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ON THE MECHANISM OF ACIDIC HYDROGEN ISOTOPIC EXCHANGE IN σ-BENZYL-π-CYCLOPENTADIENYLIRON DICARBONYL

T.Yu. ORLOVA, V.N. SETKINA * and D.N. KURSANOV
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
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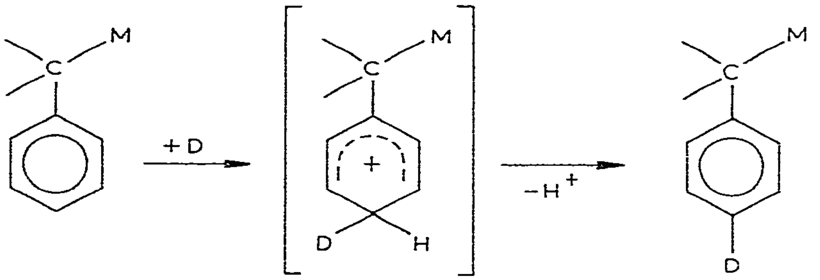
Summary

The stereochemical approach is used to show that the mechanism of acidic hydrogen isotopic exchange in σ-benzyl-π-cyclopentadienyliron dicarbonyl does not involve formation of intermediate kinetically-independent methylenecyclohexadiene.

It was found earlier that benzyl-iron, -molybdenum, and -tungsten complexes of general formula $C_5H_5(CO)_nMCH_2C_6H_5$ ($M = Fe$, $n = 2$; $M = Mo, W$, $n = 3$) exceedingly readily exchange the benzene ring hydrogen atoms for deuterium in mixtures of deuterated acetic and trifluoroacetic acids.

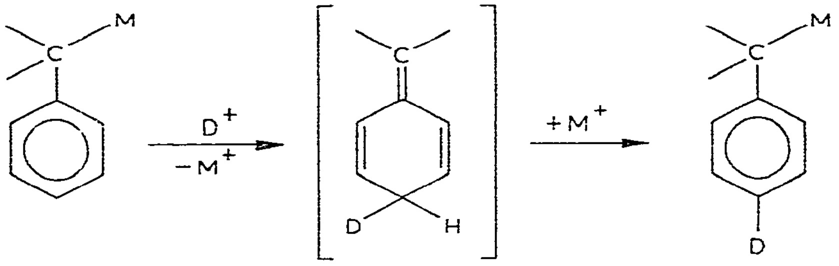
The study of the hydrogen exchange kinetics in these systems showed that the metal-containing moiety $C_5H_5(CO)_nMCH_2$ behaves as an electron-releasing group comparable in its effect with three methyl groups of mesitylene and with a stronger effect than that of the methoxy group known for its high electron-releasing power [1—3].

At present the nature of this extraordinary effect attracts much interest. In the literature, the hydrogen exchange in benzyl derivatives of transition and non-transition metals is considered a usual electrophilic exchange reaction in which the carbenium ion intermediate is stabilized by conjugation of the σ-M—C bond and the benzene ring electron system [3—5]. Stabilization of the σ—π-transition type has been suggested [3].



(Mechanism 1)

An alternative mechanism of the hydrogen exchange is possible, however, which involves fragmentation and intermediate methylenecyclohexadiene ring deuteration followed by electrophilic addition of the metal-containing moiety to the exocyclic ethylene bond.



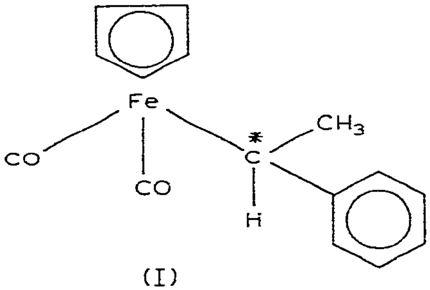
(Mechanism 2)

This possibility is discussed in detail elsewhere [6]. Participation of olefins in hydrogen isotopic exchange was shown in our study of the mechanism of hydrogen exchange in saturated hydrocarbons in acidic media [7].

The choice between the two mechanisms can be made using the stereochemical approach.

