for $C_{22}H_{24}F_{12}N_5O_4P_3$: C, 35.55; H, 3.25; N, 9.42; P, 12.50. Found: C, 35.75; H, 3.25; N, 9.49; P, 12.10.

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## Transmission of Electronic Effects in Metallocenes

BY S. A. BUTTER AND H. C. BEACHELL[1]

In a recent paper we have shown that nmr chemical shifts of phenyl and cyclopentadienyl protons in aryltitanocenes could be correlated with Hammett σ_p values.[2] The slope or ρ value in the correlation of average *ortho* and *meta* proton shifts *vs.* σ_p was equal to -0.75 unit. Our analysis of the data of other investigators for chemical shifts in *para*-substituted benzenes revealed similar ρ values of 0.70,[3] 0.75,[4] and 0.76.[5] Although the ρ values for the substituent effect of R on proton shielding values cannot be compared with the effect of R on ionization of *para*-substituted benzoic acids (where by definition $\rho = 1$) since they are of a different nature and origin, it is evident that the susceptibility of the shielding values to the substituent effect of R parallels the effect of R in the benzoic acid series.

It is of interest to compare the transmission of the substituent effect through the phenyl ring to the unsubstituted cyclopentadienyl ring in the above-mentioned titanocene system schematically represented as

I
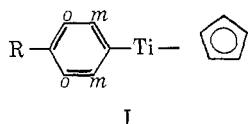
and the ρ values may be used for this purpose. The ρ ratio obtained from the slopes of the regression lines for (1) unsubstituted cyclopentadienyl proton shifts *vs.* σ_p and (2) average *ortho* and *meta* phenyl proton shifts *vs.* σ_p is 0.16/0.75 or 0.21. This value infers that 21% of the substituent effect of R is transmitted through the titanocene bonding system and relayed to the C_5H_5 protons.

Since recent studies have confirmed the presence of interannular electronic effects in the ferrocene system, it seemed desirable to look for indications of the transmission of substituent effects by the nmr technique.

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(2) H. C. Beachell and S. A. Batter, *Inorg. Chem.*, **4**, 1133 (1965).
(3) (a) J. Martin and B. P. Dailey, *J. Chem. Phys.*, **37**, 2594 (1962); (b) T. Schaefer and W. G. Schneider, *ibid.*, **32**, 1218 (1960).
(4) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 731 (1961).
(5) H. C. Beachell and D. W. Biestel, *Inorg. Chem.*, **3**, 1028 (1964).

Linear relationships have been reported between Hammett σ constants and pK_a values for substituted ferrocene carboxylic acids[6] and rate constants for esterification of these acids,[7] and in chronopotentiometric studies quarter-wave potentials have been correlated with Hammett σ values.[8] Further indication of the transmission of the electronic effect was noted in the spectra of heteroannular ferrocene carboxylic acids in which carbonyl stretch frequencies were shifted as expected from a consideration of the electronic effect of the substituent group.[9]

We have observed correlations of nmr proton shifts with σ_p constants in monosubstituted ferrocenes further confirming the transmission of electronic effects, and a quantitative estimate of the transmissivity of the substituent effect in the following system was noted.

II
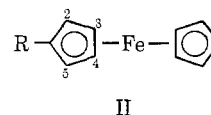
The data in Table I were taken from work by Nagai,

TABLE I

¹H CHEMICAL SHIFTS FOR MONOSUBSTITUTED FERROCENES[a]

R	δ	$\delta_{3,4}$	$\delta_{2,5}$	$\sigma_p{}^c$
CH_3	3.99	3.94	3.94	-0.17
C_2H_5	4.01	3.97	3.97	-0.15
i-C_3H_7	4.02	3.96	3.96	-0.15
t-C_4H_9	4.02	3.92	3.92	-0.197
H	4.06	4.06	4.06	0
CH_3CO	4.12	4.36	4.67	$+0.50$
$C_6H_5CO^b$	4.13	4.44	4.80	$+0.46$
$COOCH_3$	4.13	4.27	4.72	$+0.45$

