Substituent Effects on ^1H and ^{13}C NMR Chemical Shifts in Titanocene Benzoates

Yi Dang,[a] Herman J. Geise,[a,*] Roger Dommisse,[b] Jan Gelan[c] and Johan Nouwen[c]
[a] *University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium*
[b] *University of Antwerp (RUCA), Department of Organic Chemistry, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium*
[c] *Limburgs Universitair Centrum (LUC), Department of Chemistry, Universitaire Campus, B-3610 Diepenbeek, Belgium*

^1H and ^{13}C NMR chemical shifts of *meta* and *para*-substituted benzoato titanocene complexes of the type $(C_5H_5)_2Ti(O_2CC_6H_4X)_2$ have been measured. Data analysis of the phenyl carbons were performed using the dual substituent parameter approach (*para*-carbons) or triple parameter approach (*ipso*-, *ortho*-, and *meta*-carbons), showing good to excellent correlations. The signs and magnitudes of the ρ-values agreed very well with literature results, proving the accuracy of the data set and the consistency of the procedure, as well as pointing to common mechanistic origins for *ortho, meta* and *para* substituent chemical shifts (SCS) in substituted benzoato titanocenes and monosubstituted benzenes. A dual parameter approach was then used to analyse the carbons of the carbonyl group and the cyclopentadienyl rings. A reverse SCS effect was observed for the carboxylato group and an extremely long-range interaction between substituent X and the cyclopentadienyl carbon atoms was observed. The latter ρ-values follow normal field and mesomeric influences. Similar results are obtained from proton shifts. The bulky group $(C_5H_5)_2(XC_6H_4CO_2)TiCO_2$– was found to be a very weak inductive acceptor ($\sigma_F = 0.035$) and a moderate resonance acceptor ($\sigma^0{}_R = 0.142$).

During the spectral characterization of bis(substituted benzoato) complexes of bis(η-cyclopentadienyl)titanium(IV), $(C_5H_5)_2Ti(O_2CC_6H_4X)_2$, we noted[1] the dependence of ^{13}C chemical shifts upon the *non-ortho* substituent X, which prompted us to investigate this topic further. Information about electronic properties of compounds and mutual interactions of substituents may be obtained by analysing the correlation between NMR chemical shifts and substituent parameters. Over the years, different procedures have been attempted, including the Swain–Lupton approach[2] and the Hammett analysis.[3] In the latter case either a single substituent parameter (SSP) or a dual substituent parameter (DSP) procedure can be followed.[4,5] The necessary and sufficient number of parameters has sometimes been questioned.[6,7] However, there is a growing body of evidence[8–11] that the most effective procedure is the DSP approach, employing Taft's parameters σ_F and $\sigma^0{}_R$ [5,12] in conjunction with Reynolds' non-electronic, short-range factors.[13] Nevertheless, interpretative problems remain,[14,15] particularly in attempts to interpret quantitatively substituent effects on atoms close to the substituent in terms of basic mechanisms (field, inductive, resonance and polarisability).[16,17]

In this work, we report the analysis of substituent effects on the ^1H and ^{13}C chemical shifts for a series of bis(4-substituted benzoato)titanocene derivatives (*para*-series) and for a series of the 3-substituted analogues (*meta*-series). The object is to apply the Taft–Reynolds procedure as a tool in the study of the electronic properties and mutual interactions of the substituents in these complexes. The complexes are well suited for this type of research for two reasons. First, the phenyl rings may serve as probes to check the accuracy of the data as well as the internal consistency of the data set and the machinery of the procedure (SSP, DSP approach, *etc.*). Second, the carboxylato side-chains and the cyclopentadienyl rings allow the study of propagation, transmission and mutual interaction of electronic substituent effects.

Furthermore, we will compare the results of the benzoato derivatives with the results of similar correlations performed by us on the phenyl derivatives $Cp_2Ti(C_6H_4X)_2$, and on the phenoxy derivatives $Cp_2Ti(OC_6H_4X)_2$, of which the NMR spectra have been reported previously.[18–20]

Experimental

The ^{13}C NMR spectra were obtained on a JEOL NMR-FX 100 spectrometer at a frequency of 25.1 MHz with a pulse width of 6 μs (35°), using a spectral width of 6.25 kHz and 8K data points to give a maximum attainable resolution of 0.03 ppm. The chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). The spectra were recorded at low concentration 1% w/v in $CDCl_3$ in 5 mm tubes.

