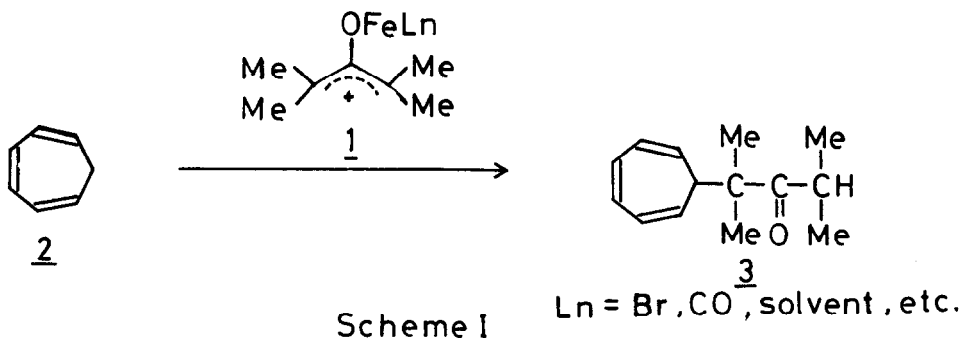


HIGH PERISELECTIVITY OF CYCLOCOUPLING REACTIONS OF 2-OXYALLYL CATION WITH CYCLOHEPTATRIENEIRON TRICARBONYL

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Summary: The cyclocoupling reaction of 2-oxyallyl-Fe(II) cation (1) with cycloheptatrieneiron tricarbonyl (4) gave the σ, π -allyliron tricarbonyl complex (6). Structure of the complex (6) was fully established by X-ray analysis. Oxidative degradation of the complex (6) with *o*-chloranil afforded a single iron free compound (7) which was indicated that a carbonyl insertion took place during oxidation.

Previously, we have described kinetic data on the reactions of 2-oxyallyl-Fe(II) cation (1) with seven-membered-ring unsaturated polyenes such as tropone and cycloheptatriene, which were chosen as model for the examination of periselectivity of 2π , 4π , 6π and 8π reactants.¹ The experimental results showed that cycloheptatriene (2) reacted with the 2-oxyallyl cation (1) to give only the ene-type product (3) *via* a concerted fashion as shown in Scheme I.



Scheme I

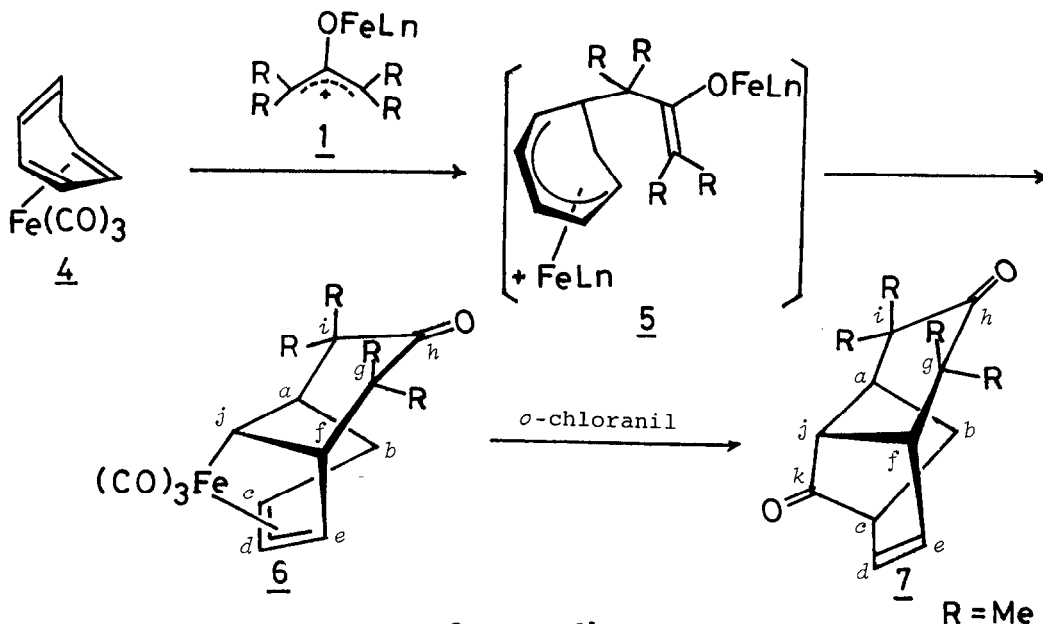
On the other hand, the ability of transition metals to alter the reactivity of co-ordinated olefins toward cycloaddition reaction is a current topic of interest.