[a] All values are in ppm downfield from internal tetramethylsilane. Chemical shifts determined by Nagai, *et al.* (ref 10), at 60 Mc in CCl_4. δ_{Cp} is the chemical shift of the unsubstituted C_5H_5 ring. [b] From Mark and Rausch (ref 11); corrected for change of solvent ($CDCl_3$) by noting shifts for acetylferrocene determined in both $CDCl_3$ and CCl_4. [c] *para*-Substituent constants based on ionization of benzoic acids. From D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

Hooz, and Benkeser[10] with the exception of benzoylferrocene which was examined by Mark and Rausch.[11] Since the latter compound was determined in deuteriochloroform while all others were in carbon tetrachloride, all shifts were converted to shielding values.[12] Figure 1 (line b) shows a plot of σ_p *vs.* the shielding value for the substituent R at the substituted ring protons 2,5 and

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(11) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963).
(12) For example, the chemical shift of ferrocene is 4.06 ppm while the substituted ring protons of methylferrocene are found at 3.94 ppm. The methyl group therefore shields the 2,5 and 3,4 protons by 0.12 ppm. Since the unsubstituted or Cp protons of methylferrocene are at 3.99 ppm, the methyl group shielding value for the unsubstituted ring protons is 0.07 ppm.
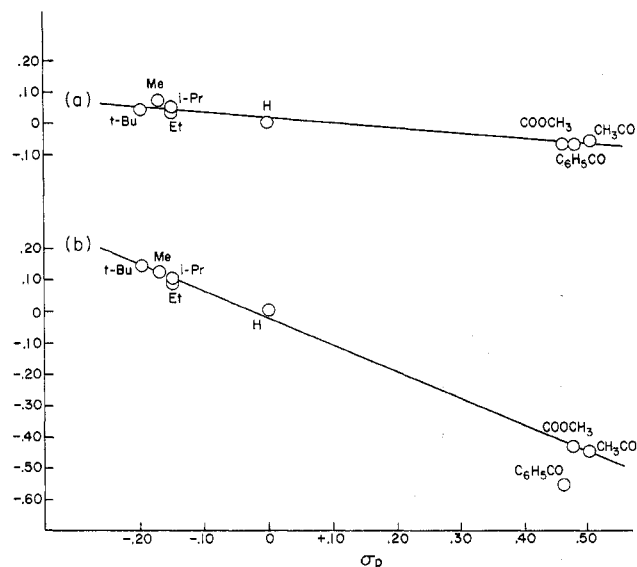
Figure 1.—Correlation of σ constants with proton shielding values of (a) unsubstituted cyclopentadienyl ring and (b) substituted ring (2,5 and 3,4 protons) for monosubstituted ferrocene.

Figure 2.—Correlation of σ constants with proton shielding values of (a) unsubstituted cyclopentadienyl ring and (b) substituted ring (2,5 and 3,4 protons) for monoarylferrocenes.

3,4 and the reasonably linear relationship with a slope equal to 0.90. For this correlation, a first-order approximation was used in that the shielding values for the three deshielding substituents—acetyl, benzoyl, and carbomethoxy—were assumed to be the average of the 2,5 and 3,4 proton shielding values. Thus the sensitivity of these proton shielding values is somewhat greater than the corresponding effect in the phenyl ring shielding values mentioned previously.[13] A linear correlation also shown in Figure 1 (line a) was found for σ_p and the shielding value for R on the unsubstituted ring. In this relationship the slope or ρ value is 0.20, which is approximately the same transmission value obtained in the phenyltitanocene system. The ρ ratio from the slopes of these two regression lines is 0.20/0.90 or 0.22 inferring a 22% transmission of the substituent effect through the ferrocene system.

