# Preliminary Notes

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## The electrophilic reactivity of (trimethylsilyl)-ferrocene, -ruthenocene, and -osmocene*

Although it has been known for some time that bis(cyclopentadienyl)-iron, -ruthenium, and -osmium can be substituted by electrophilic reagents, the only report concerning the relative reactivities of these compounds is that of a qualitative study by Rausch, Fischer and Grubert[1], who found that in Friedel-Crafts acylations reactivity decreases in the order ferrocene > ruthenocene > osmocene.

We have determined the relative reactivities by measuring the rates of acid cleavage of the cyclopentadienyl–silicon bonds in (trimethylsilyl)-ferrocene, -ruthenocene, and -osmocene. [The latter two compounds (previously unknown) were prepared by treating ruthenocene or osmocene with *n*-butyllithium, and trimethylchlorosilane, followed by purification by gas-liquid chromatography.] The acid-catalysed cleavages of aryl–silicon bonds are well established electrophilic substitutions[2]. The solvent used for our study was aqueous methanol, the catalyst was hydrochloric acid, and the reaction was followed spectrophotometrically.

TABLE 1

FIRST ORDER RATE CONSTANTS FOR $Me_3SiC_5H_4–X–C_5H_5 + H^+$ [$10^3$ $k_1$ (min$^{-1}$)]

| *HCl concn.** [*M*] | *X = Fe* | *Ru* | *Os* |
|---|---|---|---|
| 0.596 | 3.36 | 156.5 | 62.66 |
| 0.477 | 2.45 | 109.3 | 48.10 |

* Concn. of aqueous acid, 5 ml of which are added to 20 ml of an anhydrous methanol solution of the silane.

The first order rate constants at two acid concentrations are given in the table. On changing the metal atom the reactivity changes in the sequence Ru > Os > Fe. It is noteworthy that (trimethylsilyl)ruthenocene is the most reactive of the three compounds, and any mechanism proposed to explain electrophilic substitution reactions in the metallocenes must account for this fact.

The overall spread of rates is quite small: the rate of (trimethylsilyl)ruthenocene/the rate of (trimethylsilyl)ferrocene ≈ 45. The rates are of the same magnitude as that of the same reaction at the *para*-position in anisole. The relative rates for (trimethylsilyl)ferrocene/(*p*-methoxyphenyl)trimethylsilane ≈ 2.

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*Department of Chemistry, The University,*
*Hull, Yorks. (Great Britain)*

G. MARR
D. E. WEBSTER

1 M. D. RAUSCH, E. O. FISCHER AND H. GRUBERT, *J. Am. Chem. Soc.*, 82 (1960) 76.
2 C. EABORN, *J. Chem. Soc.*, (1953) 3148; and subsequent papers.

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