

STEREOSPECIFICITY IN $\text{Fe}(\text{CO})_5$ INDUCED REACTIONS OF DIVINYLPYRROLIDINES

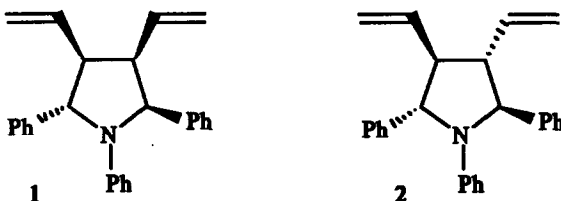
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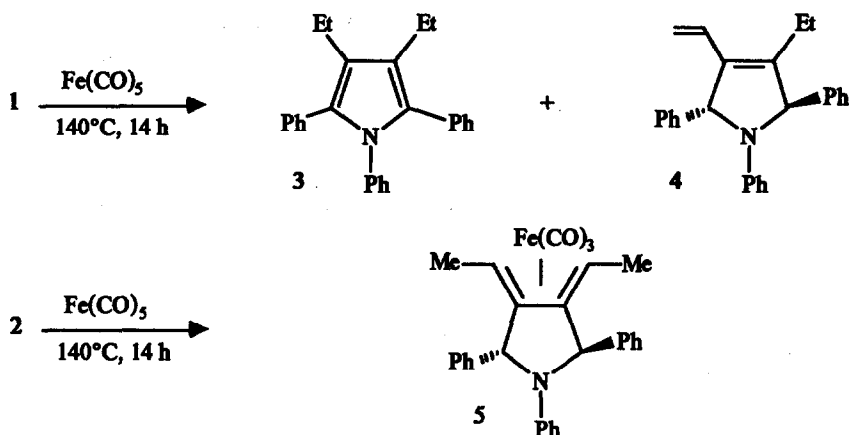
Abstract : During the reaction of $\text{Fe}(\text{CO})_5$ with *cis* (1) and *trans* (2) divinylpyrrolidines different reaction pathways are observed which may be related to the stereochemical relationships of the metal, the hydrogens and the vinyl groups in the organometallic intermediates.

The isomerization of organometallic complexes within the coordination sphere of a metal is a well known process ¹. In the case of iron derivatives many examples have already been described either as isolated complexes ² or free olefins or polyenes reacting with iron carbonyls ³. The mechanisms of these reactions have been studied in detail but there is still a need for more information about the stereochemistry involved and to this end we have prepared, in a stereocontrolled manner, the *cis*- and *trans*-divinyl pyrrolidines 1 and 2 ⁴. The purpose of this note is to report that *these two isomers react with $\text{Fe}(\text{CO})_5$ to give different products* indicating that the stereochemistry has a strong influence on the successive hydrogen shifts involved in the reaction pathway.

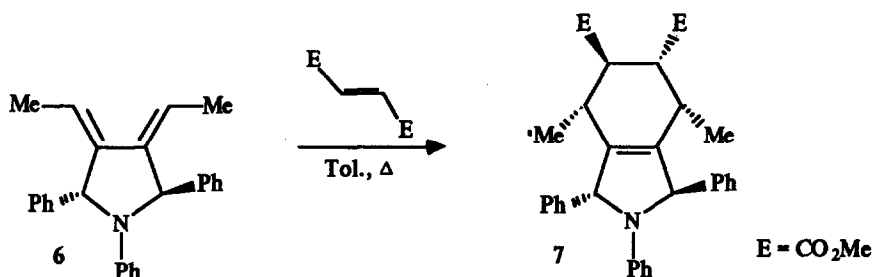


Reaction of pyrrolidine 1 with 5 equivalents ⁵ of $\text{Fe}(\text{CO})_5$ in refluxing xylene during 14 hours give a mixture of pyrrole 3 (33 %) and vinylpyrroline 4 (57 %) which are separated by chromatography and readily characterized from their physical and spectral properties ⁵. Under the same conditions, the *trans* isomer 2 give the diene-tricarbonyl iron complex 5 as the only isolated compound (68 % yield) ⁶. No trace of 3 or 4 is observed in this case. The structure of 5, established from its analytical and spectroscopic data,

is further confirmed by decomplexation to bisethylidene pyrrolidine 6 which could be used in Diels-Alder



reactions. Reaction with dimethylfumarate, for instance, produces 7, as a single cycloadduct, in 83 % yield ^{7,8}.