The ^1H NMR spectra were recorded on a Varian XL-200 spectrometer at a frequency of 200 MHz, a pulse width of 6 μs (90°), a spectral window of 2500 kHz and 64K data points giving a resolution of 0.006 ppm. The shifts are reported in ppm downfield from the TMS reference signal. They represent first-order values. The samples were measured as described for the ^{13}C NMR spectra.

The ^{19}F NMR spectra were measured on a JEOL PS-100 spectrometer at a frequency of 94 MHz in the continuous wave mode. Solutions were 1% w/v in $CDCl_3$ contained in 5 mm sample tubes with fluorobenzene as an internal standard.

For all nuclei, the spectra were obtained at constant temperature (22 °C). To investigate any concentration dependency the ^1H NMR spectra of $Cp_2Ti(O_2CC_6H_5)_2$ were measured at five concentrations ranging from 300–25 mg cm^{-3} (715–60 mmol cm^{-3}). None of the chemical shifts showed any variation with concentration.

Results and Discussion

The chemical shifts for the individual carbon and proton nuclei are given in Tables 1 and 2, respectively. The assignments are based on known[21] substituent chemical shifts (SCS) and the assigned spectrum of $Cp_2Ti(O_2CC_6H_5)_2$.[22] A few alternative assignments remain; they are specified.

The accuracy of the tabulated shifts is estimated at 0.1 ppm for ^{13}C and 0.03 ppm for ^1H shifts. One notes (Table 1) that a reversed substituent chemical shift effect is operative at the CO_2 group; *i.e.* the more electron-withdrawing the substituent becomes, the more shielded is the carboxylato carbon. The data show a normal SCS effect for the other carbons. It can also be seen that the cyclopentadienyl carbon shifts are comparable in the *para*- and *meta*-series. The shift range is rather small (<1 ppm), whereas the corresponding carboxylato and phenyl ring carbon shift ranges are between 2 and 70 ppm. The behaviour of the proton shifts (Table 2) is similar. Cyclopentadienyl protons show very small SCS variations (0.086 ppm for the *para*-series and 0.062 ppm for the *meta*-series), whereas much larger variations are noted for the phenyl protons (0.30–1.64 ppm).

As stated earlier, we decided to approach the complex body of data by analysing first the ^{13}C and ^1H shifts in the phenyl rings. This procedure allows us to see whether the mathematical machinery (SSP, DSP approach, *etc.*) can be applied to this data set, as well as to check whether the data are sufficiently accurate, before we set out to analyse the shifts of the other atoms.

The set of complexes was divided into a *para*- and a *meta*-series, each containing nine complexes carrying substituents ranging from strongly electron-donating to strongly electron-withdrawing. We employed six different, well-established correlation approaches (see Table 3 for the definition) for the analysis of the shifts of C(1) in the *para*-series, and of C(6) and H(6) in the *meta*-series. These atoms were chosen because they are in the *para*-position to the substituent X and good correlations can be expected.[23] Indicators for the goodness-of-fit of the correlations are presented in Table 3, and show that the correlations are good. Thus high values for the correlation coefficient *r* and for the *F*-test of the variance are obtained, well above the critical values ($r \geqslant 0.93$ and $F \geqslant 20$) for two and six degrees of freedom at 5% significance. Furthermore, using eqns. (5) and (6) the residual standard deviation (RSD) for the data matrix is approximately equal to the estimated experimental uncertainty. So we conclude that the data of Tables 1 and 2 are sufficiently accurate for a reliable further analysis. One can also note that the goodness-of-fit is similar for the two series, suggesting that the bulky group $(C_5H_5)_2\,(XC_6H_4CO_2)TiCO_2$– does not significantly hamper the chemical shift correlation. Finally, we observe that eqn. (5) with σ_F and $\sigma^0{}_R$ performs best, but that the difference is small compared to eqn. (6) in combination with Reynolds' set of σ_F, $\sigma^0{}_R$ values.[13] Therefore, we feel justified in using Reynolds' constants in the further analysis. We wish to do so, because later in this work we want to incorporate Reynolds' non-electronic short-range constants, which together with his σ_F, $\sigma^0{}_R$ set form a consistent, orthogonal set.

