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^{13}C AND ^{19}F NMR SUBSTITUENT CHEMICAL SHIFTS (SCS) OF SOME BRIDGEHEAD-SUBSTITUTED PHENYL- AND FLUOROPHENYLBICYCLO[2.2.2]OCTYLTRICARBONYLCHROMIUM(0) DERIVATIVES: NATURE OF ARYL ^{19}F NMR POLAR FIELD EFFECTS IN THE $Cr(CO)_3$-COMPLEXED BENZENE RING SYSTEM

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Summary

A number of $Cr(CO)_3$ complexes of bridgehead-substituted phenylbicyclo[2.2.2]octanes and (*m*- and *p*-)fluorophenylbicyclo[2.2.2]octanes have been synthesized and their ^{13}C and ^{19}F NMR spectra have been recorded, respectively. The substituent chemical shifts (SCS) of these stereochemically well-defined model systems permit an unambiguous evaluation of polar factors governing ^{13}C and ^{19}F SCS in arene-$Cr(CO)_3$ complexes. The dual nature of ^{19}F NMR polar field effects is reaffirmed and the coefficient (A) of the Buckingham equation for linear electric field effects on $C(sp^2)$—F bonds in fluoroarene-$Cr(CO)_3$ complexes has been calculated. A re-examination and re-interpretation of the ^{19}F chemical shifts of *m*- and *p*-substituted fluorophenyltricarbonylchromium derivatives is also reported. New substituent parameters (σ_I and σ_R^0) for $C_6H_5 \cdot Cr(CO)_3$ as a substituent in the neutral ground state are presented.

Introduction

In an attempt to shed further light on the nature of the chemical bond between arenes and the chromium tricarbonyl moiety ($Cr(CO)_3$), McGlinchey and coworkers [1] utilized ^{19}F chemical shifts to evaluate the efficiency of transmission of substituent electronic effects in the *meta* and *para* dispositions of fluorophenyltricarbonylchromium(0) versus the corresponding orientations in the uncomplexed ligand. The relationship between the *para* ^{19}F chemical shifts for both systems (complexed and uncomplexed) and Swain-Lupton substituent parameters (*I* and *R*) [2] was explored by multiparameter linear regression analysis. A comparison of the two correlative equations, together with the

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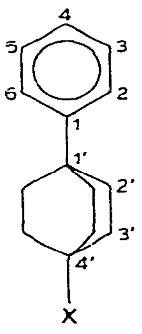
similar slopes of the apparent linear correlations between the two sets (complexed and uncomplexed) of *para* ^{19}F chemical shifts and the corresponding ^{13}C chemical shifts [3], led to the conclusion that $Cr(CO)_3$-complexation has little influence on the transmission of mesomeric or resonance effects in the *para* disposition. This conclusion is in general agreement with viewpoints from other studies [3,4].

However, for a series of substituents covering a reasonable range of electronic effects, McGlinchey and coworkers [1] found that the ^{19}F chemical shifts for the *meta*-substituted fluorophenyltricarbonylchromium(0) derivatives are confined to a very narrow range and generally show no obvious relationship with the polar influence (σ_I effect) of the substituent. This result stands in stark contrast to the corresponding shifts in the free ligand which cover a significant range, and, moreover, are directly proportional to the appropriate polar parameters (σ_I values) [5]. Based on the assumption that inductive effects perturb ^{19}F chemical shifts via the σ bonded framework [5], McGlinchey et al. [1] suggested that the *meta* ^{19}F chemical shift trends for the complexed ligand represent an additional manifestation of the strong participation of the arene ring σ bonds in the arene—metal bond [3].

More recently, studies of various model systems [6,7,8] have clearly shown that the σ_I effects of polar substituents perturb aryl ^{19}F chemical shifts by two distinct mechanisms which do not involve the electrons in the σ bonds: (i) the electric field of the substituent acting through space can polarize the π electrons in the CF bond (F_D; direct field effect); and (ii) the electric field of the substituent can polarize the entire conjugated system which may lead to a change in the π charge density at the carbon to which fluorine is attached with a concomitant response from fluorine (F_π; field-induced π polarization). Thus, the basic premise on which McGlinchey et al. [1] interpreted the unusual trend of ^{19}F chemical shifts for the *meta*-substituted fluorophenyltricarbonylchromium(0) derivatives is obviously invalid.