The best correlations were made using σ_p constants as depicted in Figure 1 although the benzoyl had a more pronounced deshielding effect on the substituted cyclopentadienyl ring which is possibly due to a solvent effect since only this value was determined in $CDCl_3$. No correlation was noted when the cyclopentadienyl shielding values were plotted vs. Taft's σ^* (or the related σ_I) substituent constants. Since σ^* depends on the net polar effect of the substituent (assuming constant resonance effect), the failure of the correlation may be due to resonance contributions of the substituents to the shielding values. A plot of σ_m vs. shielding values gave similar curves to those plotted with σ_p but since the σ_m value for benzoyl was not available and the constants for methyl, ethyl, and iso-propyl are approximately equivalent, the σ_p plots are preferred.

It is interesting that the ρ ratios in the chemical shift correlation of the unsubstituted ferrocene or titanocene cyclopentadienyl ring and the correlation of shielding values of either the *ortho* and *meta* phenyl protons or the 2,5 and 3,4 substituted ring protons in both the titanocene and ferrocene derivatives, respectively, give approximately the same value for the transmission of substituent electronic effects through the metallocene metal atom.

We have observed another interesting correlation of this type from the nmr data for monoarylferrocenes in the recent book by Rosenblum.[14] When the average 2,5, and 3,4 proton shielding values in the system

$$R-\text{\Large\bigcirc}-\overset{2}{\underset{5}{\text{\Large\bigcirc}}}\overset{3}{\underset{4}{}}-Fe-\text{\Large\bigcirc}$$

III
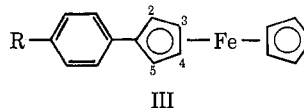
are plotted as before against σ_p, an excellent linear correlation is noted for R = OCH_3, H, $COCH_3$, and NO_2 with a slope $\rho = 0.205$. This is shown in Figure 2, and only Cl does not fall on this line. Since this ρ value is very similar to that for the unsubstituted cyclopentadienyl ring in II, a π (C_5H_5 + Fe) grouping seems as effective in transmitting the substituent effect of R as a σ-phenyl grouping (in III).

Figure 2 also contains the correlation line for σ_p vs. the shielding values for the unsubstituted C_5H_5 ring where $\rho = 0.029$. Since the phenyl ring damps out much of the substituent effect on the substituted C_5H_5 ring, less of this effect is transmitted through iron to the second C_5H_5 ring. The ρ ratio in this case is 0.029/0.205, inferring a transmission of 14% of the substituent electronic effect through the ferrocene system.

(13) Mark and Rausch (ref 11) also noted the similarity between deshielding effects of acyl substituents in acylferrocenes and the effect on *ortho* and *meta* protons in benzene derivatives.
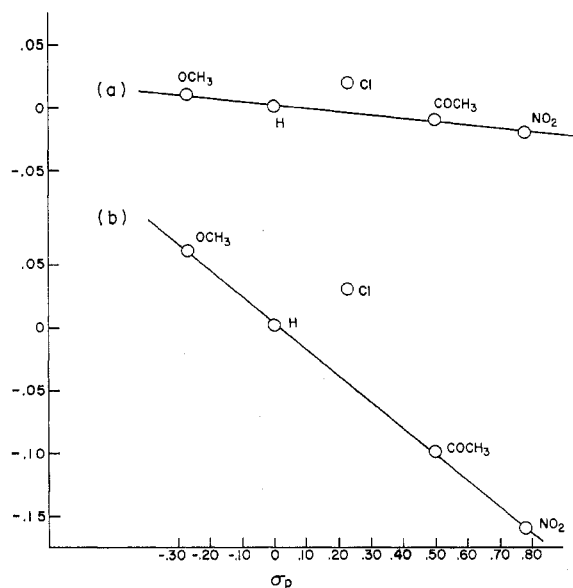
(14) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Interscience Publishers, Inc., New York, N. Y., 1965, p 215.