$$\delta = \delta_0 - \rho\sigma_p \qquad \sigma_p \text{ from ref. 24} \tag{1}$$

$$\delta = \delta_0 - \rho\sigma_p{}^+ \qquad \sigma_p{}^+ \text{ from ref. 24} \tag{2}$$

$$\delta = \delta_0 - fF - rR \qquad F, R \text{ from ref. 24} \tag{3}$$

$$\delta = \delta_0 - \rho_I\sigma_I - rR \qquad \sigma_I, R \text{ from ref. 24} \tag{4}$$

$$\delta = \delta_0 - \rho_F\sigma_F - \rho_R\sigma_R \qquad \sigma_F, \sigma_R \text{ from ref. 24} \tag{5}$$

$$\delta = \delta_0 - \rho_F\sigma_F - \rho_R\sigma_R \qquad \sigma_F, \sigma_R \text{ from ref. 13} \tag{6}$$

Correlations for Phenyl Ring Carbons and Protons.—Using eqn. (6), we sought similar correlations for the non-*para*-atoms (carbons and protons) of the phenyl ring, *i.e.*, the *ortho*, *meta* and *ipso* atoms with respect to the substituent. The results given in Tables 4 and 5, however, indicate a rather poor set of correlations. Exceptions are encountered only for C(2) (see Table 4) and H(3)/H(5) (see Table 5) in the *para*-series.

These poor correlations are not unexpected. Factor analysis[13,25] and other statistical investigations[16,17] have shown that (at least) three factors ('Triple Substituent Parameter' approach) are required to correlate the shifts of non-*para* carbon atoms in a phenyl ring. Reynolds and co-workers[13] have recently derived a set of short-range factors which can be used together with σ_F, $\sigma^0{}_R$ parameters in a TSP approach, eqn. (7). In

$$\delta = \delta_0 + \rho_F\sigma_F + \rho_R\sigma^0{}_R + \rho_X\sigma_X \tag{7}$$

eqn. (7), σ_X represents the appropriate short-range factor and ρ_X is the weighting coefficient. There are substituent factors σ_o, σ_m and σ_i to be applied to carbons in the *ortho*, *meta* and *ipso* positions to the substituent, respectively. Using their extensive styrene chemical shift data, Reynolds *et al.* have determined values of these short-range substituent constants. They have shown that it is reasonable to assume that these parameters represent an orthogonal non-electronic component of the substituent effect and that σ_F and $\sigma^0{}_R$ still give reasonable field and resonance contributions after the non-electronic effects are factored out.[13] However, the physical meaning of the 'anonymous factors' σ_o, σ_m and σ_i is not yet completely clear. For an alternative approach using electronegativity (σ_χ) and polarisability parameters (σ_α) as additional explanatory variables we refer to Cook *et al.*[16,17]

To check this point, and in the hope of improving our set of correlations, particularly for the carbons, we used the parameters given in ref. 13 in a TSP analysis. The results are given in Table 6, and indicate a remarkable improvement for some carbons, *e.g.*, C(3) in both series and C(2) in the *meta*-series, but only slight or no improvement for the other atoms in the *meta* position to the substituent, *i.e.* C(2) in the *para*-series and C(1) and C(5) in the *meta*-series. This lack of improvement has also been noted in other compounds.[8,13] Although its cause has not yet been completely elucidated, the effect seems to be associated with the presence of strongly electron-withdrawing groups. To check whether such a *meta*-effect also exists in the present titanocene benzoates, we excluded those compounds which contain the strongly electron-withdrawing substituents CN and NO_2 and repeated the TSP analysis for those atoms that had shown little or no improvement earlier.

Table 6 also shows this procedure to lead to a significant improvement. The indicators *r* and *F* increase to high values and the RSDs decrease to values close to the experimental uncertainty. Only for C(4) in the *para*- and *meta*-series does the TSP correlation remain fair, *i.e.*, the goodness-of-fit indicators *r* and *F* are well above the critical level, but the RSD is still high. A large and well-balanced set of data would be required for further investigation. Our data set is too small to decide whether this only fair result is caused by outliers (X = OMe, F in the *para*-series and X = CN, NO_2 in the *meta*-series) or whether it is the reflection of some additional effect. Below we will present an argument that such an effect, if any, could not be connected with the presence of the specific $(C_5H_5)_2(XC_6H_4CO_2)TiCO_2$ group.

We also used the TSP approach on H(2)/H(6), H(3)/H(5) in the *para*-series and on H(2), H(4), H(5) in the *meta*-series. The correlation showed no improvement, and should not, because the non-electronic σ_X parameters are derived for carbon atoms at a particular distance from the substituent, and must not apply to hydrogen atoms at a different distance. Our data set is too small to perform a reliable factor analysis and to obtain a significant set of σ_X parameters for hydrogen atoms in *ortho* and *meta*-positions to the substituent.