We now wish to report that the reaction of cycloheptatrieneiron tricarbonyl complex (4) with the 2-oxyallyl-Fe(II) cation (1) afforded a σ, π -iron bonded adduct involving initial electrophilic addition to a nonco-ordinated double bond followed by a dyotropic rearrangement.

When a solution of 2-oxyallyl-Fe(II) cation (1),² generated from 2,4-dibromo-2,4-dimethylpentan-3-one and $\text{Fe}_2(\text{CO})_9$ with cycloheptatrieneiron tricarbonyl in dry benzene was stirred at 50 °C for 10 h, a single crystalline complex (6) could

be isolated by column chromatography (mp 88-89 °C from n-hexane, 20%). The ir spectrum showed the typical carbonyl ligand absorptions at 2080 and 1980 cm^{-1} ($\text{Fe}(\text{CO})_3$) and a signal at 1695 cm^{-1} (cyclohexanone). The mass spectrum was observed characteristic peaks at m/z 344 (M^+), 316 ($M^+ - \text{CO}$), 288 ($M^+ - 2\text{CO}$) and 260 ($M^+ - 3\text{CO}$). The ^1H NMR spectrum (100-MHz, CDCl_3) exhibited signals at δ 0.92 (3 H, s, Me), 1.00 (3 H, s, Me), 1.14 (3 H, s, Me), 1.16 (3 H, s, Me), 1.28 (1 H, dd, $J = 7, 14$ Hz), 1.96-2.16 (1 H, m), 2.28 (1 H, ddd, $J = 6, 1$ Hz), 2.36-2.72 (1 H, m), 3.05 (1 H, ddd, $J = 1, 9$ Hz) and 4.24-4.56 (3 H, m). The structure assignment was further secured by proton decoupled ^{13}C NMR spectrum (25-MHz, CDCl_3) which exhibits resonance at δ 19.7 (C_j), 22.5, 25.1, 25.6, 31.7 (Me), 33.2 (C_b), 47.5, 49.7 (C_g, C_i), 52.3, 59.5 (C_a, C_f), 66.0, 71.5 (C_c, C_e), 97.0 (C_d), 202.7, 213.3, 214.3 (ligand carbonyl) and 220.2 (C_h).

From these data, the structure of compound (6) was considered to be a σ, π -allyliron complex as shown in Scheme II.



However, there are uncertain for conformation of the cyclohexanone moiety and formation of σ -bond. Thus, compound (6) was submitted to single-crystal X-ray analysis.³

A crystal of this substance proved to be triclinic, space group $P\bar{1}$, with $a = 9.840$ (6), $b = 12.176$ (6), $c = 8.076$ (4) Å, $\alpha = 95.43$ (4), $\beta = 118.31$ (3), $\gamma = 105.71$ (5)°, $V = 791.2$ (7) Å³ and $Z = 2$. The intensity data were measured on an automated four-circle Syntex $P\bar{1}$ diffractometer with Mo-K α radiation ($\lambda = 0.71069$ Å) using θ - 2θ scan technique to maximum value of $2\theta = 50^\circ$. Of 2044 independent reflections, 1865 were treated to be observed ($I > 2.3\sigma(I)$). The structure was solved by the direct method.⁴ Refinements were carried out by a

