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ELECTRONIC INFLUENCE OF RUTHENOCENYL AS SUBSTITUENT

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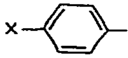
SUMMARY

Ferrocenylruthenocenylmethane was prepared in order to estimate quantitatively the electronic influence of ruthenocenyl as substituent. The formal redox potential of the ferrocenyl nucleus in this compound was determined; the pK_a of ruthenocenylcarboxylic acid was measured in 50% ethanol and the CO-stretching frequency and basicity of acetyl ruthenocene were also found. The values obtained were used in the calculation of the σ_i, σ_p and σ_p^+ constants of ruthenocenyl as a substituent. Changes in the reactivities of the five-membered aromatic rings have been found to be associated with the change in effective charge on the ring carbon orbitals, when passing from ferrocene to ruthenocene, whereas the π-electron density at the rings and its polarizability remained unaltered.

INTRODUCTION

A number of papers[1] have made a study of the reactivities of the iron group metallocenes. In our opinion, however, the essential differences and the reasons for these differences may be best resolved by investigating the σ constants of the corresponding metallocenyl substituents. On this basis, the following general approach has been worked out for discussing the reactivities of metallocenes as aromatic systems. The reactivities of metallocenes and their derivatives will be discussed in the commonly accepted terms of reactions obeying the principle of linear change of free energy (LFE)[2]. The objects to be investigated should then be as follows: X–G–Y, where substituent X is the metallocenyl group, C_5H_4ML (where $M=Fe$, $L=C_5H_5$, ferrocenyl or where $M=Ru$, $L=C_5H_5$, ruthenocenyl, etc.) Y is the reaction center, and G is the conducting system or group. In a general case, G may be absent.

Thus for the same C_5H_5–ligand, the reactivity of its combined Y group varies depending on the kind of ligand, L, and metal atom M combined with the five-membered ring via delocalized π-bonding. As in the case of other substituents, the influence of the metallocenyl group upon the reactivity of Y, should be defined, to a first approximation, by the two major interactions: the inductive and conjugation effects. A synthesis for the introduction of the metallocenyl group into the *meta*- and *para*-positions of the phenyl nucleus, towards the reaction center has been described so far only for ferrocene. Even its closest analog—ruthenocene—has not yet been arylated[3] not to speak of other metallocenes. Hence, "the classic approach" of a determination of σ-constants previously employed for ferrocenyl[4] cannot be used for the majority of other metallocenes.

Much more easily synthesized are those compounds where the metallocenyl groups and various reaction centers are directly adjacent, without a phenyl or other conducting group X–Y (a particular case of compounds X–G–Y, where G is absent). The reactivities of such compounds are usually satisfactorily described by the principle of the linear change of free energy. The value of ρ in the respective equations varies by a multiplier independent of the nature of the reaction center and the character and conditions of the reaction and is a constant for a given conducting system[2]. For example, if ρ is known for the reaction series  , then for the series X–Y this value is equal to $\rho/0.3$, since π' for the *para*-phenylene ring is 0.30 ± 0.05 [2]. Hence, by means of the π'-value one can determine quite reliably the σ-constants for a reaction series where the reaction center is directly adjacent to the metallocenyl substituent.

For a complete characterisation of the electronic influence of metallocenyls as substituents at least three types of σ should be available: the inductive aromatic constant σ_i, the Hammett constant σ_p and the electrophilic aromatic constant σ_p^+.

A later analysis discusses the model reaction series which provide the basis of the determination of σ-values for ruthenocene as a substituent.

INDUCTIVE EFFECT OF RUTHENOCENYL

At present there are a comparatively large number of model reaction series which could be employed for the determination of the inductive constants of substituents[2]. However, a more detailed analysis showed that none of the known procedures for determination of the substituent inductive parameters is available for the majority of metallocenes. First, investigators face considerable and sometimes insuperable difficulties in the preparation of, for example, metallocenyl-substituted [2.2.2]-bicyclooctanecarboxylic acids or other model compounds. Secondly, even if the preparation of such compounds is successful, then as in the case of ferrocenyl-substituted α-toluic acids, their very low solubility does not allow a correct measurement of the pK_a-values of the corresponding acids. Furthermore, the related compounds can at present be obtained only on the basis of ferrocene.

