7H_8), 2.58 (s, 3H, MeC_6H_4), 1.28 (t, 3H, OCH_2Me); *m/z* 352 (M^+).

‡ *Crystal data*: (**2**), M = 441.52, monoclinic, space group C^5_{2h}-$P2_1/n$, a = 13.993(11), b = 9.339(11), c = 14.110(10) Å, β = 95.06(6)°, U = 1836(2) Å^3, Z = 4, D_c = 1.60 g cm^{-3}; of 1975 unique reflections collected (3° ≤ 2θ ≤ 42°), 1021 observed reflections with $I > 2.5\ \sigma(I)$ were used to solve the structure by direct methods; refinement led to a final R value of 0.094.

(**3**), M = 352.22, orthorhombic, space group D^4_2-$P2_12_12_1$, a = 7.01(0), b = 12.38(1), c = 19.60(1) Å, U = 1700.3 (1.6) Å^3, Z = 4, D_c = 1.38 g cm^{-3}; of 1783 unique reflections collected (3° ≤ 2θ ≤ 50°), 1381 observed reflections with $I > 2.5\ \sigma(I)$ were used in the solution (direct methods) and refinement (block-diagonal least-squares); R = 0.046, R_w = 0.0413.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The *X*-ray structure of (**3**) (Figure 2)‡ shows that the cycloheptatriene ring of (**1**) has opened by cleavage of the original C(11)–C(17) σ-bond, and in (**3**) the C(11) atom is linked to the 'carbene' carbon C(8) forming a new σ-bond C(11)–C(8), resulting in the formation of two allyl-type molecular π-bonding orbitals, C(8)–C(11)–C(12) and C(15)–C(16)–C(17) which interact with the Fe orbitals in an η^3 side-on mode.

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