Clearly, an understanding of these "anomalous" ^{19}F chemical shifts and, therefore, whether or not they reflect pertinently on the nature of the arene—metal bond in arene-$Cr(CO)_3$ complexes, hinges critically on an unambiguous delineation of the relative magnitude and sign of the two polar mechanisms (F_D and F_π) governing electronically induced ^{19}F chemical shifts in the



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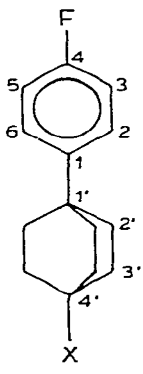

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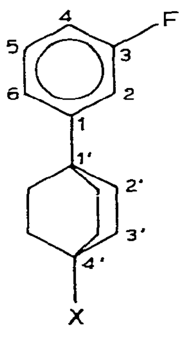

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$Cr(CO)_3$-complexed fluorophenyl ring system. Since a study [7,8] of the ^{13}C and ^{19}F chemical shifts of a number of bridgehead-substituted phenylbicyclo[2.2.2]octane derivatives led to a successful characterisation of the polarizing influences of F_D and F_π for the corresponding uncomplexed situation, we decided to initiate a similar investigation of some of the corresponding $Cr(CO)_3$ complexes of this stereochemically well-defined model system. The main virtue of the phenylbicyclo[2.2.2]octane ring system as a model for substituent effect studies is that substituent polar effects on the aryl ring can be examined in complete isolation of localized π electron interactions (mesomeric (M) and inductomesomeric effects (I_π)). Accordingly, we have synthesized a number of $Cr(CO)_3$-complexed derivatives of 1-X-4-phenylbicyclo[2.2.2]octanes (1) and 1-X-4-(*p*- and *m*-fluorophenyl)bicyclo[2.2.2]octanes (2 and 3, respectively) and measured their ^{13}C and ^{19}F NMR spectra, respectively. In addition, we have also synthesized an additional derivative of 2 ($X = C_6H_5 \cdot Cr(CO)_3$), as well as biphenyltricarbonylchromium(0), and measured their ^{19}F and ^{13}C NMR spectra, respectively. ^{19}F chemical shifts for the former system (2) have been shown to be very sensitive to the σ_I effect of bridgehead polar substituents [7], and, thus, their ^{19}F substituent chemical shifts (SCS) can be usefully employed to accurately define new σ_I values [7,9]. In the current context, we are concerned with determining the σ_I value for $C_6H_5 \cdot Cr(CO)_3$ as a substituent attached to an sp^3 hydridized carbon atom. The *para* ^{13}C SCS for the uncomplexed benzene ring of biphenyltricarbonylchromium(0), together with the dual substituent parameter (DSP) correlative equation of *para* ^{13}C SCS of mono-substituted benzenes [10], should allow an estimate of the σ_R^0 value for the $C_6H_5 \cdot Cr(CO)_3$ group acting as a substituent in the neutral ground state.

Finally, because the ^{19}F chemical shifts presented by McGlinchey et al. [1] for the *para*-substituted fluorophenyltricarbonylchromium(0) derivatives appear to contain some obvious discrepancies (in particular, fluorine as a substituent) when compared with the corresponding ^{13}C chemical shifts obtained by Bodner and Todd [3], we decided also to re-examine the ^{19}F NMR spectra of some *meta*- and *para*-substituted fluorophenyltricarbonylchromium(0) derivatives. It should be noted that the ^{13}C NMR data of Bodner and Todd [3] have recently been corroborated [11] and, therefore, are not in dispute.

Experimental

Synthesis of compounds

The bridgehead-substituted phenylbicyclo[2.2.2]octanes (systems 1, 2, and 3) were prepared as previously described [7,9,12] and, on treatment with hexacarbonylchromium, were converted to the corresponding tricarbonylchromium complexes utilizing either a procedure outlined by Strohmeier [13] (Method A) or a more recent one described by Mahaffy and Pauson [14] (Method B). All the complexes sublimed (130° C/10^{-6} mmHg) as pale yellow solids. Some relevant data is presented in Table 1.

The NMR (^1H and ^{13}C) and mass spectra of these compounds were clearly in accord with the assigned structures.