We have worked out a novel procedure for the determination of the inductive parameters of substituents, available for the majority of metallocenyl groups and probably for other polyatomic substituents. In this procedure the reaction of reversible oxidation of the substituted ferrocenes was employed. Earlier, it was shown[5] that the E_{f_0}-value of the reversible ferrocene oxidation is exceptionally sensitive to the electronic effects of substituents. Even when a substituent is separated by a methylene group from the nucleus, the potential difference for the farthest removed substituents exceeds by many hundred times the maximal value of the mean-square experimental error (300 and 2–3 mV, respectively). For the substituted ferrocenes, $C_5H_5FeC_5H_4$-CH_2X, where a substituent is separated from the nucleus by a methylene group hindering the conjugation, the redox potentials correlate well with the inductive constants of the corresponding X-substituents both in aromatic σ_i, and aliphatic σ^*, scales (Fig. 1). The characteristics outlined for the reaction series discussed, exhibiting

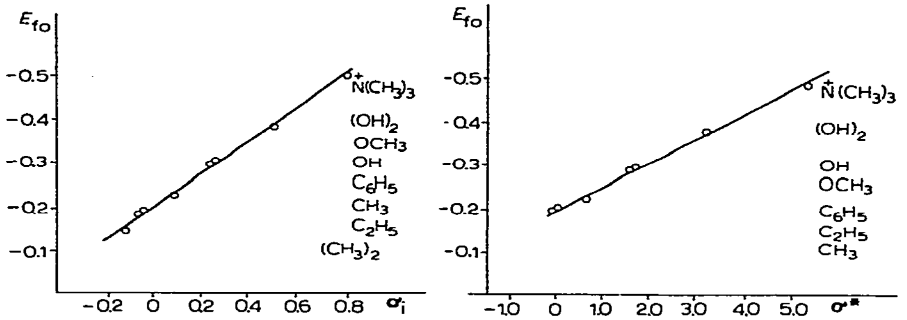


Fig. 1. Correlation of the E_{f_0} with σ_i-X and σ^*-X for $C_5H_5FeC_5H_4CH_2X$.

high negative ρ, make it satisfy all the conditions required for the model reactions and make it suitable for the determination of the new inductive parameters. The corresponding equations are as follows:

$$E_{f_0} = 0.336\,\sigma_i - 0.208; \quad r = 0.992, \quad n = 8, \quad S = 0.023 \tag{1}$$

$$E_{f_0} = -0.0546\,\sigma^* - 0.209; \quad r = 0.991, \quad n = 7, \quad S = 0.111 \tag{2}$$

The effects of substituents in the given reaction series are "purely" inductive, since a methylene group hinders, as is commonly accepted, the transmittance of the substituent conjugation effect. Moreover, the ferrocenyl nucleus itself transmits to the reaction center—the iron atom— only the inductive component of the total polar effect of substituent, as was convincingly shown in our previous paper[6].

Most of the ferrocenylmetallocenylmethanes required for the determination of the inductive parameters by this method may be synthesized by electrophilic substitution reactions of the ring hydrogens. Ferrocenylruthenocenylmethane studied in the present work, was obtained by reduction of the ferrocenylruthenocenylketone previously described with a mixture of $LiAlH_4 + AlCl_3$ in absolute ether, according to a procedure described for the reduction of substituted benzoylferrocenes[7]. The structure of ferrocenylruthenocenylmethane was established on the basis of the elementary analysis, IR and NMR spectra. The results obtained, as well as X-ray data on ferrocenylruthenocenylketone[8] and other structurally similar derivatives of ferrocene and other metallocenes[9], give grounds for assuming that ferrocenylruthenocenylmethane

