The Stereochemistry of Electrophilic Addition to Tricarbonyldieneiron Complexes

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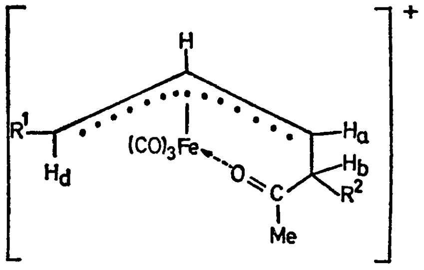
Summary The *X*-ray structural analysis of a substituted tricarbonylallyliron cationic intermediate unambiguously demonstrates that tricarbonyl(*trans, trans*-hexa-2,4-diene)iron undergoes stereospecific *endo* attack under Friedel-Crafts conditions.

The preference for nucleophilic attack on the *exo* face of a cationic organometallic species is well established, but uncertainty exists over both the regio- and stereo-specificity of electrophilic attack on unsaturated ligands. It has been predicted[1] that the electron density in the π-orbital of a complexed ligand will be greatest in the bonding region



	R^1	R^2
(1a)	H	H_c
(1b)	Me	*exo* Me
(1c)	Me	*endo* Me
(1d)	CD_3	CD_3

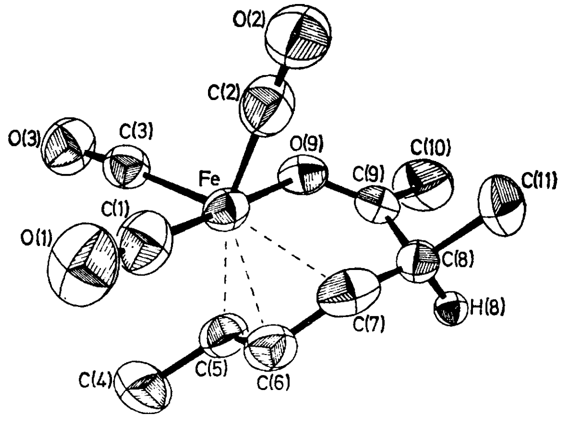


Figure. The atomic arrangement in the cation (**1c**). For clarity the only hydrogen atom shown is that at C(8). Important dimensions are: C(5)–C(6) 1·384(15), C(6)–C(7) 1·404(16), Fe–O 1·987(10), Fe–C(5) 2·210(12), Fe–C(6) 2·087(13), Fe–C(7) 2·213(14) Fe–C(1) 1·782(18), Fe–C(2) 1·809(12), Fe–C(3) 1·852(10)Å.

between the metal and the organic group, so *endo* electrophilic attack may be expected. However with various acids it has been found that *exo*-protonation[2,3] occurs with some diene-, triene-, and tetraene-Fe(CO)$_3$ complexes, *endo*-protonation[4] occurs with others, and stereochemically indiscriminate acylation[3] occurs with $C_7H_8Fe(CO)_3$. We now report that under Friedel-Crafts conditions tricarbonyldieneiron complexes react at the *endo* face.

Isolation of an intermediate in the Friedel-Crafts acylation of tricarbonylbutadieneiron has been reported[5] and its structure (**1a**) verified by *X*-ray crystallography.[6] Under similar conditions acylation of pure tricarbonyl-(*trans-trans*-hexa-2,4-diene)iron [prepared in high yield by $LiAlH_4$-$AlCl_3$ reduction of the Fe(CO)$_3$ complexes of *trans*-ethyl sorbate or *trans*-muconic acid] gave a 35% yield[7] of a single complex, corresponding to (**1b**) if acylation had occurred at the *exo*-face, or (**1c**) for *endo*-attack. Differentiation between these alternatives was expected from the ^{1}H n.m.r. value (J_{ab}), Karplus' equation and the dihedral angles ø calculated (and found) for (**1a**) [ø H_a-H_b $= -20°$ ($-34°$); ø H_a-$H_c = 100°$ ($98°$)]. However, accidental coincidence of the chemical shift of H_b and H_d and further proton–proton coupling, even for the di-CD_3 derivative (**1d**), prevented accurate evaluation of ø H_a-H_b. Therefore a single crystal *X*-ray analysis was undertaken and this has clearly identified structure (**1c**). Crystals of the hexafluorophosphate salt of (**1c**) are monoclinic, of space group $P2_1/c$, with $a = 9{\cdot}363(6)$, $b = 12{\cdot}174(9)$, $c = 16{\cdot}547(10)$ Å, $\beta = 121° \; 36 \; (3)'$, and $Z = 4$; *X*-ray data were measured on a four-circle diffractometer with graphite-monochromatized Mo-K_α radiation and yielded 1538 reflections for which $I > 3\,\sigma\,(I)$. The atomic co-ordinates were determined by Fourier methods and adjusted by least-squares calculations, the analysis converging at R 8·0%. The resulting molecular structure is shown in the Figure.

The stereochemistry of acylation of tricarbonyldieneiron complexes parallels protonation of the same complexes [and cyclohexa-1,3-diene(cyclopentadienyl)rhodium[8]]. The behaviour differs from that of ferrocene where stereochemistry of substitution is apparently dependent upon the nature of the electrophile.[9]

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[7] Under these conditions the yield of (**1a**) was 85%; for a shorter reaction time R. E. Graf and C. P. Lillya, *J. Amer. Chem. Soc.*, 1972, **94**, 8282, found that the hexadiene complex did not yield an acyl derivative under conditions where acylation of tricarbonylbutadieneiron was complete.

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