Although the relatively large esds on the ρ-values call for caution, it seems justified to say that all hydrogen shifts have positive ρ_F and ρ_R values, following the normal SCS variation,

Table 1. ^{13}C Chemical shifts (in ppm,[a] relative to TMS) of $(\eta\text{-}C_5H_5)_2Ti(O_2CC_6H_4X)_2$ in $CDCl_3$ solution.

X	C_5H_5	CO	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
(i) *para*-series								
H	118.49	172.04	133.78	129.88	128.18	131.71		
OMe	118.49	172.16	126.41	131.95	113.49	162.66		
Me	118.43	172.22	131.16	130.06	128.97	142.19		
Et	118.49	172.88	131.34	130.19	127.75	148.46		
F	118.67	171.00	130.07	132.19	115.14	165.12		
Cl	118.73	171.06	132.26	131.22	128.48	138.17		
Br	118.73	171.12	132.68	131.47	131.47	126.77		
CN	119.10	169.97	137.62	130.25	132.20	115.38		
NO_2	119.22	168.44	141.46	130.73	123.55	141.46		
(ii) *meta*-series								
H	118.49	172.04	133.78	129.88	128.18	131.71	128.18	129.88
OMe	118.61	171.86	135.18	114.47	159.67	118.19	129.15	122.39
Me	118.49	172.16	133.72	130.49	137.80	132.50	128.12	127.08
F	118.86	170.88	136.12	116.69	163.28	118.37	129.82	125.56
Cl	118.79	170.64	135.55	129.94	134.39	131.77	129.64	127.93
Br	118.73	170.33	135.67	132.81	122.39	134.63	129.94	128.36
I	118.73	170.21	135.61	138.77	94.00	140.54	130.12	128.96
CN	119.10	169.66	134.94	133.54	112.64	129.46	128.30	133.78
NO_2	119.22	169.48	135.61	124.76	148.40	126.41	129.70	135.61

[a] To avoid rounding-off errors one extra decimal is given.

Table 2. ^{1}H Chemical shifts (in ppm,[a] relative to TMS) of $(\eta\text{-}C_5H_5)_2Ti(O_2CC_6H_4X)_2$ in $CDCl_3$ solution.

X	C_5H_5	H(2)	H(3)	H(4)	H(5)	H(6)
(i) *para*-series						
H	6.621	8.030	7.442			
NH_2	6.574	7.834	6.649			
OMe	6.599	7.969	6.912			
Me	6.601	7.921	7.232			
F	6.611	7.993	7.083			
Cl	6.612	7.918	7.394			
Br	6.607	7.842	7.558			
CN	6.636	8.067	7.729			
NO_2	6.660	8.138	8.292			
(ii) *meta*-series						
H	6.621	8.030	7.442	7.489	7.442	8.030
OMe	6.617	7.561		7.059	7.317	7.610
Me	6.613	7.843[b]		7.331[b]	7.318[b]	7.836[b]
F	6.620	7.801		7.220	7.405	7.684
Cl	6.615	7.972		7.488	7.385	7.896
Br	6.614	8.129		7.636	7.339	7.937
I	6.608	8.334		7.835	7.225	7.961
CN	6.639	8.254[b]		7.801	7.631	8.228[b]
NO_2	6.670	8.803		8.365	7.707	8.405

[a] See Table 1. [b] Assignments could be reversed.

i.e., an upfield shift with increasing electron-withdrawing property of the substituent. Furthermore the sequences ρ_R (*meta*) $<$ ρ_R (*ortho*) $\approx$ ρ_R (*para*) and ρ_F (*ortho*) $>$ ρ_F (*meta*) $\approx$ ρ_F (*para*) are in accord with well-established ideas about relative mesomeric effects and with notions about the decrease of polar effects with distance.

Reversed SCS effects, indicated by negative ρ-values are noted for carbon shifts in ρ_F (*ortho*), ρ_R (*meta*) and ρ_R (*ipso*). The other carbon ρ-values indicate the usual SCS variations. The *para*-carbon ρ-values are in the ranges 5 ± 1 (ρ_F) and 20 ± 1 (ρ_R). Similar values have been reported by Taft[12,14] Reynolds[13] and Brownlee[15] in organic compounds.