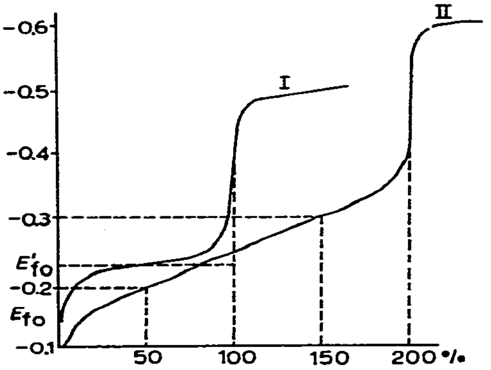


Fig. 2. Amount of oxidized iron. Total quantity of iron in diferrocenylmethane was taken as 200%.

may also exist predominantly in a "*trans*" configuration with undistorted (due to the direct contact) ruthenocenyl and ferrocenyl nuclei.

The potentiometric and polarographic oxidation of ferrocenylruthenocenylmethane was investigated. The potentiometric titration curves of ferrocenylruthenocenylmethane (I) and diferrocenylmethane (II) are compared in Fig. 2. It can be seen from this figure, that under the conditions described the titration curve of ferrocenylruthenocenylmethane represents a one-electron one-step reversible oxidation. In order to determine which of the two nuclei undergoes oxidation under these conditions, separate titrations of ferrocene and ruthenocene, and of their equimolar mixture, were carried out. Only ferrocene titration curves were observed in all cases. It should be pointed out that the presence of ruthenocene in solution had no effect upon the formal redox potential of ferrocene.

The polarographic oxidation of ferrocenylruthenocenylmethane, ruthenocene and ferrocene were also studied on platinum electrode in acetonitrile. Ferrocenylruthenocenylmethane shows two well defined reversible one-electron waves with half-wave potentials close to those of the individual metallocenes (Fig. 3). The ruthenocenyl nucleus is, by approximately 0.5 V, more difficult to oxidise than the ferrocene nucleus. Hence, the potentiometric oxidation of ferrocenylruthenocenylmethane involves only that of the ferrocenyl nucleus since, as we have shown earlier, no oxidation of ferrocenes containing strong electron-withdrawing substituents was observed when E_{f_0} differed by more than 0.35 V from that of ferrocene.

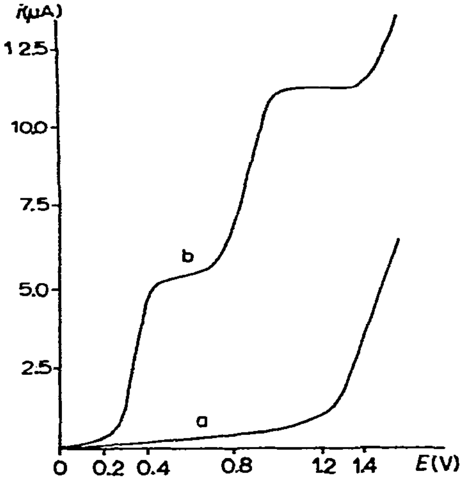


Fig. 3. Polarogram of oxidation of ferrocenylruthenocenylmethane on the smooth platinum electrode in CH_3CN with 0.1 N $(C_2H_5)_4NClO_4$ as supporting electrolyte.

The formal redox potential of the ferrocenyl nucleus in ferrocenylruthenocenylmethane is -0.222 V. This value is compared with the corresponding potentials of ferrocene, methylferrocene and diferrocenylmethane. As can be seen from Table 1, the introduction of the ferrocenyl nucleus into the methyl group of methylferrocene decreases the formal redox potential. On the other hand, the positive charge appearing at the iron atom in one ferrocenyl nucleus inhibits the oxidation of the second nucleus not only in respect to that of the initial methylferrocene but to unsubstituted ferrocene as well. The introduction of the ruthenocenyl nucleus into the methyl group