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Chloroaquo Complexes of Vanadium(III)

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During our earlier investigations of vanadium(III) chloride complexes,[2a] we reexamined the red alkali compounds of $VCl_5 \cdot H_2O^{2-}$, first described by Stähler[2b] and reported in a method for the preparation of K_2-$VCl_5 \cdot H_2O$ and for its dehydration to K_2VCl_5. In 1963 Crayton and Thompson[3] described a green compound $K_2VCl_5 \cdot 4H_2O$ which was dehydrated to pink K_2VCl_5 at 100–125°. These results were not duplicated by Horner and Tyree,[4] who found that from hydrochloric acid solutions only $KVCl_4 \cdot 6H_2O$ could be obtained. This compound was dehydrated to $KVCl_4 \cdot 1.5H_2O$. Because this latter work partially contradicts our results, a reinvestigation was undertaken. Additionally, the systems $CsCl–VCl_3–H_2O$ and $RbCl–VCl_3–H_2O$ have been studied and the magnetic susceptibilities and the densities of the compounds measured.

Experimental Section

Preparation of Compounds. (A) Isolation of Cs Compounds. —When a solution containing 5 g of $VCl_3 \cdot 6H_2O$ and 3.5 g of CsCl in 40 ml of 6 *M* HCl was saturated with gaseous HCl at temperatures below 60°, a green precipitate was obtained. (In our experiments the temperature was maintained at 0°.) The green precipitate was separated by suction, washed with ether, and dried *in vacuo*. *Anal.* Calcd for $Cs_2VCl_5 \cdot 4H_2O$: V, 9.00; Cl, 31.32. Found: V, 9.32; Cl, 31.38.

In the presence of a $CaCl_2$ desiccant and under reduced pressure the green precipitate was dehydrated to the red $Cs_2VCl_5 \cdot H_2O$ at a temperature of 80–90°. (ΔH_2O: Calcd, 9.54%; Found, 9.80%.) Dehydration was also observed when the substance was kept for some time in ethanol. *Anal.* Calcd for $Cs_2VCl_5 \cdot H_2O$: V, 9.95; Cl, 34.62. Found: V, 10.02; Cl, 33.66.

(B) Isolation of Rb Compounds.—After introducing gaseous HCl into a solution of 5 g of $VCl_3 \cdot 6H_2O$ and 3 g of RbCl in 40 ml of 6 *M* HCl below 0°, green $RbVCl_4 \cdot 6H_2O$ precipitated. This precipitate was washed with ether and dried in a flow of nitrogen gas. *Anal.* Calcd for $RbVCl_4 \cdot 6H_2O$: V, 13.19; Cl, 36.71; H_2O, 27.90. Found: V, 13.23; Cl, 36.90; H_2O, 27.50.

At temperatures above 60° dehydration occurred in a vacuum desiccator to yield a red mixture of $Rb_2VCl_5 \cdot H_2O$ and hydrates of vanadium(III) chloride. Pure $Rb_2VCl_5 \cdot H_2O$ was obtained from the above solution by the method of Stähler.[2] The solution, in the presence of gaseous HCl, was heated on a water bath to reduce the volume of the liquid phase. *Anal.* Calcd for Rb_2-$VCl_5 \cdot H_2O$: V, 12.21; Cl, 42.49. Found: V, 12.37; Cl, 42.90.

(C) Isolation of K Compounds.—Crayton and Thompson[3] reported the formation of a green compound $K_2VCl_5 \cdot 4H_2O$ by introducing gaseous HCl into a solution 12 *M* in HCl, 0.5 *M* in VCl_3, and 1.0 *M* in KCl; the temperature of the solution was maintained at −30°. The experiments of Horner and Tyree[4] yielded a green mixture of $KVCl_4 \cdot 6H_2O$ and KCl, by the above