Mechanism 1 leaves the M—C bond intact, whereas according to mechanism 2, this bond undergoes rupture during the reaction. Thus hydrogen exchange in optically-active complexes with chiral centers on the metal or adjacent carbon atom should accompany retention of configuration at the chiral center in the case of mechanism 1, or lead to racemization in the case of mechanism 2.

In order to solve the problem, we studied hydrogen exchange in the optically active iron complex I with the chiral center on the carbon atom.



(I)

First, we studied hydrogen exchange in the corresponding racemic mixture to show that the compound reacts at approximately the same rate as $C_5H_5(CO)_2FeCH_2C_6H_5$ does. Thus, the substitution of the CH_3 group for the methylene hydrogen atom does not affect the reaction rate to a significant extent [8].

(+)-σ-Phenylethyl-π-cyclopentadienyliron dicarbonyl (I) was prepared using the procedure reported by Alexander and Wojcicki [9]. With hydrotropic acid of 80% optical purity as starting material, we isolated complex I in the form of an oil, $[\alpha]_{546}^{22}$ +54° (*c* 0.5 hexane) *. Manifold Al_2O_3 chromatographic purifica-

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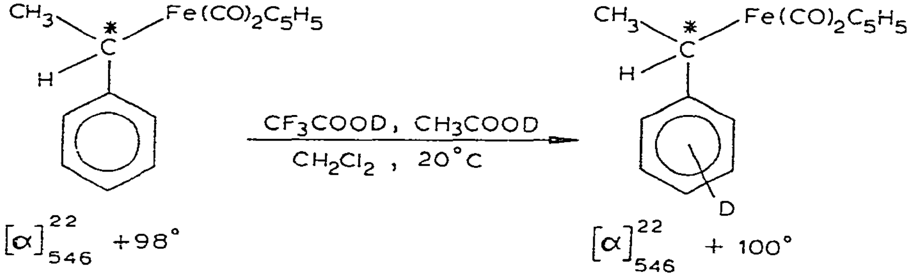
* Rotation was measured on a Jouan—Roussel (France) polarimeter. The values cited were averaged over 4—5 measurements. Rotation values of samples differed within 5° due to the instability of complex 1 in solution.

tion of the product followed by low-temperature crystallization yielded I in the crystalline form, $[\alpha]^{22}_{546}$ +98° (hexane) *, and unidentified optically inactive hydrocarbon. Unpurified complex I ($[\alpha]^{22}_{546}$ + 54°) was subjected to hydrogen exchange under the conditions described in ref. 8 (mixture of deuterated acetic and deuterated trifluoroacetic acids in methylene chloride, ambient temperature). The reaction was allowed to proceed for 7 h to give conversion of about 20% of the equilibrium value. Complex I isolated from the reaction mixture and purified as described above gave $[\alpha]^{22}_{546}$ + 100° (hexane).

Thus, we did not observe racemization of complex I during acidic hydrogen exchange. We found the same value for optical rotation in the initial complex I and in the complex isolated from the reaction mixture.



From our results we inferred that the Fe—C bond remains intact, i.e. in the exchange reaction methylenecyclohexadiene formation does not take place.

We came to the same conclusion by studying the effect of Fe-salt addition on hydrogen exchange rates in $C_5H_5(CO)_2FeCH_2C_6H_5$. (If mechanism 2 were the case this salt would accelerate the exchange reaction [6]). Indeed an addition of excess $C_5H_5(CO)_2FeOCOCF_3$ (5 *M* to 1 *M* $C_6H_5(CO)_2FeCH_2C_6H_5$) did not affect the reaction rate. Under identical conditions *k* is 3.0×10^{-6} sec^{-1} and 3.4×10^{-6} sec^{-1} with and without the addition, respectively. The data obtained permit us to exclude Mechanism 2 in the case of $C_5H_5(CO)_2FeCH_2C_6H_5$.

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* Complex I was reported [9] to be a dark brown oil, $[\alpha]^{27}_{546}$ +78° (chloroform). The substance described earlier thus appears to be impure.