Stereocontrolled Tandem Alkylations: Michael Additions and Subsequent Alkylations of α,β-Unsaturated Acyl Ligands bound to [(η⁵-C_5H_5)Fe(CO)(PPh_3)]

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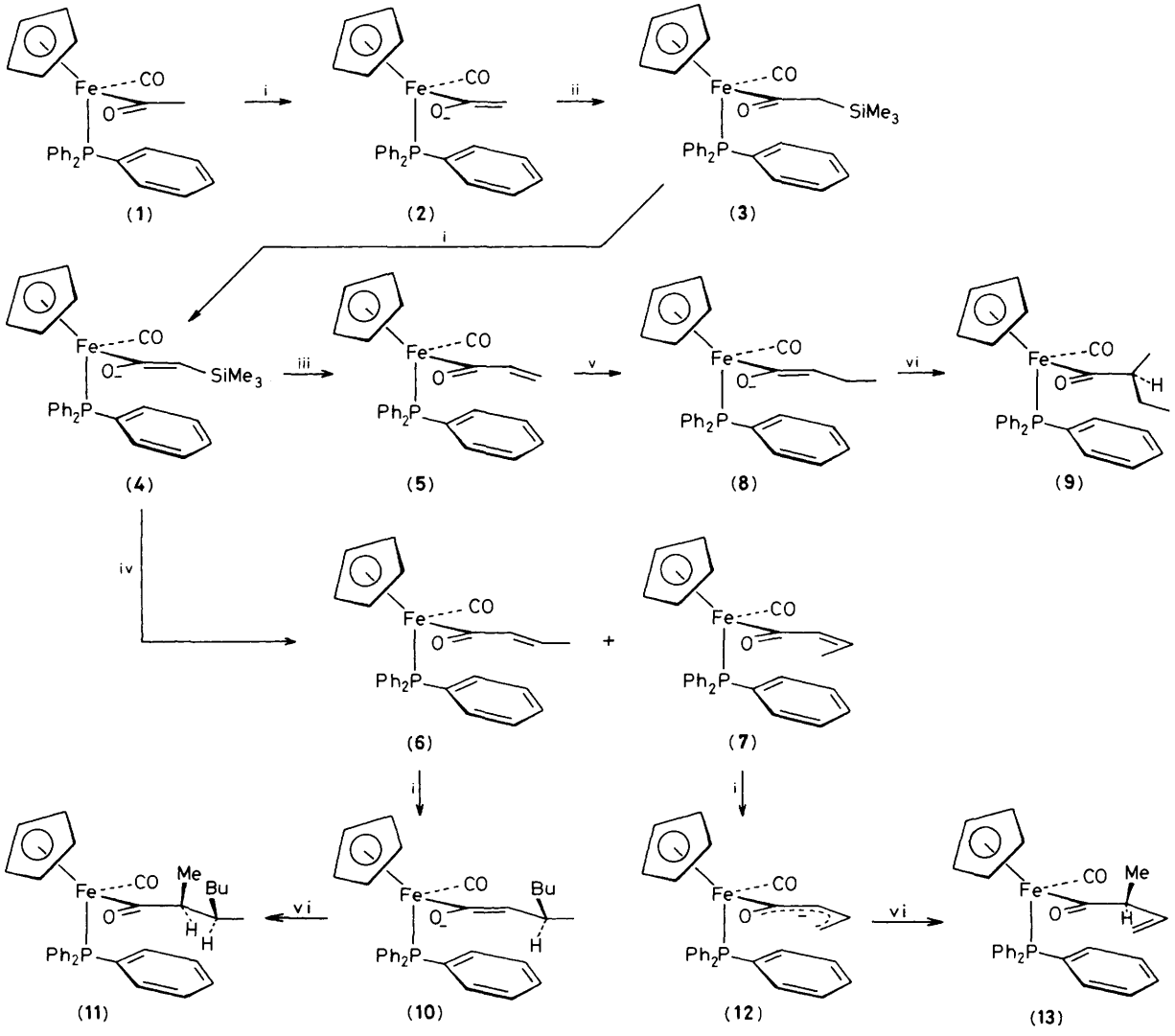
α,β-Unsaturated acyl complexes of [(η⁵-C_5H_5)Fe(CO)(PPh_3)] can be prepared by the Peterson olefination reaction and are found to undergo tandem stereoselective Michael additions and subsequent methylations which result in the stereocontrolled synthesis of α- and β-substituted iron acyl complexes.

