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Preliminary communication

Iron mediated diene activation: facile nucleophile addition to a coordinated diene: the crystal structure of $[(\eta^5\text{-}C_5Me_5)Fe(methylhexa\text{-}2,4\text{-}dienoate)CO][BF_4]$

Patrick McArdle *, David MacHale, Mary Mahon and Desmond Cunningham
Chemistry Department, University College, Galway (Ireland)

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Abstract

The site of attack on the cation $[(\eta^5\text{-}C_5Me_5)Fe(methylhexa\text{-}2,4\text{-}dienoate)CO]^+$ by borohydride or methoxide is determined by the electronic effect of the carbomethoxy group and by the steric interaction between the olefinic dienemethyl and one of the cyclopentadienylmethyls.

Since the addition of very strong nucleophiles to neutral coordinated dienes had been observed [1], it was to be expected that cationic complexes would show greater reactivity. Although cationic diene complexes are relatively rare, there are well established examples for molybdenum, ruthenium and cobalt systems [2,3,4]. The known iron systems all contain an η^5-olefinic group and CO as supporting ligands, but they are either unstable [5], difficult to prepare [6,7], or undergo nucleophilic attack at the η^5-ligand [8]. In an effort to obtain iron systems which could have applications in asymmetric synthesis the pentamethylcyclopentadienyl ligand has been used to provide stable cationic diene complexes of iron which are easy to prepare [9]. The reactions of these systems, which contained isoprene and a range of substituted cyclohexadienes, towards nucleophiles were disappointing; the products of nucleophilic attack were observed in solution but could not be isolated, [10]. This communication reveals an improvement in the value of these systems when the diene is changed to a derivative of sorbic acid.

Irradiation (Pyrex filtered 125 watt medium pressure Hg at 25 ° C) of a dichloromethane solution of methyl sorbate, 3 cm^3, and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(THF)][BF_4]$, from 2 g of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I)$ [11], gave $[(\eta^5\text{-}C_5Me_5)Fe(methylhexa\text{-}2,4\text{-}dienoate)CO][BF_4]$, (**1**), in an overall 60% yield. Reaction of **1**. 0.1 g, with an excess of sodium methoxide in methanol, 20 cm^3, for 3 min followed by extraction with diethyl ether, evaporation, and distillation onto a cold finger gave **2a** in almost quantitative yield. **2b** was obtained similarly, by use of sodium borohydride in tetrahydrofuran. The ^1H NMR spectra clearly showed that in both cases nucleophilic

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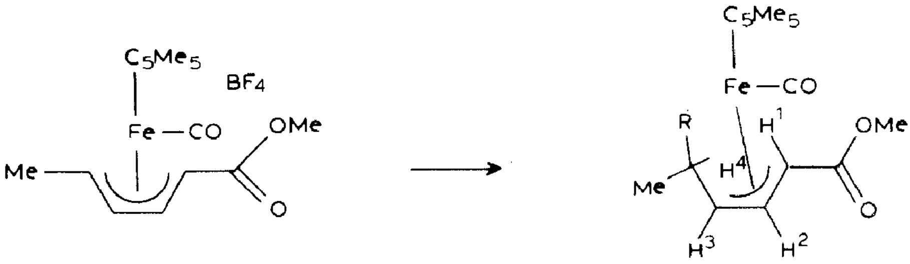

(**1a** : R = OMe ,
R = H)

(**2a** : R = OMe ,
R = H)

attack had taken place at the C(5) carbon of the diene ligand *. No other products were observed.

The site of nucleophilic attack in these systems would, by analogy with the molybdenum systems, be expected to be at one of the terminal diene carbons. To throw further light on the reactivity of this complex the crystal structure of **1** was determined, and the structure of the cation is illustrated in Fig. 1 *.

The coordinated diene and the cyclopentadienyl ring are oriented in such a way that the carbomethoxy group is placed between the methyl groups on C(9) and C(13) while the C(6) methyl makes a close approach to the methyl group on C(11). The distance between the carbon of the C(11) methyl and C(6) is 3.45 Å. This distance is close to the shortest non-bonded C...C distance reported for a 1,8-di-t-butylnaphthalene system, of 3.37 Å (a classic case of steric congestion) [12]. The steric pressure developed is sufficient to lengthen the Fe–C(5) bond, 2.265(18) Å, relative to the Fe–C(2) bond, 2.152(16) Å. This difference of 0.1 Å is greater than the corresponding difference, of 0.04 Å, observed for the neutral (η^4-(hexa-2,4-dienoic acid)Fe(CO)$_3$ complex. The structures of the related iron complexes of 2,4-hexadiene and cyclohexa-1,3-diene [6,10], and of a cyclopentadienylruthenium complex [3], all show essentially symmetrical iron–diene bonding. In the present case the electron-withdrawing carbomethoxy group probably increases backbonding at