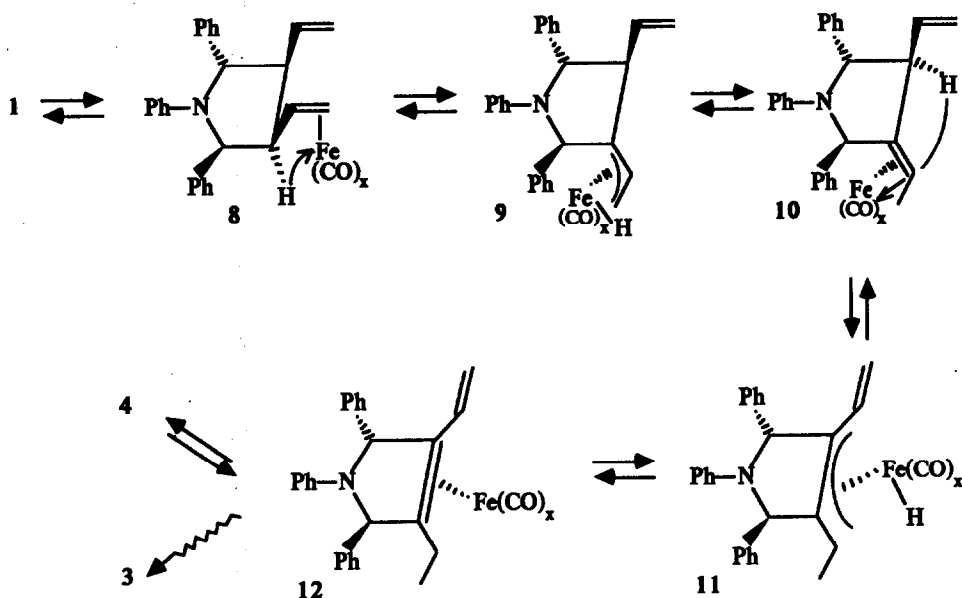


A detailed study of the mechanisms involved in the reactions of 1 and 2 with Fe(CO)_5 will require experiments using labelled compounds. However, a tentative explanation for the difference in the reaction pathways followed by the two stereoisomers assumes that these transformations follow the generally accepted mechanism of 1,3 hydrogen migration via π -allylic intermediates ¹.

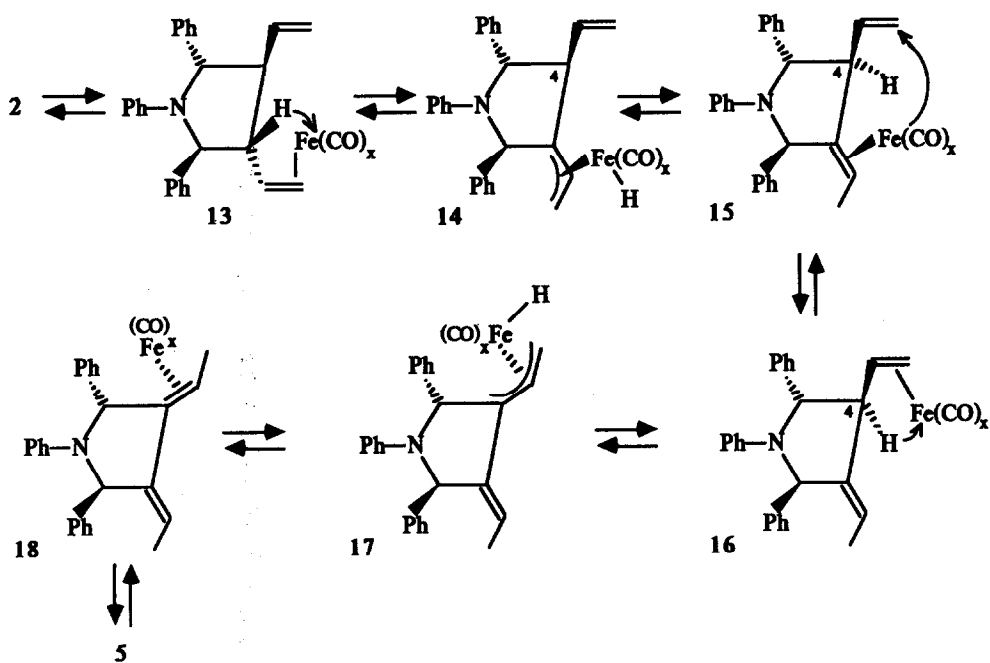
Starting from 1, the first 1,3 hydrogen shift would lead, via the η^2 intermediate 8 and the π -allyl hydride 9, to the complex 10 (scheme 1). *In this intermediate the H_4 hydrogen is cis to the metal and thus in good position for a second 1,3 shift to give 12 via 11.* The complex 12 leads by ligand displacement to the vinyl-pyrroline 4. Pyrrole 3 may be formed from 12 after several 1,3 hydrogen shifts ⁹.