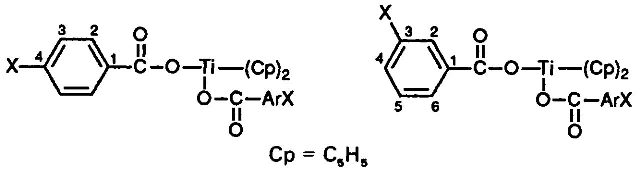
We also note that in the TSP analysis ρ_i and ρ_o are close to unity, while ρ_m deviates from unity, even if we exclude the compounds containing the electron-withdrawing substituents CN and NO_2. A comparison of our ρ-values in the *para*-series with those obtained in 4-substituted styrenes[13] shows consistency for the ρ_m and ρ_o values. Finally it is very gratifying to see that our ρ_F and ρ_R values for the *ortho*-, *meta*- and *para*-carbons with respect to X are in agreement in sign as well as magnitude with the values obtained by Cook.[17]

Although not all questions could be settled, our set of phenyl data (^{13}C and ^{1}H) is in excellent agreement with the state-of-the-art results available in recent literature. Thus, we feel confident in concluding that the explanations in terms of physical effects can be applied here as well.[16,17] For example, the mechanisms (electronegativity, field, polarisability and resonance effects) influencing *ortho*, *meta* and *para* phenyl-carbon shifts are probably equal in the substituted benzoato titanocenes and monosubstituted benzenes. In other words there does not seem to be a significant interference by the presence of the complex group $(C_5H_5)_2(XC_6H_4CO_2)TiO_2C$.

Correlations for Side-chain Carbons and Protons.—We now move our attention to the side-chains: the carboxylato carbons and the cyclopentadienyl carbons and protons. The following conclusions of Cook *et al.*[16,17] will be used here: for atoms at a distance larger than *meta* to X a DSP approach suffices and σ_F contains only significant contributions of the field effect (*F*), where the dipole of the substituent (X) induces electronic perturbations in the probe fragment by through-space interactions. The correlations for the side chain atoms using the DSP approach are listed in Tables 4 and 5. The significance of the correlation is easily judged by the goodness-of-fit parameters *r*, *F* ratio and RSD. We observe an excellent correlation for the cyclopentadienyl carbon shifts in both series and a good correlation for the carboxylato carbons, also in both series. For the attempted correlation of the cyclopentadienyl protons in the *meta*-series we cannot reject the null-hypothesis that no correlation exists and that the observed shift variation is due to the random noise. This is hardly surprising since the total ppm range in this series is only twice the experimental esd. For the cyclopentadienyl protons in the *para*-series (range three times the experimental esd), however, the correlation is acceptable, namely, the null-hypothesis can be rejected.

Nevertheless, additional evidence would be most welcome. We believe that this can be found for the *para*-series by examining the sensitivity of the cyclopentadienyl proton shifts to substitution in the phenyl ring as a function of the size of the intermediate group. To this end, we compare the carboxylato derivatives $Cp_2Ti(O_2CC_6H_4X)_2$ (series I) with the phenoxy derivatives $Cp_2Ti(OC_6H_4X)_2$ (series II) and the phenyl derivatives $Cp_2Ti(C_6H_4X)_2$ (series III). The size of the intermediate group decreases in each series: –Ti–OC(O)– > –Ti–O– > –Ti–. If the polar effect predominates, the susceptibility of the cyclopentadienyl protons will increase in the order I < II < III, and the chemical shift range observed in our *para*-series (0.086 ppm) should be smaller than the ranges observed in the series II[20] and III.[18] The carboxylate series contains almost the same set of substituents as the phenyl series. Hence, a direct comparison is allowed: 0.086 (series I) < 0.11 (series III) ppm. Unfortunately, only a very limited set of substituents is available for the phenoxy series [$Cp_2Ti(OC_6H_4X)_2$ with X = H, OMe, Me, Cl, Br]. Nevertheless, if we compare the ranges taken over the same set of substituents we find 0.02 (series I) < 0.05 (series II) < 0.09 (series III) ppm. From the combined evidence we conclude that the chemical shift variation observed for the cyclopentadienyl ring protons in the *para*-series is caused by the substituent variation in the phenyl ring. These and other correlations prove that very long-range substituent effects exist in the titanocene benzoates.

Table 3. Selection of results of the correlation analysis for $(\eta\text{-}C_5H_5)_2Ti(O_2CC_6H_4X)_2$ derivatives with different approaches.



