

The Electronic Factor in the Face Selection of Iron Tricarbonyl Complexation

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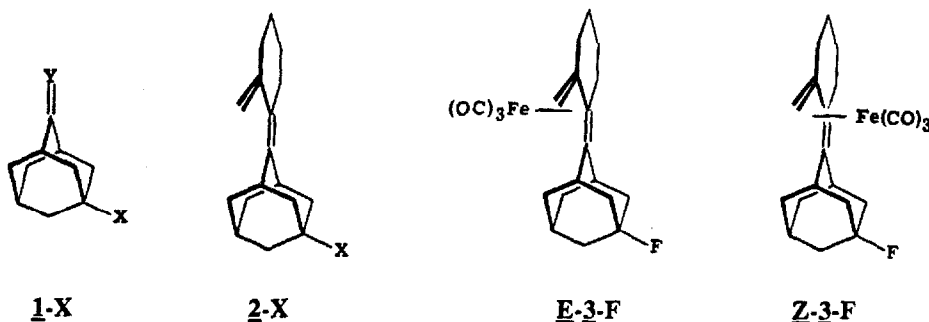
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Abstract: The iron tricarbonyl complexes of 1-(2-adamantylidene)-2-methylenecyclohexane and of the 5-fluoroadamantylidene analog have been prepared. Both the syn and anti isomers were obtained in the latter case; the major product has the syn configuration as established by means of X-ray diffraction. The reaction therefore joins several others in which reagents of various types were added to a trigonal center C_2 in adamantanes carrying an electron withdrawing substituent at C_5 ; this attack also, occurs preferentially at the zu face.

The addition of a reagent to a trigonal center has the important stereochemical consequence that two isomers may form depending on the face selected for attack, in all cases except C_{2v} symmetrical substrates. The choice can be influenced by many factors, among which steric crowding and conformational preference are two obvious ones. Much recent interest has been lavished upon the electronic factor, by means of which sometimes rather remote substituents can effect the isomer ratio.¹ To study this effect, we have made much use of 5-substituted adamantanes 1-X with a trigonal center at C_2 , since this probe is free from the dual problems of simultaneous steric hindrance and of conformational uncertainty. It was found that electron withdrawing substituents X promote syn approach



of the reagent and electron donors promote anti approach. We have interpreted the cause of this effect in terms of transition state hyperconjugation, a concept proposed by Cieplak² to account for the preferred axial addition of nucleophiles to the carbonyl carbon of rigid cyclohexanones. The presumption is that

the antiperiplanar bonds hyperconjugate with the incipient σ^* orbital, and that syn approach will therefore be preferred if X is strongly electronegative.

Little is known³ about electronic effects on the stereochemistry of complexation of dienes by the iron tricarbonyl group, and we have adopted our probe so as to provide us with a species **2-X** that contains an *s-cis* 1,3-diene moiety but retains the advantages of sterically equivalent faces and conformational rigidity.⁴

Heating of the parent diene with a fourfold excess of iron pentacarbonyl in *n*-butyl ether for 24 hours did not result in the complete consumption of **2-H** (see experimental), and complex **3-H** could be isolated in analytical purity with a 43% yield. The same reaction with **2-F** gave a 70% yield of a mixture of *E*- and *Z*-**3-F** which could be analyzed by means of ¹⁹F NMR integration; a 3:2 ratio of adducts was found. Thick layer chromatography allowed complete separation of the two isomers. Both were found to be stable under the conditions of their formation; several variations in the ratio of the reactants or reaction time did not change the product ratio.

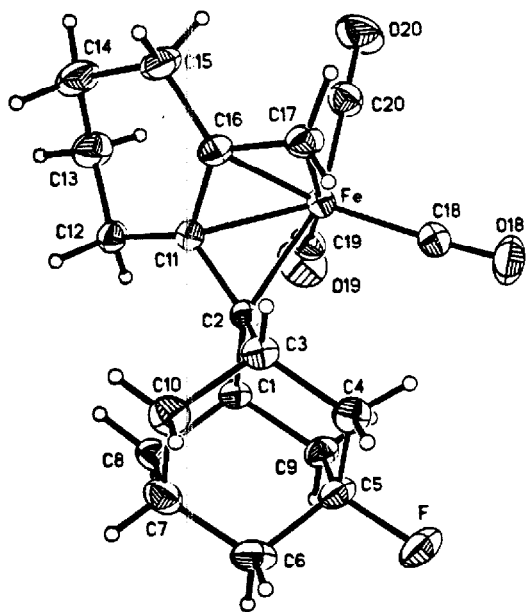


Fig. 1 --Ortep of **Z-3-F**

The ¹³C NMR spectra of **3-H** and of *E*- and *Z*-**3-F** all showed the twenty signals required by their structures; seven of the signals of each of the **3-F** isomers are split by the ¹⁹F atom as expected. The signals of **3-H** were found to be unaffected by the shift reagent Eu(fod)₃, hence the C₄ and C₈₋₁₀ signals could not be assigned. Consequently, the ¹³C NMR chemical shifts additivity method⁵ could not be applied to assign the configurations of **3-F**. Fortunately, good quality crystals of the major isomer could be obtained and analysed by means of X-ray diffraction: this isomer has the *Z*-configuration (Fig. 1). The reaction that produced it is therefore evidently subject to the same electronic factor that appears to control all other additions to trigonal carbon that we have studied to date.

