Stereoselective Synthesis of Quaternary Carbon Atoms

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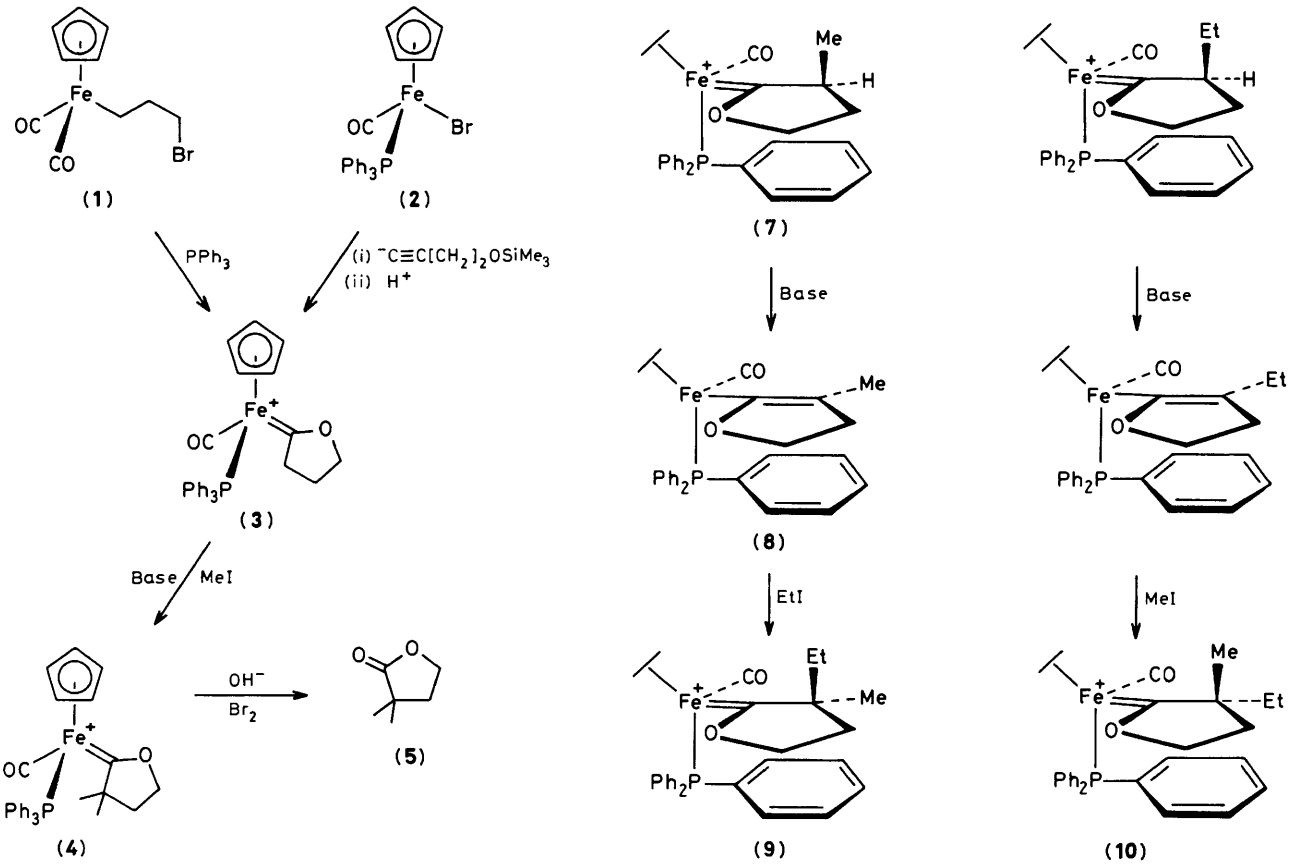
Repeated deprotonation and alkylation of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(=\overline{COCH_2CH_2CH_2})]^+$ allows the stereoselective synthesis of quaternary carbon centres to be achieved with decomplexation leading to 2,2-dialkylbutyrolactones.

Quaternary carbon centres (*i.e.* a carbon atom bonded to four other carbon atoms) are a common feature of many natural products. Reactions that allow the elaboration of quaternary centres are, however, very limited.[1] Furthermore no general method for the asymmetric synthesis of a quaternary carbon centre has been demonstrated; the few methods available having severe restrictions.[1,2] Our preceeding communication describes the use of (alkoxyvinyl)iron complexes to achieve stereoselective carbon–carbon bond formation.[3] We describe here the extension of this methodology for the stereoselective construction of quaternary carbon centres.



The cyclic alkoxycarbene cation (**3**) can be prepared from complex (**1**) and triphenylphosphine[4] or by treatment of the bromide (**2**) with the anion from 1-trimethylsiloxybut-3-yne followed by acidification. Treatment of cation (**3**) with an excess of base (di-isopropylethylamine) and an excess of methyl iodide elaborates a quaternary carbon centre and yields, *via* alkoxylvinyl intermediates, the dimethylated complex (**4**). The ^{1}H n.m.r. spectrum of (**4**) contained a singlet for the methyl group shielded by the triphenylphosphine at δ 0.62 and a second singlet for the other methyl group at δ 1.45. Decomplexation by successive treatment with hydroxide and bromine releases 2,2-dimethylbutyrolactone (**5**).

The elaboration of the quarternary centre in (**5**) can be achieved in a stepwise manner and all the intermediates isolated. Deprotonation of (**3**) with methoxide produces the alkoxyvinyl complex (**6**). Treatment of (**6**) with methyl iodide gives the monoalkylated cation (**7**) (Me doublet at δ 1.33). The new chiral centre in (**7**) is formed stereoselectively (≫ 98%) with reaction having occurred onto the unhindered face of the alkoxyvinyl ligand in the *anti*-conformation consistent with our previous observations on this type of complex.[5] Further treatment of (**7**) with base generates (**8**) which reacts with ethyl iodide to yield (**9**) (Me singlet at δ 0.38). Again high stereoselectivity (≫ 98%) is observed in this alkylation, with none of the other possible diastereoisomer (**10**) being observed. As expected, introduction of the ethyl group prior to the methyl group stereoselectively elaborated the alternative diastereoisomer (**10**) (Me singlet at δ 1.26).

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