Eqn.	RSD	*r*	*F*
para-series	C(1)		
(1)	1.949	0.9085	33
(2)	1.081	0.9728	123
(3)	1.189	0.9718	51
(4)	1.306	0.9658	42
(5)	0.574	0.9935	228
(6)	0.628	0.9922	190
meta-series	C(6)		
(1)	1.799	0.9524	33
(2)	0.982	0.9889	154
(3)	0.705	0.9883	66
(4)	0.784	0.9855	101
(5)	0.089	0.9998	8061
(6)	0.119	0.9997	4518
meta-series	H(6)		
(1)	0.1222	0.9421	26
(2)	0.0760	0.9788	78
(3)	0.0709	0.9689	46
(4)	0.0767	0.9635	39
(5)	0.0407	0.9899	146
(6)	0.0439	0.9882	125

With the correlations firmly established we will now try to interpret the observed ρ-values.

For the carboxylato groups in both series we observe negative values for ρ_F and ρ_R, indicative of the reverse SCS effect, *i.e.*, electron-withdrawing substituents cause an upfield shift instead of the usual downfield shift. It is of great interest to note that the ρ_F value, which describes the field-inductive contribution, is equal for the *para*- and *meta*-series, while the ρ_R value, which describes the mesomeric contribution, is twice as large in the *para*-series compared with the *meta*-series. It is even larger than in organic acid derivatives.[26] Indeed, in the *para*-series the substituent is situated such that a larger mesomeric component is to be expected. In the *para*-series the inductive and mesomeric components are equal within the error limits [ρ_R/ρ_F = 0.81(0.23)], whereas in the *meta*-series the inductive component seems to dominate [ρ_R/ρ_F = 0.41(0.12)]. This supports the view of Brownlee *et al.* who consider the reverse SCS effect to be the best evidence to date in support of the hypothesis that π-polarisation is the major contributor to the inductive component, as illustrated by the structure in Fig. 1.[26]

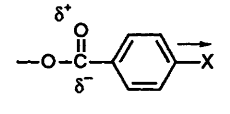


Fig. 1. The concept of localised polarisation.

Table 4. Correlation analysis [DSP approach, eqn. (6) together with set of σ_F/σ^0_R from ref. 13] on carbon chemical shifts for $(\eta\text{-}C_5H_5)_2Ti(O_2CC_6H_4X)_2$ derivatives.

Carbon	δ^a	δ_0	ρ_F	ρ_R	ρ_R/ρ_F	*r*	*F*	RSD
(i) *para*-series								
C(1)	133.78	133.66(0.42)	5.73(0.89)	21.3(1.3)	3.72(0.62)	0.9922	190	0.628
C(2)/C(6)	129.88	129.67(0.19)	2.16(0.41)	−4.32(0.59)	−2.00(0.61)	0.9577	33	0.285
C(3)/C(5)	128.18	130.44(3.85)	−5.58(8.29)	26.7(12.1)	−4.78(7.42)	0.6701	2.4	5.821
C(4)	131.71	134.97(8.73)	−3.5(18.8)	−62.8(27.5)	18.1(97.5)	0.7015	2.9	13.21
CO	172.04	172.01(0.26)	−3.83(0.55)	−3.09(0.80)	0.81(0.23)	0.9649	41	0.387
C_5H_5	118.49	118.52(0.03)	0.86(0.07)	0.72(0.10)	0.83(0.13)	0.9890	134	0.048
(ii) *meta*-series								
C(1)	133.78	133.54(0.26)	3.50(0.52)	−2.50(0.69)	−0.71(0.32)	0.9424	24	0.328
C(2)	129.88	132.69(5.92)	−4.2(12.1)	26.5(16.0)	−6.30(18.5)	0.5623	1.4	7.58
C(3)	128.18	125.42(18.06)	3.2(37.0)	−56.2(48.9)	−17.6(204)	0.4339	0.7	23.15
C(4)	131.71	134.33(5.71)	−6.9(11.9)	20.6(15.7)	−29.9(56.4)	0.4780	0.9	7.42
C(5)	128.18	128.01(0.49)	2.57(0.99)	−2.18(1.31)	−0.8(0.6)	0.7465	3.8	0.622
C(6)	129.88	129.85(0.09)	4.08(0.19)	20.66(0.25)	5.06(0.24)	0.9997	4521	0.119
CO	172.04	172.01(0.16)	−3.80(0.33)	−1.56(0.43)	0.41(0.12)	0.9844	94	0.205
C_5H_5	118.49	118.50(0.06)	0.91(0.13)	0.40(0.18)	0.44(0.21)	0.9579	33	0.083

[a] Parent complex.

Table 5. Correlation analysis [DSP approach, eqn. (6) together with set of σ_F/σ^0_R from ref. 13] on hydrogen chemical shifts for $(\eta\text{-}C_5H_5)_2Ti(O_2CC_6H_4X)_2$ derivatives.