block-diagonal least-squares method using *UNICS II* program system.⁵ The final R value was 0.033 for the observed reflections. The molecular structure drawn by the ORTEP program⁶ is shown in Figure 1 with numbering sequence used in this paper. From these results, the coupling constants of the ¹H NMR spectrum for compound (6) ($J_{a,j} = 7$ Hz, $J_{f,j} = 14$ Hz) were consistent well with the dihedral angles of X-ray result (44° and 23°). The carbon atoms C(15) and C(12) lie 0.2 Å above and 0.68 Å below the best plane through atoms (13), C(14), C(16) and C(17), respectively, indicating that the cyclohexanone ring is constrained in a chair conformation. The angles of C(12)-C(13)-H(13), C(14)-C(13)-H(13) and C(12)-C(13)-C(14) are 123.0°, 109.8° and 114.0°, respectively, suggesting that sp³ hybridization develops between Fe(1) and C(13) to form σ bonding.

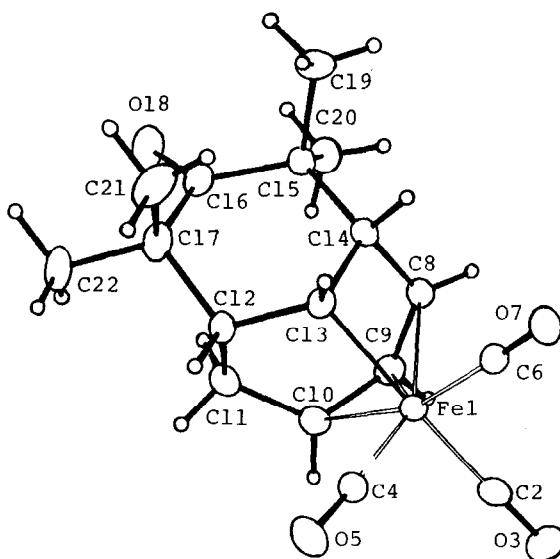


Figure 1. ORTEP drawing of complex 7.

Oxidation of compound (6) with *o*-chloranil afforded a single iron free product (7) which was isolated by column chromatography (mp 93-95 °C from *n*-hexane, 47%) as shown in Scheme II. The elemental analysis and the mass spectrum (m/z 232 (M^+)) indicated that a carbonyl insertion took place during oxidation. The ir spectrum showed two carbonyl absorptions at 1750 cm^{-1} (cyclopentanone) and 1690 cm^{-1} (cyclohexanone). These data together with ¹H NMR spectrum (100-MHz, CDCl_3) [δ 1.11 (3 H, s, Me), 1.17 (3 H, s, Me), 1.31 (3 H, s, Me), 1.34 (3 H, s, Me), 1.72 (1 H, ddd, $J_{a,b} = 11$ Hz, $J_{b,c} = 7$ Hz, $J_{b,b'} = 1$ Hz, H_b), 2.18 (1 H, ddd, $J_{a,b} = 7$ Hz, $J_{a,j} = 1$ Hz, H_a), 2.36-2.48 (1 H, m, H_j), 2.52-2.64 (1 H, m, H_c), 3.04 (1 H, ddd, $J_{b',c} = 5$ Hz, $H_{b'}$), 3.14-3.28 (1 H, m, H_f), 5.62 (1 H, dd, $J_{d,e} = 9$ Hz, $J_{e,f} = 4$ Hz, H_e) and 6.14 (1 H, dd, $J_{c,d} = 7$ Hz, H_d)], and the ¹³C NMR spectrum (25-MHz, CDCl_3) [δ 23.4, 24.5, 28.1, 31.0 (Me), 36.0 (C_b), 43.6, 44.1, 45.9 (C_a ,

C_j, C_f), 45.1, 47.2 (C_g, C_i), 57.2 (C_c), 127.0, 135.6 (C_d, C_e), 213.2 (C_k) and 217.3 (C_h)] supported the structure assignment of 7.

The experimental results showed that initial electrophilic attack of the 2-oxyallyl cation (1) may occur on free double bond of cycloheptatrieneiron tricarbonyl (4) forming a dipolar transient (5) followed by ring closure to σ, π -allyl isomer (6) which is obtained by a thermodynamically controlled process.⁷

References and Notes:

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