Diastereocontrol of η^4-α,β-Unsaturated Ketone–$Fe(CO)_3$ Complexation by an Adjacent Metal-complexed Chiral Centre

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The reaction of tricarbonyl-[η^6-3-(*o*-methyl- or *o*-methoxyphenyl)-1-phenylprop-2-en-1-one]chromium with nonacarbonyldi-iron gives specifically one diastereoisomer of the η^4-$Fe(CO)_3$–α,β-unsaturated ketone–η^6 $Cr(CO)_3$–*ortho*-substituted arene complex, the relative configuration (*RS,SR*) of which was unambiguously established by *X*-ray analysis; the equivalent reaction using the 3-*m*-methoxyphenylpropenone isomer gives a 1 : 1 mixture of two diastereoisomers.

Chiral arene tricarbonylchromium complexes have proved to be highly useful tools for asymmetric induction. There is much current interest in developing methodology which uses chiral arene tricarbonylchromium for induction operations on benzylic or lateral chiral carbon.[1] The chiral benzylic function can be used to control the configuration of the metallocenic chiral centre.[2]

Here we report on a novel metal complex-induced formation of a new chiral metal-complexed centre. Treatment of a prochiral α,β-unsaturated ketone with $Fe_2(CO)_9$ leads to the

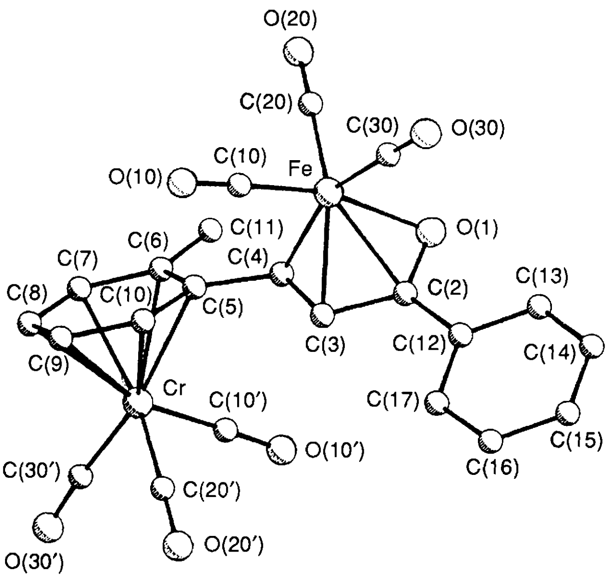
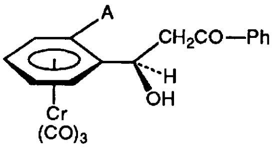


Figure 1. Molecular structure of complex (**5**). Bond distances (Å): Fe-O(1) 2.017(2), Fe-C(2) 2.108(4), Fe-C(3) 2.060(4), Fe-C(4) 2.118(4), Cr-C(5) 2.239(2), Cr-C(6) 2.265(2), Cr-C(7) 2.233(2), Cr-C(8) 2.223(2), Cr-C(9) 2.231(3) Cr-C(10) 2.207(2).

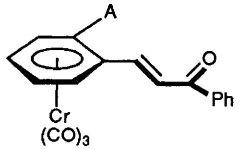
formation of an (α,β-unsaturated ketone)tricarbonyliron(0) complex with discrimination between the two diastereotopic sides of the ligand.

We recently reported the stereospecific aldol reaction of methyl phenyl ketone with *ortho*-substituted-benzaldehyde-tricarbonylchromium complexes to give the propanone complexes (**1**) and (**2**).[1b] Treatment of (**1**) and (**2**) with NaOH in ethanol-water gives the corresponding α,β-unsaturated ketones (**3**) and (**4**) respectively in 70 and 73% yields.