Proton	δ[a]	δ_0	ρ_F	ρ_R	ρ_R/ρ_F	*r*	*F*	RSD
(i) *para*-series								
H(2)/H(6)	8.030	7.996(0.062)	0.07(0.13)	0.31(0.14)	4.4(8.4)	0.7350	3.5	0.079
H(3)/H(5)	7.442	7.465(0.106)	0.59(0.22)	1.82(0.24)	3.1(1.2)	0.9698	48	0.135
C_5H_5	6.621	6.616(0.007)	0.03(0.01)	0.09(0.02)	2.7(1.1)	0.9498	28	0.009
(ii) *meta*-series								
H(2)	8.030	8.051(0.122)	0.59(0.25)	1.53(0.33)	2.59(1.23)	0.9003	18	0.157
H(4)	7.489	7.536(0.128)	0.66(0.26)	1.64(0.35)	2.47(1.11)	0.9315	20	0.164
H(5)	7.442	7.406(0.086)	0.22(0.18)	0.56(0.23)	2.55(2.28)	0.7912	5.0	0.110
H(6)	8.030	8.028(0.034)	0.22(0.07)	1.29(0.09)	5.86(1.91)	0.9882	124	0.044
C_5H_5	6.621	6.620(0.011)	0.03(0.02)	0.06(0.03)	2.0(1.7)	0.7742	4.5	0.014

[a] Parent complex.

Table 6. Correlation analysis [TSP approach, eqn. (7) together with set of $\sigma_F/\sigma^0_R/\sigma_X$ from ref. 13] on carbon and hydrogen chemical shifts for $(\eta\text{-}C_5H_5)_2Ti(O_2CC_6H_4X)_2$ derivatives

Atom	X[a]	δ[c]	δ_0	ρ_F	ρ_R	ρ_X	*r*	*F*	RSD	*N*
(i) *para*-series										
C(2)/C(6)	*m*	129.88	129.77(0.26)	1.92(0.54)	−3.81(0.78)	0.63(0.55)	0.9655	18.4	0.3011	8
C(3)/C(5)	*o*	128.18	128.20(0.04)	−3.71(0.09)	23.46(0.11)	1.02(0.00)	1.0000	41 922	0.0537	8
C(4)	*i*	131.71	131.74(1.05)	6.49(2.16)	−50.5(2.9)	0.82(0.04)	0.9982	368	1.3443	8
C(2)/C(6)[b]	*m*	129.88	129.86(0.07)	0.08(0.45)	−4.99(0.33)	1.87(0.33)	0.9986	238	0.0806	6
H(2)/H(6)	*m*	8.030	7.970(0.066)	0.13(0.14)	0.24(0.16)	−0.13(0.13)	0.6277	2.7	0.0788	9
H(3)/H(5)	*o*	7.442	7.474(0.579)	0.58(0.23)	1.84(0.27)	0.00(0.01)	0.9709	27.4	0.1458	9
(ii) *meta*-series										
C(1)	*m*	133.78	133.63(0.21)	3.17(0.44)	−1.98(0.60)	0.59(0.28)	0.9705	27.0	0.2587	9
C(2)	*o*	129.88	129.81(0.20)	−3.66(0.41)	23.9(0.5)	1.01(0.01)	0.9997	2 543	0.2571	9
C(3)	*i*	128.18	128.35(0.25)	13.8(0.5)	−39.2(0.7)	1.00(0.01)	0.9999	12 946	0.3193	9
C(4)	*o*	131.71	131.60(1.57)	−6.45(3.15)	18.1(4.2)	0.96(0.11)	0.9770	35.1	1.9714	9
C(5)	*m*	128.18	128.20(0.37)	1.90(0.79)	−1.13(1.07)	1.19(0.50)	0.8916	6.5	0.4636	9
C(1)[b]	*m*	133.78	133.63(0.15)	3.46(0.72)	−1.79(0.72)	0.44(0.37)	0.9907	53.0	0.1839	7
C(5)[b]	*m*	128.18	128.19(0.06)	2.55(0.30)	−0.72(0.29)	0.86(0.15)	0.9979	243	0.0751	7
H(2)	*o*	8.030	8.041(0.135)	0.59(0.27)	1.52(0.36)	0.00(0.01)	0.9294	10.4	0.1692	9
H(4)	*o*	7.489	7.524(0.140)	0.67(0.28)	1.63(0.37)	0.00(0.01)	0.9343	11.4	0.1757	9
H(5)	*m*	7.442	7.368(0.050)	0.36(0.11)	0.35(0.14)	−0.25(0.07)	0.9489	15.1	0.0623	9

[a] Position of C(*i*) and H(*i*) with respect to substituent X. *m* = *meta*-substituted, *o* = *ortho*-substituted and *i* = *ipso*-substituted. [b] CN and NO_2-substituted complexes excluded. [c] Parent complex.

