Journal of Organometallic Chemistry, 402 (1991) C56–C58
Elsevier Sequoia S.A., Lausanne
JOM 21562PC

Preliminary communication

Self-recognition by the iron chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ in the formation of $(RR,SS)\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2]_2CH_2$

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(Received November 6th, 1990)

Abstract

Complete self-recognition of chirality is observed in the Michael addition of the enolate derived from $R,S\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COCH_3]$ to the acryloyl complex $R,S\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COCH{=}CH_2)]$ to generate exclusively the single diastereoisomer of the glutaroyl complex $RR,SS\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2]_2CH_2$.

The iron chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ exerts powerful stereocontrol during the reactions of attached acetate enolates [1] and during Michael additions to attached α,β-unsaturated acyl ligands [2]. We describe here complete self-recognition in the Michael addition of the lithium enolate derived from the iron acetyl complex **1** and the iron acryloyl complex **2**.

Treatment of an orange tetrahydrofuran solution of the racemic acetyl complex **1** with one equivalent of butyllithium at $-78\,^\circ C$ generated the corresponding red lithium enolate. Addition of the acryloyl complex **2** and warming to $-40\,^\circ C$ before quenching with methanol afforded on work-up 95% of the glutaroyl complex **3** as a single diastereoisomer. The ^1H NMR spectrum of **3** [3*] allowed the stereochemistry within **3** to be assigned unambiguously as *RR,SS* as the two central methylene protons were equivalent appearing as a 2H quintet at δ 1.11 ppm. In the alternative *RS,SR-meso* diastereoisomer **4** the central methylene protons would be diastereotopic. The $\{^1H\}^{31}P$ NMR spectrum exhibits a single peak at δ 73.13 confirming the diastereoisomeric purity of **3**.

The remarkable self-recognition of chirality in the above reaction results from the complete discrimination by one of the enolate enantiomers between the two enantiomers of the acryloyl complex in favour of its own configuration. Given that Michael addition to α,β-unsaturated acyl complexes are chelation controlled with the chelated nucleophile attacking the unhindered face of the α,β-unsaturated acyl

* Reference number with asterisk indicates a note in the list of references.

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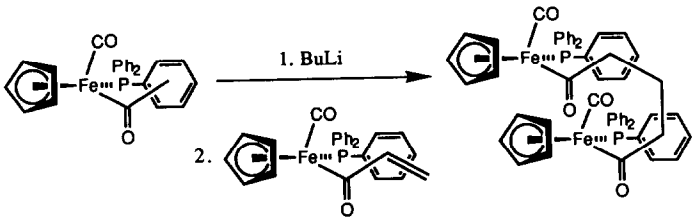
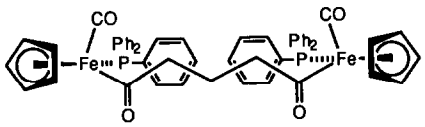


R(S)-1 R(S)-2 RR(SS)-3



RS(SR)-4

in the *anti* (O to CO) *cisoid* conformation [2] and that electrophiles add to iron acyl enolates from the unhindered face in their *anti* O^- to CO conformation [1], the self-recognition of chirality between the iron chiral auxiliaries may be rationalised. Both these sets of criteria can only be satisfied for the *R*-enolate adding to the *R*-acryloyl complex (Fig. 1). For the mismatched pair with the *R*-enolate adding to the *S*-acryloyl complex lithium chelation would require either the enolate or acryloyl complex to react in the *syn* (O to CO) form or for one of them to react from the hindered face.

Moss and Scott have recently reported the synthesis of the iron glutaroyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2]_2CH_2$ via treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2]_2CH_2$ (**5**) with two equivalents of triphenylphosphine [4]. Moss and Scott, while apparently not appreciating the possibility of this type of glutaroyl complex existing as diastereoisomers **3** and **4**, describe their product, on the basis of low resolution ^1H NMR spectroscopy, as a single compound with diastereotopic central methylene protons. As indicated above this would correspond to the *meso RS,SR*-compound **4**. We were intrigued by this result since not one of the numerous investigations in our laboratory to find such a stereoselective phosphine induced migratory insertion reaction using chiral iron alkyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2R^*$ or chiral phos-