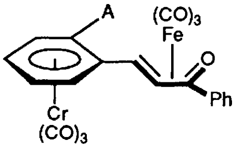
Reaction of (**3**) and (**4**) with nonacarbonyldi-iron[3] led to isolation of air-stable red–brown crystals which were identified as the (α,β-unsaturated ketone)tricarbonyliron(0) complexes (**5**) and (**6**) (yields 75 and 98%); HPLC analysis and the 400 MHz ^1H NMR spectrum of (**5**) and (**6**) indicate that only one diastereoisomer is obtained. Crystals of (**5**) were grown by cooling the ethanol solution and were examined by single crystal *X*-ray diffraction.[†] The relative configuration was



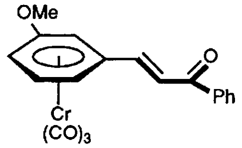
(**1**) A = Me
(**2**) A = OMe



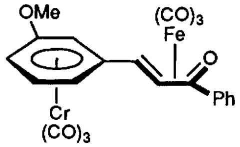
(**3**) A = Me
(**4**) A = OMe



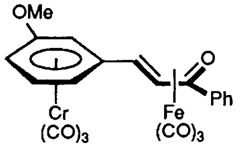
(**5**) A = Me
(**6**) A = OMe



(**7**)



(**8**) (*RS, SR*)



(**9**) (*RR, SS*)

identified as (*RS,SR*). The high stereoselectivity observed could presumably originate from steric interaction between the *ortho*-substituent and the unsaturated ketone and also between the bulky $Cr(CO)_3$ moiety and $Fe_2(CO)_9$, which would arise in a transition state. The use of the *meta*-substituted chiral α,β-unsaturated ketone (**7**) is accompanied by the total loss of the ability of the $Fe(CO)_3$ unit to discriminate between the two diastereotopic sides of the ligand. Thus, treatment of tricarbonyl-[η^6-3-(*m*-methoxyphenyl)-1-phenylprop-2-en-1-one]chromium with nonacarbonyldi-iron gave a mixture of the two diastereoisomers (**8**) and (**9**) (yield 95%), in a 1:1 ratio as determined by HPLC analysis and 400 MHz ^1H NMR spectroscopy. The specific preparation of one of the diastereoisomers is not possible.

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[†] *Crystal data* for (**5**): $C_{22}H_{14}CrFeO_7$, M_r = 498.19, triclinic, space group $P\bar{1}$, a = 9.719(1), b = 11.143(2), c = 11.860(3) Å, α = 100.76(15), β = 113.70(16), γ = 107.98(15) °, V = 1045(4) Å^3, Z = 2, D_c = 1.58 g cm^{-3}. Data were collected with an Enraf-Nonius CAD4 diffractometer, maximum 2θ 50°, using Mo-K_α radiation, $\bar{\lambda}$ = 0.71069 Å, μ(Mo-K_α) = 11.4 cm^{-1}, T = 293 K, crystal dimensions 0.3 × 0.6 × 0.4 mm, 3675 reflections were measured, 3361 were considered observed [$I/\sigma(I) \geqslant 3.0$] and used in refinement; they were corrected for Lorentz and polarisation effects, but not for absorption and extinction effects. The Fe and Cr atoms were located from Patterson synthesis and the light atoms found on Fourier syntheses (including H-atoms). Phenyl H-atoms were inserted at calculated positions and not refined; the methyl group was treated as a rigid CH_3 unit, with its original orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. No H-atom co-ordinates were refined. Final refinement was on F by least-squares methods refining 280 parameters. Final R = 0.027, with unit weights. Maximum shift/error in final cycle 0.03. Computing with SHELXS86 (Sheldrick, 1985) for Patterson synthesis and SHELX76 (Sheldrick, 1976) for refinement, on a Micro-VAC II. Scattering factors in the analytical form and anomalous dispersion factors taken from International Tables (1974). 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.

References

1 See for recent examples: (a) S. G. Davies and C. L. Goodfellow, *J. Organomet. Chem.*, 1989, **370**, (1,2,3) C5; *Synth. Lett.*, 1989, 59; A. Solladie-Cavallo, S. Quazzotti, S. Colonna, and A. Manfredi, *Tetrahedron Lett.*, 1989, **30**, 2933; J. S. Brocard, M. A. Mahmoudi, L. Pelinski, and L. A. Maciejewski, *ibid.*, 1989, **30**, 2549; (b) *Tetrahedron*, in the press.

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