Conversion of 6,6-Dimethylfulvene into 1-Isopropenyl-1′-isopropylferrocene by Cocondensation with Iron Vapour

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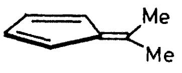
Summary Cocondensation of dimethylfulvene with iron vapour yields solely 1-isopropenyl-1′-isopropylferrocene by intramolecular disproportionation.

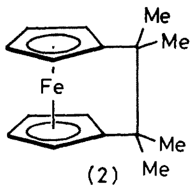
Cocondensation of 6,6-dimethylfulvene (**1**) with iron vapour has been reported as a direct route to the [2]ferrocenophane (**2**).[1] In our effort to use this method for the synthesis of other metallocenophanes we reinvestigated this conversion and observed contradictory results.

Under the usual cocondensation conditions[2] (static reactor, metal evaporation from a resistively heated alumina crucible, vacuum 10^{-4} to 10^{-5} mmHg, liquid nitrogen cooling), iron vapour and (**1**) yielded as the sole isolable product the previously unknown 1-isopropenyl-1′-isopropylferrocene (**4**), isolated by column chromatography on alumina [*ca.* 40% yield based on cocondensed metal, yellow oil, b.p. 60—70 °C at 0·1 mmHg; mass spectrum (electron impact, 70 eV): *m/e* (rel. int.) 268 (M^+, ^{56}Fe, 100%) and 253 ($M^+ - CH_3$, 20%); ^{1}H n.m.r. ($CDCl_3$): δ 1·14 (d, *J* 7 Hz, 6H, $CHMe_2$), 2·02 (m, 3H, $=C{\cdot}CMe$), 2·57 (sept., *J* 7 Hz, 1H, $CHMe_2$), 3·93 (~t, *J* 1·5 Hz, 2H, isopropyl cp) (cp = cyclopentadienyl), 3·95 (~t, *J*, 1·5 Hz, 2H, isopropyl cp), 4·13 (~t, *J* 1·5 Hz, 2H, isopropenyl cp), 4·29 (~t, *J* 1·5 Hz, 2H, isopropenyl cp), 4·81 (m, 1H, =CH), and 5·09 (m, 1H, =CH)].

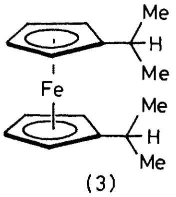
Neither in an experiment with neat (**1**) nor in dilution with hexane could the earlier[1] reported products (**2**) or (**3**) be detected. Both systems have been synthesized by published methods[3,4] and were clearly distinguished (t.l.c. and n.m.r.) from product (**4**).



(1)



(2)



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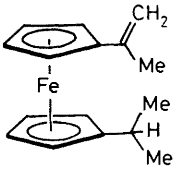

(4)

The formation of (**4**) as the only product implicates an intramolecular hydrogen transfer from one fulvene unit to another within a preformed iron complex. This conclusion is supported by the following isotopic labelling experiments. (a) Cocondensation of iron with [$^2H_6$]dimethylfulvene (from [$^2H_6$]acetone and cyclopentadiene) diluted with hexane reveals hydrogen transfer from one isopropylidene group to another and no hydrogen abstraction from the solvent or the cyclopentadiene ring of the substrate. (b) A 1 : 1 mixture of (**1**) and [$^2H_6$] (**1**) upon cocondensation with iron vapour yields only products stemming from intramolecular hydrogen and deuterium transfer, respectively, from one fulvene unit to another Thus only $[^2H_0]$-, $[^2H_6]$-, and $[^2H_{12}]$-(**4**) is formed and no random loss or introduction of hydrogen or deuterium respectively can be observed (from the mass spectrum)

In contrast with these results homofulvene (spiro [2 4]hepta-4,6-diene) upon concondensation with iron vapour yields a nearly random mixture of disproportionation and coupling products[5]

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[1] T S Tan J L Fletcher and M J McGlinchey *J Chem Soc Chem Commun* 1975 771

[2] P L Timms and T W Turney *Adv Organomet Chem* 1977 **15** 53

[3] H L Lentzner and W E Watts *Tetrahedron* 1971 **27** 4343

[4] G R Knox and P L Pauson *J Chem Soc* 1961 4610

[5] These results found in our laboratory (reported at the Chemiedozententagung 1979 Darmstadt) have been observed independently J A Gladysz J G Fulcher R C Ugolick A J Lee Hanlan and A B Bocarsly *J Am Chem Soc* 1979 **101** 3388 A J Lee Hanlan, R C Ugolick J G Fulcher S Togashi A B Bocarsly and J A Gladysz *Inorg Chem* submitted for publication