TABLE 1

FORMAL REDOX POTENTIALS OF SOME SUBSTITUTED FERROCENES

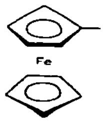
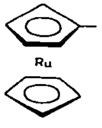
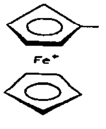
No.	Compound $C_5H_5FeC_5H_4$–X	E_{f_0}
1	$-CH_2C_5H_4FeC_5H_5$	−0.189
2	$-CH_3$	−0.198
3	$-CH_2C_5H_4RuC_5H_5$	−0.222
4	–H	−0.245
5	$-CH_2-C_5H_4\overset{+}{Fe}C_5H_5$	−0.302

of methylferrocene also increases the oxidation potential, *i.e.*, inhibits the oxidation in comparison with the initial methylferrocene. The formal redox potential of the ferrocenyl nucleus in ferrocenylruthenocenylmethane is intermediate between those of ferrocene and methylferrocene. It can thus be assumed that the ferrocenyl substituent should display electron-releasing (and ruthenocenyl, electron-withdrawing) properties with respect to hydrogen.

Earlier[10] an overall quantitative estimation of the electron-releasing properties of the ferrocenyl nucleus was given in some of our papers and those of other authors. In the present work, using the E_{f_0}-values obtained we calculated the inductive aromatic σ_i and aliphatic σ^* constants for the metallocenyl groups investigated and determined the group electronegativities of the corresponding radicals; the results are given in Table 2.

TABLE 2

INDUCTIVE CONSTANTS OF METALLOCENYL GROUPS

Compound	σ_i	σ^*	Group electronegativity χ^a
	−0.05	−0.33	2.08±0.13
	+0.04	+0.26	2.27±0.10
	+0.30	+1.85	2.76±0.02

[a] Estimated from equations[11] $\chi_1=0.370\sigma^*+2.06$; $\chi_2=0.26\sigma^*+2.30$; values of $\chi=(\chi_1+\chi_2)/2$ are given.

As can be seen from this Table, the inductive parameters of the metallocenyl groups investigated provide a clear quantitative estimation of the effects of the nature of the metal and charge upon the reactivity of the π-bonded cyclopentadienyl group. Unfortunately, it is not possible to evaluate σ_i for the non-coordinated cyclopentadienyl anion as a substituent. It can be assumed only that the effective electronegativity of carbons in the C_5H_4-group should be small, whereas the inductive constant should be considerably negative in value (~ -0.20), comparable with the known values for other negatively charged substituents[2] (for $-O^-$, $\sigma_i = -0.12$; for $-COO^-$, $\sigma_i = -0.15$ to -0.17).

It can be seen that the absolute magnitude of the inductive aromatic constant of the $(C_5H_4)^-$-group decreases somewhat, although still remaining negative, after coordination. This shows that the effective carbon electronegativity of the five-membered aromatic ring in the ferrocene molecule is lower with respect to that of hydrogen. These results are in good agreement with the data from quantum chemical calculation taking into account the σ-framework[12] and showing a total effective negative charge at the carbons and a positive one at the hydrogen atoms. In the general case, polarization of the σ $C^{\delta-}-H^{\delta+}$ bond should result in the following general chemical transformations: increasing activity in the reactions of electrophilic substitution of hydrogen and decreasing acidity of the C–H bond*; moreover, activity of the C–X bond might be expected to decrease in the nucleophilic exchange of X. Corresponding characteristics of the reactivities of the ferrocenyl derivatives have been dealt with in a number of papers[1].

The removal of an electron from the highest occupied orbital of ferrocene and the positive charge appearing at the iron atom of the ferricinium cation considerably influence the electronegativity of the aromatic carbon atoms. It is reasonable to compare the changes in inductive constants σ_i and σ^* when passing from ferrocenyl to ferrocenylium ($\Delta\sigma_i = 0.35$; $\Delta\sigma^* = 2.18$) with the analogous changes, for example, in a series: amino group–ammonium group[2] ($\Delta\sigma_i = 0.75$, $N(CH_3)_2 \rightarrow \overset{+}{N}(CH_3)_3$); ($\Delta\sigma_i = 0.50$, $NH_2 \rightarrow \overset{+}{N}H_3$). With the possibility of charge delocalization increasing there are less carbon electronegativity changes in the ferrocenyl group with respect to those of nitrogen in the above substituents. This agrees with the quantum chemical calculations of Shustorovich and Dyatkina[14], where a part of the total positive charge in the ferricinium cation has been shown to concentrate on the rings. An approximate estimation indicated that with the release of an electron by the molecule the carbon electronegativity of the five-membered aromatic rings changes by 0.7 unit. This is a relatively large value, because the entire range of electronegativity change for the carbon-containing groups involves 0.9 electronegative units[11]

