Stereoselective Reduction of (*R,S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(=$\overline{COCH_2CH_2CMe_2}$)]$^+$ and Complete Epimerisation of the Kinetic (*RR,SS*)-Diastereoisomer to the Thermodynamic (*RS,SR*)-Diastereoisomer of the Product [(η^5-C_5H_5)Fe(CO)(PPh_3){$\overline{C(H)OCH_2CH_2CMe_2}$}]

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Hydride reduction of the cation [(η^5-C_5H_5)Fe(CO)(PPh_3)(=$\overline{COCH_2CH_2CMe_2}$)]$^+$ occurs completely stereoselectively to give the kinetic product (*RR,SS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){$\overline{C(H)OCH_2CH_2CMe_2}$}] which subsequently under mild acid conditions epimerises completely to the thermodynamically more stable (*RS,SR*)-diastereoisomer; a simple conformational analysis rationalises both these phenomena.

Recently we proposed a conformational analysis for ligands attached to the chiral auxiliary (η^5-C_5H_5)Fe(CO)(PPh_3) which established the following guidelines for predicting the most stable conformation.[1] Stable conformations resemble that shown in Figure 1 with the size of the sites at C_α being A $\gg$ B $>$ C. Large C_α substituents (*e.g.* Bu^t) are restricted to site A whereas site C is only accessible to small C_α substituents. We describe here the remarkable degree of stereocontrol that can be achieved during reactions at carbon centres directly attached to the chiral auxiliary (η^5-C_5H_5)Fe(CO)(PPh_3).

Sodium borohydride reduction of the alkoxycarbene complex (**1**)[2] in tetrahydrofuran (THF) proceeds completely stereoselectively to give (**2**) as a single diastereoisomer (92%). During chromatography on silica gel complete epimerisation of (**2**) to give (**4**) (97%) as a single diastereoisomer occurs. The

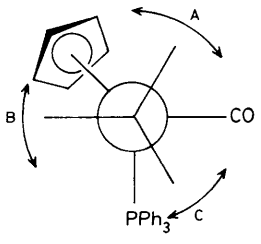
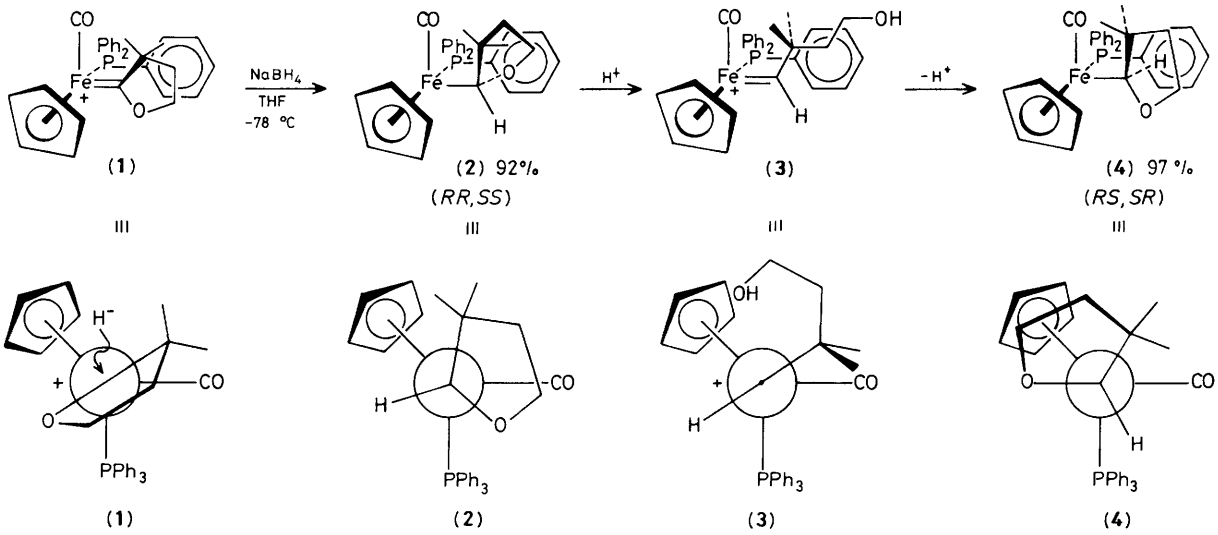