The possibility of the tandem stereocontrolled formation of two chiral centres *via* Michael additions of carbanions to α,β-unsaturated carbonyl compounds and subsequent alkylation of the enolate thus formed has been recognised for some time.[1] In general, the use of a chiral auxiliary on the α,β-unsaturated carbonyl group has proved the more successful approach[1–3] although the use of chiral nucleophiles has also given interesting results.[1,4] In particular, where part or all of the α,β-unsaturated carbonyl moiety is contained in a ring system, moderate to good stereocontrol can be achieved in the formation of both the α- and β-centres.[1,2] For the corresponding acyclic cases however, good stereocontrol has only been achieved in the initial Michael addition, *i.e.* at the β-centre.[1,3,4] We describe here highly stereoselective Michael additions and subsequent alkylations of α,β-unsaturated acyl ligands bound to the chiral [(η⁵-C_5H_5)Fe(CO)(PPh_3)] moiety.

Deprotonation of the acetyl complex (**1**) at −78 °C with Bu^nLi generated the enolate (**2**) which on addition of trimethylsilyl chloride underwent exclusive C-silylation[5] to generate after work-up the α-trimethylsilyl complex (**3**) (86%). Treatment of (**3**) in tetrahydrofuran (THF) at −78 °C with Bu^nLi produced the enolate (**4**) which after addition of a freshly prepared solution of formaldehyde in THF gave the α,β-unsaturated acyl complex (**5**). A similar Peterson reaction was observed between enolate (**4**) and acetaldehyde to yield a 2:1 mixture of the *trans* (**6**) and *cis* (**7**) isomers. Compounds



Reagents: i, Bu^nLi; ii, Me_3SiCl; iii, CH_2O; iv, MeCHO; v, MeLi; vi, MeI.

(**6**) and (**7**) were readily separable by chromatography and the double bond geometries were assigned on the basis of the coupling constants between the olefinic protons (J_{cis} 11; J_{trans} 15 Hz).

Addition of MeLi to a solution of the α,β-unsaturated acyl complex (**5**) in THF at −78 °C in the presence of methyl iodide stereoselectively (>30:1) generated the (*RS,SR*)-diastereoisomer (**9**) of the s-butyl acyl complex. The observed preferential formation of (**9**) is consistent with MeLi attacking (**5**) in the *cisoid* conformation to generate the *E*-enolate (**8**) which, as we have shown previously, is methylated with high facial stereoselectivity to give (**9**).[6]

The *trans*-isomer (**6**) reacted with Bu^{n}Li at −78 °C to give the enolate (**10**). Subsequent addition of methyl iodide stereospecifically gave the (*RSS,SRR*)-diastereoisomer (**11**); no other diastereoisomers could be detected by ^{1}H n.m.r. spectroscopy. The relative configuration in (**11**) of the α-chiral centre to the iron was established by methods described previously[7] (^{1}H n.m.r. α-Me δ 0.98) and indicated that, as for complex (**5**), Michael addition was occurring to (**6**) in the *cisoid* conformation. The relative configuration of the β-centre was assigned on the assumption that the Bu^{n}Li would attack (**6**) in the *cisoid* conformation, with the carbonyl oxygens *anti*, from the unhindered face, *i.e.* the face opposite the blocking phenyl group of the triphenylphosphine ligand.[8]

In contrast to the above Michael additions, the *cis*-isomer (**7**) underwent exclusive deprotonation with Bu^{n}Li to give the dienolate (**12**). Subsequent methylation of (**12**) gave the (*RS,SR*)-diastereoisomer (**13**) as the only detectable product indicating that the *cisoid*-conformation of (**7**) had been deprotonated.

The above results demonstrate the stereocontrolled tandem alkylations of α,β-unsaturated acyl ligands bound to [(η^5-C_5H_5)Fe(CO)(PPh_3)] involving the diastereofacially selective *cis* formation of two carbon–carbon bonds. Since the starting acetyl complex can be resolved[9] and the resulting acyl complexes can be converted under mild conditions into a variety of carbonyl functionalities,[10] this methodology is currently being extended to asymmetric synthesis.

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