CARBON-METAL HYPERCONJUGATION IN METALLOCENES
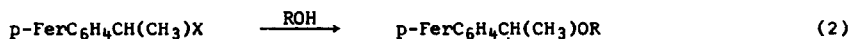
HYDROGEN EXCHANGE IN PHENYLFERROCENE[1]

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In the previous communication,[2] carbon-metal hyperconjugation[3] has been demonstrated

in the facile deuteriodeprotonation observed during electrophilic cleavage of dibenzylmer-

cury and benzylboronic acid. In this report we discuss the same phenomenon with respect

to the ferrocene system.

Traylor and Ware[4a,b] have suggested that the high reactivities in reactions 1 and 2

(where Fer = $C_5H_5FeC_5H_4$) are, in part, due to Fe-C bond hyperconjugation

$$FerCH(CH_3)X \xrightarrow{ROH} FerCH(CH_3)OR \ (retention) \tag{1}$$

$$\underline{p}\text{-}FerC_6H_4CH(CH_3)X \xrightarrow{ROH} \underline{p}\text{-}FerC_6H_4CH(CH_3)OR \tag{2}$$

illustrated below for reaction 2. These workers have demonstrated a strong resonance
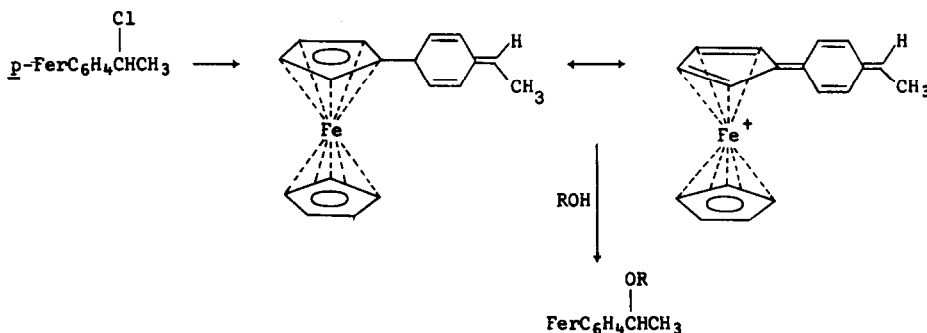
stabilizing effect for the ferrocenyl group in the para position of a benzene ring in

reaction 2. We now report a similar effect for isotopic hydrogen exchange in phenyl-

ferrocene.

Phenylferrocene was prepared from ferrocene and phenyldiazonium sulfate according

to the procedure of Broadhead and Pauson,[5] and was purified by column adsorption chroma-

tography on alumina. The hydrogen exchange rate for this compound was determined in

4.31 $\underline{M}$ trifluoroacetic acid-d (98% O-D) in benzene at 25°C, H_o-1.38. Kinetic analysis was made by isolating aliquots at various time intervals, purifying the material by chromatography, and comparing the integrated areas of the sample peaks with respect to methylene chloride as internal standard in a Varian HR-60 nmr spectrometer. This method enabled the determination of specific rate constants for all positions in phenylferrocene.[6] Results are seen in Table 1. Infrared analysis[7] of material isolated at various points of a kinetic run showed the presence of two strong bands at 635 cm^{-1} and 608 cm^{-1}, which we assign to the ortho and para carbon-deuterium bending frequencies of the phenyl ring.[8,9]

TABLE 1

Specific Rate Constants for Isotopic Hydrogen Exchange at 25°C, H_o-1.38

Compound	$k_{obs.}$ (sec^{-1})	Rel. Rate
Phenylferrocene:		
2 position	8.54×10^{-4}	1447
1' position	3.35×10^{-4}	568
3 position	2.71×10^{-4}	459
phenyl ring (o and p)	0.59×10^{-6}	1
phenyl ring (m)	too slow to measure	
total rate[10]	3.68×10^{-4}	
Ferrocene[11]	5.59×10^{-4}	947
Anisole	1.25×10^{-6}	
Toluene	6.28×10^{-10}	

In order to compare the rates of these isotopic hydrogen exchanges with those of other aromatic compounds we have measured exchange rates for toluene and anisole under our conditions. Tritiodeprotonation rates for these substrates in 4.31 $\underline{M}$ trifluoroacetic acid-H[3] at 25°C are shown in the table. A log $k_{rel.}$ versus σ^+ plot using these two rates as calibration points (ρ -6.9) leads to a value of -0.72 for para-ferrocenyl. This can be compared to the value of -0.71 obtained from solvolysis[4] data.