Carbon electronegativity in the five-membered aromatic rings of the ferricinium molecule far exceeds that of hydrogen, thus the bond is polarized as $C^{\delta+}-H^{\delta-}$. This should result in a serious hindering of electrophilic hydrogen substitution, and increase in C–H bond acidity and should facilitate the nucleophilic substitution reactions of X in the C–X bond. Unfortunately, the reactivity of the ferricinium cation has not yet been studied sufficiently. It was shown only that the ferricinium salts are entirely inactive in hydrogen electrophilic substitution reactions[15].

At the present time there is insufficient information on the metallic complexes of the IInd and IIIrd transition periods, to be able to assume the kind of changes that

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* When investigating the polarographic reduction of diferrocenylmercury Gubin and Denisovich[13] found the pK_a of ferrocene, as C–H acid, to be equal to 40.

occur in similar complexes when passing from the light to heavier metals. It is known that in the same series the heavier transition metal atoms have a higher electronegativity, according to the Pauling scale, than their lighter analogs[16] (for Fe, for example, $\chi=1.8$; for Ru, $\chi=2.2$.) Thus in similar complexes the heavier metal atoms should bear larger effective positive charges than those at the corresponding light elements. The behaviour for ruthenocene is probably analogous: the effective positive charge at the ruthenium atom in the C_5H_5–Ru-group influencing the carbon atoms of the coordinated C_5H_4-ring is somewhat higher than the analogous charge in ferrocene. This results in a noticeable increase of the carbon electronegativities; thus the inductive σ_i constant of the $C_5H_5RuC_5H_4$– group becomes positive.

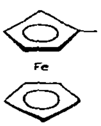
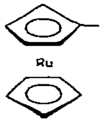
Therefore, it can be expected that in comparison with ferrocene, ruthenocene activity in hydrogen substitution electrophilic reactions should be lower and in nucleophilic substitution reactions the activity of C–X bonds will be somewhat higher. Data available on the relative reactivities of ferrocene and ruthenocene are in a good agreement with this conclusion[1].

THE HAMMETT CONSTANT OF RUTHENOCENYL AS SUBSTITUENT

For the determination of Hammett constants the dissociation constants of aromatic carboxylic acids measured in 50% aqueous ethanol are usually employed as a standard reaction series. In the present work the dissociation constant of ruthenocene carboxylic acid was determined under the same conditions. This acid was found to be 1.4 times weaker than benzoic and 1.7 times stronger than ferrocene carboxylic acid. The σ_p constants calculated are shown in Table 3. In the McDaniel and Brown scale of Hammett constants[17], σ_p of ruthenocenyl is closest to that of the $Si(CH_3)_3$-group ($\sigma_p= -0.07$).

TABLE 3

σ-VALUES OF METALLOCENYL GROUPS INVESTIGATED

Compound	σ_p	σ_c $(\sigma_p-\sigma_i)$	σ_p^+	σ_c^+ $(\sigma_p^+-\sigma_i)$
	−0.10	−0.05	−0.55[a] −0.68[b]	−0.50
	−0.05	−0.09	−0.44[a] −0.69[b]	−0.48

[a] Obtained from eqn. (4). [b] Obtained from ketone basicities.

The carboxylic group is a weak electron-deficient reaction center. Its influence, however, is essential for the +C-effect of the ruthenocenyl substituent to compensate for the slight −*I*-effect of this group; thus the total Hammett constant is negative. Table 3 compares the σ_c-values characterizing the conjugation of metallocenyl substituents with the carboxylic group for ruthenocenyl and ferrocenyl. These values are seen to be very close.