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* Selected spectroscopic data. **1**: IR (ν(C–O) CH_2Cl_2) 2028 cm^{-1}. **2a**: IR (ν(C–O) CH_2Cl_2 1937 cm^{-1}, ^{1}H NMR 270 MHz $CDCl_3/Cs_2$ 1/1 δ 4.57 (dd, J(H(1)–H(2)) 10.25 Hz, J(H(2)–H(3)) 8.4 Hz, 1H, H(2)), 3.65 (s, 3H, OMe), 3.08 (s, 3H, OMe), 2.64 (dd, J(H(2)–H(3)) 8.4 Hz, J(H(3)–H(4)) 10.26 Hz, 1H, H(3)), 1.77 (m, 1H, H(4), 1.68 (s, 15H, Me), 1.45 (d, J(H(1)–H(2)) 10.25 Hz, 1H, H(1)), 1.24 (d, J(CH_3–H(4)) 6.8 Hz, 3H, Me). **2b**: IR (ν(C–O) CH_2Cl_2 1937 cm^{-1}, ^{1}H NMR 270 MHz $CDCl_3/CS_2$ 1/1 δ 4.32 (dd, J(H(1)–H(2)) 10.25 Hz, J(H(2)–H(3)) 8.06 Hz, 1H, H(2)), 3.64 (s, 3H, OMe), 2.93 (q, J(CH_2–H(3)) = J(H(2)–H(3)) = 8.06 Hz, 1H, H(3)), 1.48 (d, J(H(1)–H(2)) 10.26 Hz, 1H, H(1)), 1.67 (s, 15H, Me), 0.97–0.81 (m, 5H, Me, CH_2).

* Crystal data for compound. **1**: $C_{18}H_{25}O_3BF_4Fe$ Monoclinic; Space group, $P2_1/c$; a 8.990(3), b 14.469(3), c 15.239(3) Å; β 93.31(2)°; $Z = 4$; $U = 1978.92$ Å; μ 7.55 cm^{-1}; $F(000) = 896$; 2975 unique reflections measured of which 936 were observed with $I > 3\sigma(I)$ using a CAD4 diffractometer and Mo-K_α radiation; $2\Theta_{max}$ 48°. The structure was solved by direct methods, SHELX86 [14], and refined with 154 variable parameters using SHELX76 [15]. After full matrix refinement; R 7.02 and R_w 6.73%. The maximum and minimum excursions in the final difference map were 0.22 and −0.23 e/Å^3. The ORTEP program was used to obtain the drawing [16]. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

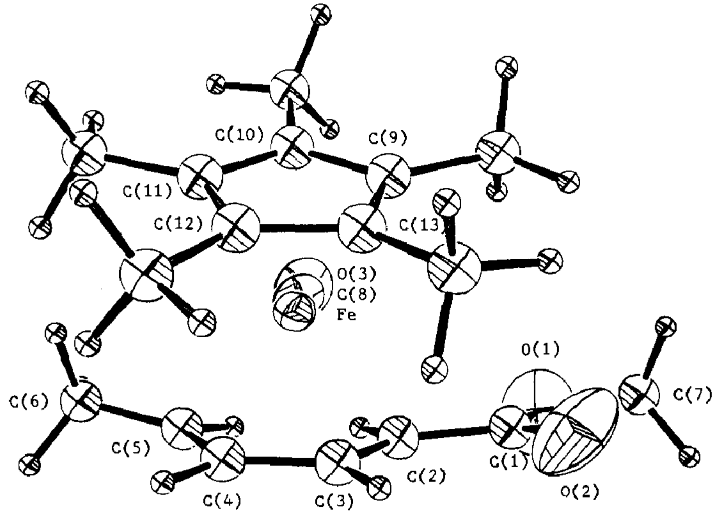

Fig. 1. Ortep drawing of the cation of **1**. Selected interatomic distances are: Fe–C (2) 2.152(16), Fe–C(3) 2.020(18), Fe–C(4) 2.077(17), Fe–C(5) 2.265(18), C(1)–C(2) 1.446(21), C(2)–C(3) 1.398(20), C(3)–C(4) 1.405(20), C(4)–C(5) 1.434(21), C(5)–C(6) 1.435(22). The angle between the plane defined by the ring, C(9)...C(13), and the diene unit, C(2)...C(5) is 22°.

C(1) relative to that at C(5). Since both ends of the coordinated diene cannot simultaneously lie over spaces between the methyl groups on the cyclopentadienyl ring it is tighter Fe–C(1) bonding which determines that the C(5) substituent takes up the most sterically crowded position.

Atomic charges calculated for the cation of **1**, by the extended Hückel method [13], give for the diene carbons: C(2) 0.026; C(3) 0.024; C(4) 0.022; C(5) 0.032. Michael-type addition to free methyl sorbate would be expected to take place at C(3) or C(5). Thus a combination of, the directing effect of the carbomethoxy group, relief of steric strain, and charge all ensure that nucleophilic attack is at C(5).

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