The fact that the ferrocenyl group accelerates exchange on benzene by 10^5 whereas the phenyl group (or even the methoxy group[10]) scarcely changes reactivity on the ferrocene group is also consistent with σ-π conjugation. Thus the resonance structure (I) is

important in the exchange on phenyl but (II) would not be important for exchange in the ferrocenyl group because it is an unstable structure.

$$(I) \qquad\qquad (II)$$
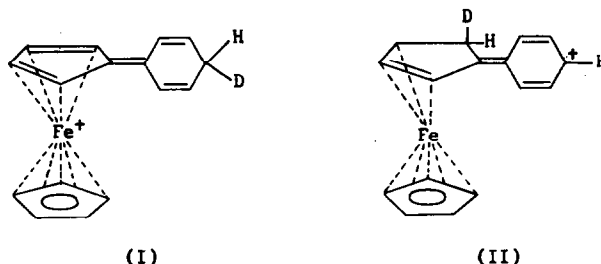
The above and previous[3] results make it abundantly clear that carbon-metal hyperconjugation is a general phenomenon in the reactions of organometallic compounds, whether they be σ bonded metals[2] or the π bonded metallocenes.

Curiously the rate of deuteriodeprotonation of ferrocene leads to a $\sigma^+_{\alpha-Fer} = -1.1$ which is contrasted to $\sigma^+_{\alpha-Fer} = -1.4$ for the solvolysis reaction 1. The following communication shows how this discrepancy has lead to a general mechanism for electrophilic substitution on metallocenes.

References

1. Supported by the Air Force Office of Scientific Research grant AF-AFOSR-514-66.

2. W. Hanstein and T. G. Traylor, _Tet. Letters_ 0000 (1967).

3. (a) A. N. Nesmeyanov and I. F. Lutsenko, _Doklady Akad. Nauk, SSSR_ 59, 707 (1948).

    (b) A. N. Nesmeyanov, K. A. Perchskaya, A. N. Akramovich and L. M. Miakova, ibid. 121, 660 (1958). (c) A. N. Nesmeyanov and I. I. Kritskaya, ibid. 477 (1958).

4. (a) T. G. Traylor and J. C. Ware, _J. Am. Chem. Soc._ 89, 2304 (1967).

    (b) J. C. Ware and T. G. Traylor, _Tetrahedron Letters_ 18, 1295 (1965).

5. G. D. Broadhead and P. L. Pauson, _J. Chem. Soc._ 367 (1955).

6. The nmr spectrum of phenylferrocene (10% in carbon tetrachloride solution) consists of four groups of lines; a multiplet for phenyl protons at 2.73τ, a triplet for the 2,5 protons at 5.47τ, a triplet for the 3,4 protons at 5.82τ, and a singlet for the unsubstituted ring protons at 6.07τ.

7. Infrared spectra were recorded on a Cary-White 90 spectrometer, in carbon disulfide solution.

8. Assuming the <u>ortho</u>- and <u>para</u>-toluene-d_1 intensity ratios of Tiers,[9] leads to an <u>ortho</u>/_{<u>para</u>} rate ratio of $\frac{1}{2}$ $^{D}o/D_p$ = 0.91 - 0.96. These two values are for phenylferrocene isolated after 30% and 50% exchange of phenyl protons.

9. (a) G. V. D. Tiers, <u>J. Chem. Phys.</u> <u>19</u>, 1072 (1951). (b) G. V. D. Tiers and J. H. Tiers, ibid. <u>20</u>, 761 (1952).

10. M. N. Nefedova, D. N. Kursanov, V. N. Setkina, E. N. Perevalova, and A. N. Nesmeyanov, <u>Doklady Akad. Nauk. SSSR</u> <u>166</u>, 374 (1966) reported that the total rate of exchange in phenylferrocene was 0.6 that in ferrocene at 25°C, 7.3 wt % trifluoroacetic acid-d in methylene chloride.

11. John A. Mangravite and T. G. Traylor, unpublished observations.

12. It was necessary to determine the ρ slope under our condition since apparently hydrogen exchange selectivity is highly dependent on conditions. Stock and Brown[13a] report a ρ slope for detritiation of -8.2; Lauer[13b] reports the rate of exchange in toluene to be 100 times that of benzene in trifluoroacetic acid-d-deuterium oxide, which would be a ρ slope of -6.6.

13. (a) L. M. Stock and H. C. Brown in "<u>Advances in Physical Organic Chemistry</u>," Vol. I, Academic Press, London, 1963, p. 96. (b) W. M. Lauer, G. W. Matson and G. Stedman, <u>J. Am. Chem. Soc.</u> <u>80</u>, 6433 (1958). (c) ibid. 6437. (d) W. M. Lauer and G. Stedman, ibid. 6439.