1,1′-Tetramethylethyleneferrocene: A Direct Synthesis From Fulvenes and Iron Vapour

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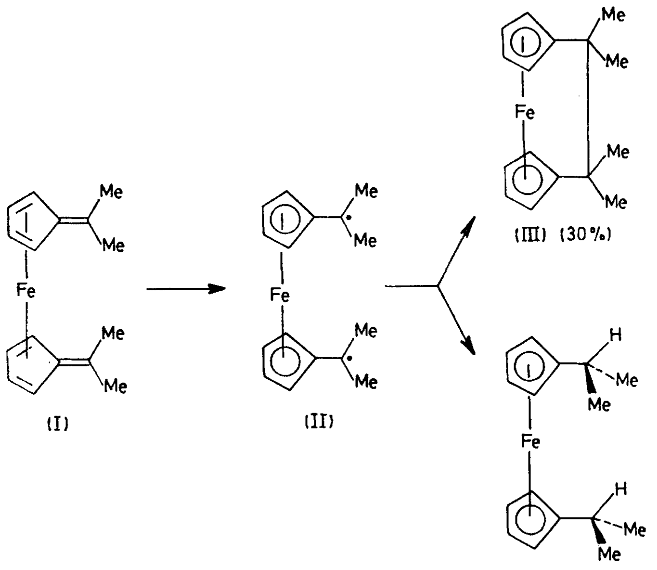
Summary Cocondensation of 6,6-dimethylfulvene and iron vapour yields 1,1′-tetramethylethyleneferrocene and 1,1′-di-isopropylferrocene.

Although several routes to 1,1′-alkyl bridged ferrocenes have been devised,[1] even the most direct synthesis of 1,1′-ethyleneferrocenes leads to many side products.[2] The major problem appears to be that the intermediate dianion formed by treating fulvene with sodium probably adopts a configuration such that the rings are directed away from each other; formation of the alkyl bridged ferrocene is thus disfavoured upon subsequent addition of $FeCl_2$.



(I) (II) (III) (30%) (IV) (25%)

We have used the reaction of the fulvene directly with iron vapour using the low temperature cocondensation procedure,[3] and thus have dimerised the fulvene on the metal template. The initial reaction may well produce bis(dimethylfulvene)iron (I), a 16-electron system somewhat analogous to bis(cyclo-octadiene) iron synthesised by Timms.[4] Radical coupling, *via* the intermediate (II), could then readily produce the desired bridged compound (III). The presence of a diradical intermediate is supported by the isolation in good yield of 1,1′-di-isopropylferrocene (IV) which presumably arises *via* hydrogen abstraction by (II) from the excess of fulvene.

In a typical experiment, a large excess of the fulvene was codeposited with *ca.* 5 mmol of iron vapour, the fulvene was removed *in vacuo*, and the residue was separated by chromatography on alumina using light petroleum (b.p. 60—80°). The products were identified by comparison of their mass and n.m.r. spectra and physical properties with the published data.[2,5]

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