ELECTROPHILIC AROMATIC σ_p^+ CONSTANTS OF RUTHENOCENYL

Electrophilic aromatic constants, of ruthenocenyl were determined by two methods. First, a linear correlation between the CO-stretching frequencies in $X-C_6H_4-COCH_3$ and the σ^+ constants of the X substituents was used for the determination of the electrophilic aromatic σ_p^+ constant. Earlier[18] the stretching CO vibrations were found to depend considerably upon the effective positive charge at the carbon atom and to be mechanically separated from the vibrations of other bonds in the molecule, *i.e.*, they are highly characteristic. In a number of papers[18] dependences between the ν-stretching frequencies of the CO-groups in aromatic ketones and the σ-constants were investigated. It was found that the contribution of the +C conjugation effect of the substituents in the given reaction series is so great that it can be described satisfactorily only by the σ_p^+ constants. It was also established[19] that the CO-stretching frequencies are linearly related to the rates of S_N1 solvolysis of chlorides or acetates to the corresponding carbinols. The latter reactivities are known to be described by the aromatic σ^+ electrophilic constants. Thus, "a given reaction series" is suitable for the determination of new electrohpilic aromatic constants. The corresponding equation, calculated using the frequencies of ref. 20 as well as those measured in this work, is as follows:

$$\nu = 11.30\,\sigma^+ + 1690.9\ (\text{cm}^{-1}) \qquad (3)$$

$$(r=0.997,\quad n=11,\quad S=0.494)$$

The CO-stretching frequency of acetylruthenocene measured (1681 cm^{-1}) is higher than the value found for acetylferrocene (1677 cm^{-1}). The electrophilic aromatic constants calculated using these data are listed in Table 3. The σ_p^+ constant of ferrocenyl calculated from the CO vibrations in acetylferrocene coincides well with the value obtained for *para*-ferrocenylacetophenone from eqn. (3) (−0.59). Although σ_p^+ of ruthenocenyl is somewhat lower than the ferrocenyl constant, their σ_c^+ values, characterizing only the ability to enter the conjugation between these substituents and the neighbouring electron-deficient reaction center, are practically equivalent.

For the determination of the electrophilic constants of the metallocenyl groups the basicities (dissociation constants of conjugated BH^+ acids) of acetylruthenocene and acetylferrocene were also measured. The determination of the basicities of the aromatic ketones has been investigated in detail[2]. The pK_a-values of BH^+ substituted acetophenones were found to correlate with σ^+ constants of the corresponding substituents ($\rho = -2.17$). A comparatively small negative ρ testifies that the reaction center in this reaction is highly sensitive to the electronic effects of the substituents but is rather weakly affected upon passing from one to another substituent. This is perhaps associated with the specific structures of arylketone conjugated acids.

In the present work the basicities of acetylruthenocene and acetylferrocene were measured employing the Hammett indicator method in aqueous sulfuric acid (Stewart conditions). No special study of the conjugated acid structures was made. The latter are assumed to be analogous to the structure of acetylferrocene conjugated acids already established[22], based on a detailed IR spectral investigation of the protonated ketones. Ruthenocene and ferrocene acetyl derivatives are the strongest bases among the aromatic ketones studied. *para*-Hydroxyacetophenone, for example, is the strongest base investigated by Stewart[21] ($pK_a = -4.73$) and it is still, by two orders, weaker than the acyl derivatives of ruthenocene and ferrocene.

The electrophilic aromatic constants calculated from these data are given in Table 3. They are practically equivalent and markedly exceed the values estimated from the CO-stretching frequencies but do not exceed the deviations usually observed for electrophilic constants calculated from different reaction series[2].