Regarding the cyclopentadienyl carbon shifts we observe much smaller ρ_F and ρ_R values compared with the carboxylato shifts. This is obviously due to the much greater distance between the substituents and the cyclopentadienyl carbons. Nevertheless, the distributions of mesomeric and inductive-polar components for the Cp-variations are equal to those of the CO-variations, *i.e.* ρ_F-values are approximately equal for the *para*- and *meta*-series, whereas ρ_R in the *para*-series is *ca.* twice as large as ρ_R in the *meta*-series. Again, we interpret the polar component as acting *via* through-space interactions.

The Effect of the $(C_5H_5)_2(XC_6H_4CO_2)TiCO_2$ *Group.*—We conclude this study by investigating the effect the group $(C_5H_5)_2(XC_6H_4CO_2)TiCO_2$– has as a substituent on the phenyl ring. The SCS constants for the unsubstituted complex are in ^{13}C NMR spectroscopy: C(1), 5.3; C(2)/C(6), 1.4; C(3)/C(5), 0.2; C(4), 3.2 ppm and in ^1H NMR spectroscopy: H(2)/H(6), 0.77; H(3)/H(5), 0.18; H(4), 0.23 ppm. The group thus behaves as an electron-attracting group with a weak-inductive attracting and a moderate mesomeric-attracting component. In fact, the ^{13}C SCS values are in between those of a CO_2Me and a $-CO_2^-$ group, as one might expect of a compound having a Ti–O bond intermediate between ionic and covalent. The inductive and resonance components can be examined quantitatively from the σ_F and σ^0_R constants, respectively. These are most readily obtained from a combination of ^{13}C and ^{19}F chemical shifts. Taft *et al.*[27] have shown that the ^{19}F chemical shift for a *meta*-substituted fluorobenzene (here for the 3-F substituted compound measured as 68.26 ppm) compared with fluorobenzene itself (68.61 ppm), in the same solvent, is related to the inductive effect of the substituent by eqn. (8). This inductive constant is then used in eqn. (9) with the *para*-carbon chemical shift of the monosubstituted compound [here C(4) of the unsubstituted compound, 131.71 ppm] compared with benzene itself (128.50 ppm) in the same solvent. Using $CDCl_3$ as solvent we have:

$$\delta(meta\text{-F}) = 7.1\sigma_F - 0.6 \qquad (8)$$

$$\delta(para\text{-C}) = 4.54\,\sigma_F + 21.54\,\sigma^0_R \qquad (9)$$

The field and resonance constants derived for the $(C_5H_5)_2(XC_6H_4CO_2)TiCO_2$ group are compared (Table 7) with those of $-CO_2^-$ and $-CO_2R$. The organometallic group is again found to be a very weak inductive acceptor and a moderate resonance acceptor. If we interpret these findings in mechanistic

Table 7. Comparison of some σ_F and $\sigma^0{}_R$ values.

Substituent	σ_F	$\sigma^0{}_R$
$(\eta\text{-}C_5H_5)_2(XC_6H_4CO_2)TiCO_2$–	0.035	0.142
^-O_2C–	−0.19[a]	—
RO_2C–	0.11[a]	0.19[a]

[a] See ref. 23.

terms we must realize[16,17] that σ_F in general contains three terms: (i) the field effect (F) where the substituent dipole induces electronic perturbations by through-space interactions, (ii) the inductive effect (χ) where the electronegativity of the substituent results in through-sigma-bond charge transfer and (iii) the polarisability effect (P), where a charge or a dipole on the probe results in polarisation of the substituent. The F, χ and P parameters are interrelated. For a substituent bonded to the phenyl group by a first-row atom [here C(O)] the electronegativity parameter is approximately as follows: $\sigma_\chi = a\sigma_F - b\sigma^0{}_R$. Using Cooks regression coefficients[16] we find the $(C_5H_5)_2(XC_6H_4CO_2)TiCO_2$ group to have virtually no through-bond electronegative effect ($\sigma_\chi \simeq 0$). With the low C–C bond polarisability this means that the field effect of the group is mainly due to the dipole moment set up in the group by a resonance mechanism.

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