procedure. The crystals that formed were removed by filtration and dried first in a flow of nitrogen gas and then by being pumped on with a vacuum pump for 1–2 hr at room temperature. In our experiments KCl was precipitated from the above solution and also from solutions containing a VCl_3:KCl ratio of 1:1 by introduction of HCl gas. The green, crystalline precipitate, isolated at −30°, deliquesced in nitrogen to yield HCl. This strongly suggests that the mixture included hydrates of HCl which were stable below −15°.[5] After drying under reduced pressure the product was found to contain 7.2% V, 45.3% Cl, 13.5% H_2O, and 34.0% K, corresponding formally to a mixture of about 65% KCl and 35% $VCl_3 \cdot 6H_2O$. Since the X-ray pattern exhibited lines other than those for KCl and $VCl_3 \cdot 6H_2O$, at least one new compound must be present. By analogy to the results of Horner and Tyree[4] and to the rubidium system this new compound should be $KVCl_4 \cdot 6H_2O$.

Details for the preparation of the red $K_2VCl_5 \cdot H_2O$ have been given earlier.[2a] An excess of $VCl_3 \cdot 6H_2O$ was heated with KCl in a stream of HCl gas; the temperature was 100–120°. After treatment the excess of the vanadium(III) chloride hydrate was washed with absolute ethanol. *Anal.* Calcd for $K_2VCl_5 \cdot H_2O$: V, 15.70; Cl, 54.64. Found: V, 15.90; Cl, 54.62.

The red monohydrate can be dehydrated in a stream of HCl gas at 250–300° to the red-brown K_2VCl_5.

X-Ray Powder Patterns and Densities.—Powder patterns were determined by using a Berthold goniometer and Cu Kα radiation (Figure 1). There is considerable evidence that the compounds $Rb_2VCl_5 \cdot H_2O$ and $K_2VCl_5 \cdot H_2O$ are isomorphous with the compound $K_2FeCl_5 \cdot H_2O$ described by Bellanca.[6] This compound crystallized in the orthorhombic $Cl_2[Rh(NH_3)_5Cl]$ type. $Cs_2VCl_5 \cdot H_2O$ should have a different structure. This is supported by the pycnometrical determinations in petroleum (Table I). By subtracting the increments I of the alkali ions M^+ ($2I_{K^+} = 32$ cm^3, $2I_{Rb^+} = 40$ cm^3, $2I_{Cs^+} = 52$ cm^3, as reported by Biltz[7]) from the molar volumes of the compounds $M_2VCl_5 \cdot H_2O$, the increment for the $VCl_5 \cdot H_2O^{2-}$ ion is obtained. The values for this ion are 108 and 107 cm^3 for the K and Rb compounds, respectively, and 120 cm^3 for the Cs compound. This indicates that the cesium compound is less tightly packed.

Magnetic Measurements.—Magnetic measurements were carried out with a Gouy balance. The magnetic field was standardized with $Hg(Co(CNS)_4)$,[8] and the temperatures were controlled by means of the dependence of the susceptibilities of nickel ammonia sulfate.[9] The χ_{mol} values were calculated as the average of measurements made on two samples. The values for μ_{eff} were obtained from the expression $\mu_{eff} = 2.84 (\chi_{mol}^{cor} T)^{1/2}$. The values of θ were determined graphically from a plot of $1/\chi_{mol}$ *vs.* T. The error for μ_{eff} is ±0.03 BM and for θ is ±5°. The values of the oxidation state 3.00 for vanadium were extrapolated assuming that a change in the oxidation state of 0.01 would produce a change in μ_{eff} of 0.01 BM. Table II shows that at room temperature the values for μ_{eff} range from 2.80 to 2.90 BM which correspond to the spin-only value of 2.83 BM for two unpaired electrons. For those compounds with much water θ is zero within experimental error. For compounds with little water θ values range from −10 to −30°.

Analyses.—Vanadium was determined by titration with potassium permanganate. In determinations of the oxidation state of vanadium, the halides were removed by precipitation with a solution of silver sulfate (error ±0.03). The halides were determined by argentometric titration. Water was determined by the method commonly used for carbon–hydrogen analyses of organic compounds.

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