In the case of the trans derivative 2 (scheme 2) after the first 1,3 hydrogen shift (giving 15), the *metal is now trans to the H_4 hydrogen and thus, not well oriented for migration.* However the metal is cis in relation to the next vinyl system and so in the best orientation for an intramolecular shift leading to 16. From this intermediate, a final 1,3 hydrogen shift of H_4 gives 18 and hence the complex 5.

Acknowledgments : Fruitful discussions with Professor R. Carrié and Dr D. Bremner are gratefully acknowledged.



Scheme 1



Scheme 2

References and notes

- 1 - "Principles and Applications of Organotransition Metal Chemistry" Collman J.P., Hegedus L. Ed., University Science Books, N.Y., 1980.
- 2 - "The Organic Chemistry of Iron" Koerner von Gustorf E.A., Grevels F.W., Fischler I., Ed., Acad. Press., N.Y. 1978 (vol. 1) and 1981 (vol. 2).
- 3 - Rodriguez J., Brun P., Waegell B., Bull. Soc. Chim. Fr. (in print).
- 4 - Lassalle G., Grée R., Bull. Soc. Chim. Fr. (to be submitted for publication).
- 5 - Compounds 2 and 3 are also obtained with only 1 eq. of $\text{Fe}(\text{CO})_5$ but the reaction is slower.

3 : m.p. = 154-5°C (MeOH). ^1H NMR (80 MHz, CDCl_3) : 7.20-6.67 (m, 15 H, Arom.) ; 2.55 (q, 4 H, $J = 7.4$, CH_2) ; 1.11 (t, 6 H, CH_3).

4 : F = 135-6°C (Ether/pentane 1/1). ^1H NMR (80 MHz, CDCl_3) : 7.47-6.37 (m., 15 H, Arom.) ; 6.19 (d.d., 1H, $J = 17.0$, $J = 11.0$, - $\text{CH} = \text{CH}_2$) ; 6.24 (d., 1 H, $J = 5.2$, CHPh) ; 5.56 (d. 1 H, CHPh) ; [5.25 (d., 1 H) and 5.07 (d., 1 H) - $\text{CH} = \text{CH}_2$] ; 2.60-1.51 (m., 2 H, $\text{CH}_2\text{-CH}_3$) ; 1.00(t., 3 H, $J = 7.4$, CH_3).

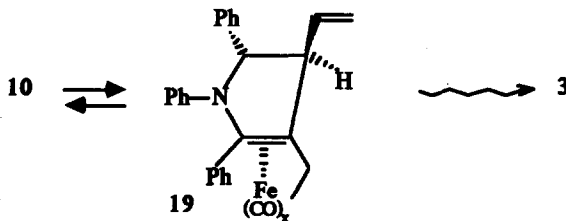
6 - 5 : m.p. = 175-6°C (Ether). IR (Nujol, $\nu \text{ cm}^{-1}$) : 2035, 1962, 1930, ($\text{C} = \text{O}$) ; 1620 ($\text{C} = \text{C}$, Arom.) ;

^1H NMR (80 MHz, CDCl_3) : 7.60-6.45 (m, 15 H, Arom.) ; 6.35 (broad s., 1 H, CHPh) ; 6.15 (broad s., 1 H, CHPh) ; 1.32 (d., 3 H, $J = 6.4$, Me) ; 1.24 (d., 3 H, $J = 6.4$, Me) ; 0.81 (q., 1 H, CH-Me) ; 0.75 (q., 1 H, CH-Me). ^{13}C NMR(20.1 MHz, CDCl_3) : 211.5 (CO) ; 143.8 ; 143.0 ; 141.8 ; 130.1 ; 129.3 ; 128.7 ; 128.5 ; 128.3 ; 128.0 ; 127.7 ; 127.3 ; 117.2 ; 116.5 (Arom.) ; 109.4 and 106.9 ($\text{C} = \text{C-Me}$) ; 68.0 and 67.7 (CHPh) ; 48.1 and 45.9 ($\text{C} = \text{C-Me}$) ; 17.0 and 15.6 (CH_3).

7 - The configuration attributed to 7 corresponds to a cycloaddition from the less hindered side ; however it could not be definitely established from the spectroscopic data.

8 - Cleavage of the double bond in 7 using ozone or a $\text{KMnO}_4 + \text{NaIO}_4$ mixture could not be achieved. In each case, only aromatisation leading to the corresponding pyrrole was observed.

9 - The detailed mechanism of this transformation cannot be established at this moment and bimolecular processes may also be involved. Furthermore, it is interesting to note that no type 19 complexed enamine



has been found, although it is possible intermediate in the transformation of 10 to 3 ; we thank a referee for this suggestion.