DISCUSSION

The investigations conducted provided a series of σ-constants required for the quantitative estimation of the effect of ruthenocenyl as substituent. Table 3 shows, together with the experimentally obtained σ-constants, the σ_c and σ_c^+ values characterizing the ability of ruthenocenyl and ferrocenyl to enter into conjugation with neighbouring reaction centers, and the π-electron polarizability of the C_5H_5-rings in these compounds, calculated in this work. This Table shows that for the two metallocenyl substituents investigated all three sets of σ-values coincide, within the accuracy of the experiment. Hence, when going from ferrocene to ruthenocene there is no change in the ability of these substituents to enter into conjugation with the neighbouring reaction centers; on the other hand, the polarizability of the π-electron cloud of the five-membered aromatic rings also does not vary. In other words, coordination of the C_5H_5-ligand with the RuC_5H_5-group does not change the ligand π-electron density with respect to that in the five-membered aromatic ring of ferrocene. Differences observed in the reactivities of metallocenes should not be assigned to the π-electron density differences in the five-membered aromatic rings as has usually been done so far. However, the effective electro-negativity differences at the ring carbon atoms observed (change of effective charge on the σ-orbitals) satisfactorily explain the reactivity differences observed for the five-menbered aromatic rings in ferrocene and ruthenocene molecules.

EXPERIMENTAL

Compounds

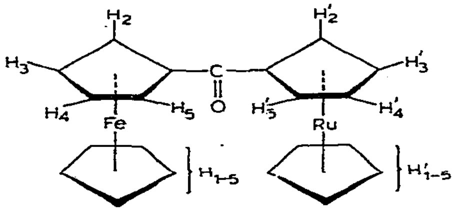
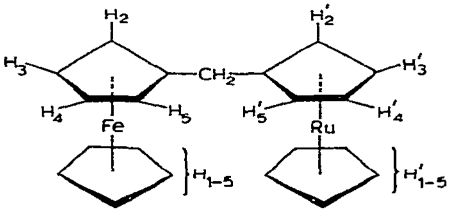
Acetylruthenocene and ruthenocenecarboxylic acid were prepared by procedures already described and had analyses and characteristics corresponding to published data[3].

Ferrocenylruthenocenylketone was obtained by reaction of ferrocenoyl chloride with ruthenocene in the presence of aluminium chloride[3]. The compound was identified by its m.p., IR, and PMR spectra (see Table 4).

Synthesis of ferrocenylruthenocenylmethane. A suspension of 0.12 g (0.0033 *M*) of $LiAlH_4$ in 40 ml of ether was added to a cold mixture of 0.42 g of $AlCl_3$ (0.0033 *M*) in 40 ml of absolute ether under an argon atmosphere. A solution of 1.48 g (0.0033 *M*) of ruthenocenylketone in 250 ml of ether was then added with vigorous stirring for 2 h at room temperature. The mixture was heated for 4 h on a water bath then cooled and decomposed with water. The ethereal layer was separated, washed with water and dried. After evaporation of the solvent, the solid was chromatographed on an alumina column and eluted with benzene. The reduction product, ferrocenylruthenocenylmethane, was recrystallized from n-hexane; 1.37 g (97.7%) of a yellow product was obtained, m.p. 139–140°. (Found: C, 58.42, 58.72; H, 4.48, 4.57. $C_{21}H_{20}FeRu$ calcd.: C, 58.75; H, 4.69%). The IR spectrum shows the bands characteristic of the C_5H_5-ring and a CH deformation frequency at 2921 cm^{-1}. The proton chemical shifts in the PMR spectra are shown in Table 4.

TABLE 4

PMR SPECTRA OF FERROCENYLRUTHENOCENYLKETONE AND FERROCENYLRUTHENOCENYLMETHANE ($CDCl_3$)

Compound	Type of protons	δ (ppm)	Type of signal
Ferrocenylruthenocenylketone 	H'_{1-5}	4.55	singlet
	$H'_{2,5}$	5.32	triplet
	$H'_{3,4}$	4.79[a]	triplet
	H_{1-5}	4.20	singlet
	$H_{2,5}$	4.90[a]	singlet
	$H_{3,4}$	4.49	triplet
Ferrocenylruthenocenylmethane 	H'_{1-5} $H'_{2,5}$ $H'_{3,4}$	4.45	—[b]
	H_{1-5}	4.07	singlet
	$H_{2,5}$ $H_{3,4}$	4.03	singlet
	H_{-CH_2-}	3.25	singlet

[a] Accurate signal assignment was performed using double resonance techniques. [b] The singlet of unsubstituted ring protons produces a wide peak coinciding with a signal from the substituted ring protons.