Figure 1



(1) (2) (3) (4)

configurations of the C_α centres relative to the iron centre in (**2**) and (**4**) were assigned by ^1H n.m.r. spectroscopy;† H_α for (**2**) appeared at δ 5.07 with J_{PH} 5.5. Hz whereas H_α for (**4**) appeared at δ 4.12 with J_{PH} 17.7 Hz. Application of the Karplus equation to these data indicates that H_α is approximately antiperiplanar to the carbon monoxide ligand in (**2**) and approximately orthogonal to the carbon monoxide ligand in (**4**). Furthermore the large upfield shift of H_α in (**4**) relative to H_α in (**2**) is consistent with H_α in (**4**) lying over one of the phenyl rings of the triphenylphosphine ligand.[3] Given the requirement that the bulky quaternary carbon centre is sterically constrained to remain between the cyclopentadienyl and the carbonyl ligands (site A, Figure 1) the relative configurations of (**2**) and (**4**) must be (*RR*,*SS*) and (*RS*,*SR*) respectively. This same steric constraint may also be used to rationalise the remarkable stereoselectivities observed for the reduction and epimerisation reactions. Thus in the starting alkoxycarbene complex (**1**) the oxygen must lie *anti* to the carbonyl ligand and the reducing agent can only approach the face of the carbene opposite the blocking phenyl group of the triphenylphosphine[4] to give (**2**). The conformation of (**2**) is fixed by the quaternary carbon centre which forces the OCH_2 group to lie in the least favourable site, between the triphenylphosphine and the carbonyl ligand (site C, Figure 1). Under mildly acidic conditions epimerisation can occur by opening to the carbene (**3**) and readdition to the opposite face. Since by placing H_α in the smallest site very unfavourable steric interactions are removed the epimerisation goes to completion.

The results described above demonstrate the remarkable stereocontrol exerted by the chiral auxiliary (η^5-C_5H_5)Fe(CO)(PPh_3) in reactions on the α-carbon where reduction of (**1**) proceeds completely stereoselectively to give the kinetic product (**2**) which then epimerises, also completely stereoselectively, to the thermodynamic product (**4**). These results are readily explicable in terms of a simple conformational model and the phenomenon can be expected to be general for all cases where there is a very bulky C_α substituent.

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† ^1H N.m.r. data (300 MHz, C_6D_6): complex (**2**), δ 7.70—7.60 (6H, m, Ph), 7.10—6.90 (9H, m, Ph), 5.07 (1H, d, $^3J_{PH}$ 5.5 Hz, FeCH), 4.18 (5H, d, $^3J_{PH}$ 1.2 Hz, C_5H_5), 3.24 (1H, m, CH_2CHO), 2.64 (1H, m, CH_2CHO), 1.63 (1H, m, $CHCH_2O$), 1.44 (3H, s, Me), 1.25 (1H, m, $CHCH_2O$), and 1.05 (3H, s, Me); complex (**4**), δ 7.70—7.70 (6H, m, Ph), 7.10—6.90 (9H, m, Ph), 4.43 (5H, d, $^3J_{PH}$ 1.12 Hz, C_5H_5), 4.12 (1H, d, $^3J_{PH}$ 17.7 Hz, FeCH), 3.93 (1H, m, CH_2CHO), 3.47 (1H, m, CH_2CHO), 1.52 (1H, m, $CHCH_2O$), 1.42 (1H, m, $CHCH_2O$), 1.21 (3H, s, Me), and 0.97 (3H, s, Me_3).

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