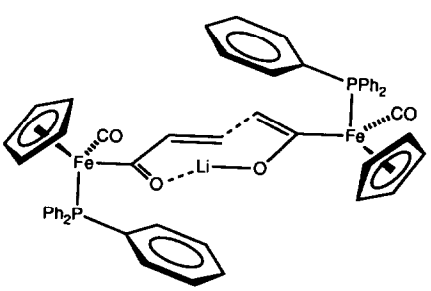
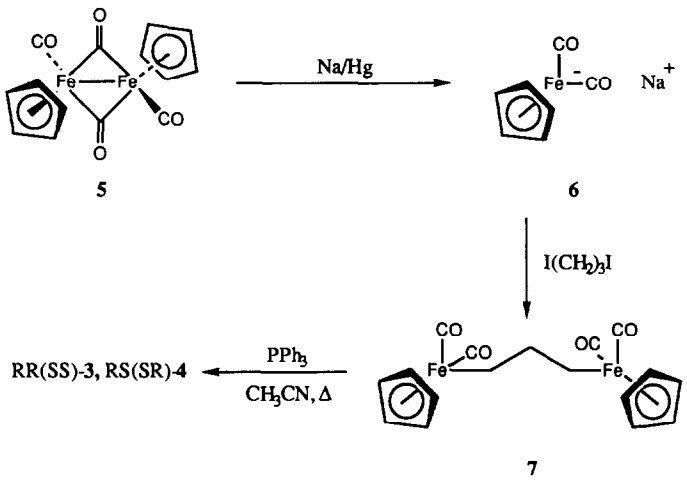


Fig. 1. Proposed transition state for the reaction of the lithium enolate of **1** with **2**.

phines has ever shown any diastereoselectivity. Following the method of Moss and Scott [4], reductive cleavage of complex **5** generated the iron anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ (**6**), which with 1,3-di-iodopropane generated complex **7**. This crude product was reacted with two equivalents of triphenylphosphine in tetrahydrofuran at reflux for 65 h in the absence of light. Work-up gave 51% of iron glutaroyl species which was shown to be a 1 : 1 mixture of diastereoisomers **3** and **4** by $\{^1H\}^{31}P$ NMR spectroscopy. Although complete separation of **3** and **4** was not possible the structure and stereochemistry of **4** could be assigned from its ^1H NMR data [5*] obtained by difference. The highly diastereotopic nature of the central methylene protons of **4** mandates its assignments as the *meso RS,SR*-isomer and hence unambiguously confirms the assignment for **3**.



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Acknowledgements. We thank the S.E.R.C. for a studentship (to SCP) and N.S.E.R.C. of Canada for a post-doctoral award (to GJB).

References and notes

1 S.L. Brown, S.G. Davies, D.F. Foster, J.I. Seeman and P. Warner, Tetrahedron Lett., 27 (1986) 623; S.G. Davies, Aldrichim. Acta, 23 (1990) 31.

2 S.G. Davies, I.M. Dordor-Hedgecock, K.H. Sutton, J.C. Walker, R.H. Jones and K. Prout, Tetrahedron, 42 (1986) 5123; S.G. Davies, I.M. Dordor-Hedgecock, R.J.C. Easton, S.C. Preston, K.H. Sutton and J.C. Walker, Bull. Soc. Chim. Fr., (1987) 608.

3 Compound **3**: ^1H NMR = 7.48 (2H, m, ArH_{ortho}), 7.38 (3H, m, ArH_{meta}, ArH_{para}), 4.39 (10H, d, J(PH) = 1.2 Hz, C_5H_5), 2.66, 2.20 (4H, AB part of an ABXY system, J_{AB} = 15.7 Hz, J_{AX} = 9.3 Hz, J_{AY} = 6.3 Hz, J_{BX} = 5.5 Hz, J_{BY} = 9.4 Hz, $-CH_2CH_2CH_2$), 1.10 (2H, quintet, J = 7.4 Hz, $-CH_2CH_2CH_2-$). ^{13}C NMR = 276.15 (br s, C=O, 220.58 (d, J(PC) = 31.7 Hz, C=O), 136.56 (d, J(PC) = 42.5 Hz, ArC_{ipso}), 133.29 (d, J(PC) = 7.3 Hz, ArC_{ortho}), 129.56 (s, ArC_{para}), 127.92 (d, J(PC) = 7.8 Hz, ArC_{meta}), 85.18 (s, C_5H_5), 65.48 (s, $-CH_2CH_2CH_2-$), 21.01 (s, $-CH_2CH_2CH_2-$); ^{31}P NMR = 73.13 ppm.

4 J.R. Moss and L.G Scott, J. Organomet. Chem., 363 (1989) 351.

5 Compound **4**: ^1H NMR = 7.48 (2H, m, ArH_{ortho}), 7.38 (3H, ArH_{meta}, ArH_{para}) 4.37 (10H, d, J(PH) = 1.2 Hz), 2.66, 2.20 (4H m, $-CH_2CH_2CH_2-$) 1.28, 0.84 (1H, m, $CH_2CH_2CH_2$); ^{13}C NMR = 276.15 (br s, C=O), 220.58 (d, J(PC) = 31.7 Hz, CO), 136.56 (d, J(PC) = 42.5 Hz, ArC_{ipso}), 133.29 (d, J(PC) = 7.3 Hz, ArC_{ortho}), 129.56 (s, ArC_{para}), 127.92 (d, J(PC) = 7.8 Hz, ArC_{meta}), 85.18 (s, C_5H_5), 65.48 (s, $-CH_2CH_2CH_2-$), 21.01 (s, $-CH_2CH_2CH_2-$); ^{31}P NMR = 72.84.