Experimental

Iron π -1-(2-adamantylidene)-2-methylenecyclohexane tricarbonyl (**3-H**). Diene **2-H**⁴ (100 mg, 0.44 mM) was dissolved in *n*-butyl ether (3 mL, distilled from P₂O₅), under nitrogen; Fe(CO)₅ (343 mg, 1.76 mM) was added and the mixture heated to reflux for 24 hours. The diene was not completely consumed, but longer reaction times resulted in the formation of unidentified side products. The solvent was removed under pressure and the residue was chromatographed (silica gel, hexane). Complex **3-H** was isolated as a pale yellow solid that was crystallized from hexane at -78° C (70 mg, 43%). Mp, 109.5-110.5° C. ¹H NMR, 300 MHz, CDCl₃, δ 0.9-3.4 (m); ¹³C NMR, 75 MHz, CDCl₃, δ 22.31, 23.08, 27.82, 27.90 (CH, by APT), 28.62 (CH), 31.23, 31.80 (CH), 36.66, 38.26, 38.44, 38.63, 40.41, 41.31 (CH), 43.44, 87.30, 102.70, 104.58, 209.64, 210.00, 212.50. Anal. calcd. C, 65.23; H, 6.56. Fd. C, 65.42, H, 6.68.

Iron π -1-(5-fluoroadamant-2-ylidene)-2-methylenecyclohexane tricarbonyl (**3-F**). --Diene **2-F**⁴ (106 mg, 0.45 mM) was treated to the same conditions except that the heating was to 80° for 17 h and then to reflux for 11 h. The residue showed the presence of 2 spots of similar R_F value. ¹⁹F NMR of the crude mixture showed two peaks in the ratio of 60:40. Plate chromatography (hexane) gave samples of both complexes in pure form.

Major isomer (**Z**-): Mp 142-143° C. ¹⁹F NMR, 300 MHz, CDCl₃, δ -58.0. ¹H NMR, 300 MHz, CDCl₃, δ 1.0-3.0 (m). ¹³C NMR, 75 MHz, CDCl₃, δ 22.22, 22.92, 28.27, 31.04, 31.76 (J_{CF} = 8.5 Hz), 34.36 (J_{CF} = 6.5 Hz), 36.87, 38.85 (J_{CF} = 10.9 Hz), 41.15, 41.40, 43.03 (J_{CF} = 17.1 Hz), 43.88 (J_{CF} = 10.3 Hz), 44.56 (J_{CF} = 17.7 Hz), 81.77, 92.01 (J_{CF} = 184.3 Hz), 103.21, 103.98, 209.05, 209.39, 216.50.

Minor isomer (**E**-): Mp 122-123° C. ¹⁹F NMR, 300 MHz, CDCl₃, δ -57.4. ¹H NMR, 300 MHz, CDCl₃, δ 1.0-3.0 (m). ¹³C NMR, 75 MHz, CDCl₃, δ 22.22, 22.92, 27.62, 31.05, 31.31 (J_{CF} = 8.9 Hz), 33.58 (J_{CF} = 5.4 Hz), 34.97, 38.55, 39.01, 42.50 (J_{CF} = 17.1 Hz), 43.01 (J_{CF} = 10.7 Hz), 43.13 (J_{CF} = 7.8 Hz), 46.70 (J_{CF} = 16.5 Hz), 80.85, 91.93 (J_{CF} = 184.2 Hz), 103.55, 104.41, 208.96, 209.44, 216.68.

X-ray diffraction study. --A pale yellow crystal of **Z-3-F** of dimensions 0.45x0.25x0.2 mm was mounted on an R3m/ μ update of a Nicolet P2₁ diffractometer. Unit cell dimensions were obtained from a least squares refinement of 25 reflections. Crystal data: C₂₀H₂₃O₃FFe, M_r = 386.30, monoclinic; P2₁/n; a = 13.434 (5), b = 10.064 (3), c = 14.597 (4) Å; β = 116.41 (2)°; V = 1767.6 (8) Å³; Z = 4, D_x = 1.450 gcm⁻³; μ = 8.76 cm⁻¹; F(000) = 808. Intensity data were collected by the Ψ -scan technique (3 \leq 2 Θ \leq 55°) with a variable scan rate (4-29.3° min⁻¹) and graphite monochromated radiation (Mo K α , λ = 0.71073 Å). A total of 5168 reflections were collected of which 4038 were independent (R_{int} = 0.0064) yielding 3257 with intensities greater than 3 σ (I). Lorentz and polarization corrections and a Ψ -scan based absorption correction were applied. The structure was solved by direct methods and refined by a block-cascade least-squares technique. The structure was refined to R = 0.0452 and wR = 0.0467 with 313

parameters and 3257 reflections giving $S = 1.597$, $(\Delta/\sigma)_{\max} = 0.023$ and the largest peaks in a final difference map of -0.28 and $0.55 \text{ e}\text{\AA}^{-3}$. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized with $w = [\sigma^2(F_o) + 0.00017 F_o]^{-1}$. All programs were supplied by Nicolet Instrument Corp. for Desktop 30 Microclipse and Nova 4/C configuration with atomic scattering factors and anomalous dispersion corrections from International Tables for X-ray Crystallography.

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References and footnotes

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