E_{f_0} *determination*

The formal redox potentials E_{f_0} were determined by potentiometric titration with 0.01 *N* dichromate solution in a mixture of acetic and perchloric acids at 25±0.1° using a procedure already described[23]. To increase the solubility of ferrocenylruthenocenylmethane, 10% of benzene was added instead of water. Preliminary experiments with ferrocene showed that such an addition does not change the shape of the titration curve.

Polarographic measurements

Polarographic measurements were conducted on the platinum electrode in CH_3CN at 25±0.1° under an argon atmosphere saturated with solvent vapour. A 0.1 *N* solution of $(C_2H_5)_4NClO_4$ was employed as a supporting electrolyte. All potentials are referred to a saturated aqueous calomel electrode (Table 5).

TABLE 5

POLAROGRAPHIC CHARACTERISTICS OF THE OXIDATION WAVES OF FERROCENYLRUTHENOCENYLMETHANE, FERROCENE AND RUTHENOCENE

(CH_3CN, 0.01 *N* $(C_2H_5)_4NClO_4$; *C*, $1 \cdot 10^{-3}$ *M*).

Compound	1st wave $E_{\frac{1}{2}}$ (V)	2nd wave $E_{\frac{1}{2}}$ (V)
Ferrocenyl-ruthenocenyl-methane	0.35	0.83
Ferrocene	0.39	—
Ruthenocene	—	0.81

Determination of pH of acid solutions

The measurements and calculation of pK_a-values were carried out as described in our previous work[4]. The pK_a-values obtained were 5.83 and 5.85.

Measurement of basicity of acetylruthenocene

The basicity of acetylruthenocene was determined by the Hammett indicator method using the procedure previously described[24]*. The pK_a(BH^+) and K_a(BH^+) of the acetyl derivatives of ferrocene and ruthenocene are shown in Table 6.

TABLE 6

THE pK_a(BH^+) AND K_a(BH^+) OF THE ACETYL DERIVATIVES OF FERROCENE AND RUTHENOCENE

Compound	$-$pK_a (BH^+)	K_a (BH^+)$\cdot 10^4$
$C_5H_5FeC_5H_4COCH_3$	2.65	22.40
$C_5H_5RuC_5H_4COCH_3$	2.70	20.0

Determination of the carbonyl vibration frequencies of metallocenyl ketones

Spectra were taken on a double-beam UR-20 spectrometer in CCl_4 solutions at concentrations of 0.002–0.004 *M* and a layer thickness of 1 mm. The instrument was calibrated by the absorption bands of water vapour at 1700–1600 cm^{-1}; the error was about 0.5 cm^{-1}. All the ketones investigated were analytically pure. CO-frequencies were measured for acetylferrocene and acetophenone.

The values obtained are in a good agreement with reported data[20] enabling the CO-frequencies obtained by Traylor and Ware to be used for the derivation of the correlational equation. Use was made only of 11 points giving good linear dependency of ν(CO) on σ^+.

Calculation of σ constants

These constants were calculated from the following equation:

$$\log \frac{K_X}{K_{C_6H_5}} = \frac{\rho}{\pi'} (\sigma_X - \sigma_{C_6H_5}) \qquad (4)$$

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* Measured by I. P. Shepilov.

obtained by subtracting eqn. (6) from eqn. (5). In all calculations π' was taken as 0.30 [2].

$$\log \frac{K_X}{K_{H-Y}} = \frac{\rho}{\pi'} \sigma_X \qquad X\text{–}Y \tag{5}$$

$$\log \frac{K_{C_6H_5}}{K_{H-Y}} = \frac{\rho}{\pi'} \sigma_{C_6H_5} \qquad C_6H_5\text{–}Y \tag{6}$$

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