All other tricarbonylchromium complexes reported in this study are known compounds [1,3,15—17] and were prepared in variable yields (6—82%) by

TABLE 1

SYNTHETIC METHOD, YIELDS, AND MELTING POINTS OF THE TRICARBONYLCHROMIUM COMPLEXES OF SYSTEMS 1, 2, AND 3 [a]

System	Substituent (X)	Method	Yield (%)	Mp (°C)
1	H	A	54	164—166
1	F	A	26	202.5—204
1	Cl	A	43	153—155
1	Br	A	38	163—165
1	OAc	A	49	167—169
1	COMe	B	45	132—134
1	OMe	A	43	155.5—157
1	Me	B	45	147—148.5
1	t-Bu	B	46	152—156
2	H	B	51	119—120
2	F	B	18	179—181
2	OAc	A	30	160—162
2	OMe	B	51	153.5—154.5
2	Me	B	63	131—133
3	H	B	51	104—105.5
3	F	B	30	147—149
3	OMe	B	56	151—152

[a] System 2, X = $C_6H_5 \cdot Cr(CO)_3$: Method B, Yield 23%, mp 156—159°C.

treatment of the appropriate arene either with hexacarbonylchromium (Method B) or triamminetricarbonylchromium [10]. Purification was effected by sublimation (100°C/10^{-6} mmHg). It should be noted that mass spectral analysis indicated that some of the substituted fluorophenyltricarbonylchromium(0) derivatives (*p*-t-Bu, *p*-Cl, *p*-F, and *m*-Cl) were contaminated with the $Cr(CO)_3$ complexes of benzene and mono-substituted benzenes. Apparently, reductive loss of substituents can occur during treatment of the appropriate substituted fluorobenzene with hexacarbonylchromium. Several attempts to prepare the $Cr(CO)_3$ complexes of *m*- and *p*-fluorobenzotrifluoride as well as *m*-difluorobenzene were unsuccessful.

Full details of the ^1H NMR spectra for all the complexes reported in this study may be found elsewhere [19].

Spectra

The broad-band proton-decoupled ^{13}C NMR spectra of all the $Cr(CO)_3$ complexes of systems 1, 2, and 3 were recorded in the pulse Fourier transform mode on a Bruker spectrometer operating at 67.89 MHz (spectral width 15,000 Hz, 16K/8K data points, resolution of 0.03 ppm and spectral width 5000 Hz, 32K/16K data points, resolution of 0.004 ppm) using $DCCl_3$ solutions (0.1—0.2 *M*) with Me_4Si or $DCCl_3$ (central resonance peak) as an internal reference. All other ^{13}C NMR spectra ($DCCl_3$ solutions, ~0.2—0.3 *M*) were obtained with a Bruker spectrometer operating at 22.625 MHz with a spectral width of 6024 Hz (16K/8K data points, resolution of 0.03 ppm).

The ^{19}F NMR spectra of solutions ($c\text{-}C_6H_{12}$, C_6H_6, CH_2Cl_2, or $HCCl_3$ as solvent) of systems 2 and 3 as well as their corresponding $Cr(CO)_3$ complexes and some of the substituted fluorophenyltricarbonylchromium(0) derivatives were obtained under proton-decoupled conditions in the pulse Fourier transform mode with a Bruker spectrometer operating at 84.66 MHz. A spectral width of 1202 Hz was used and the data collected into 16K/8K data points giving a resolution of better than 0.01 ppm. Each sample consisted of a mixture of the unsubstituted compound (10—15 mg) and substituted compound (5—10 mg) dissolved in 0.5 ml of the appropriate solvent.

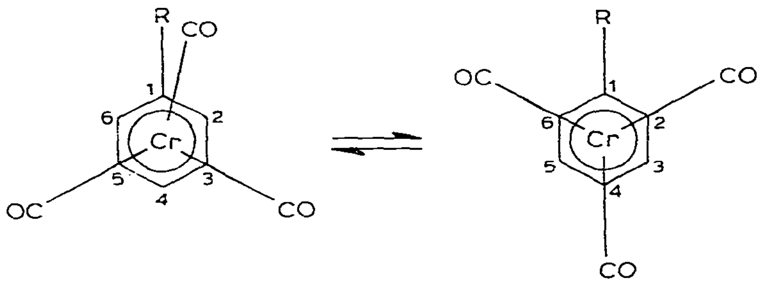
All other ^{19}F NMR spectra reported in this study were measured with a Varian DP-60 spectrometer operating at 56.4 MHz under proton-coupled conditions using solutions containing 5% (W/W) of the compound and 3% (W/W) of hexafluorobenzene as internal reference and lock. The instrument had been modified to obtain spectra in the HA mode which were calibrated using a Racal SA35 universal counter timer. The chemical shifts can be considered accurate to ±0.03 ppm.

^{1}H NMR spectra were measured with a Varian A-60 spectrometer.

Results and discussion

^{13}C NMR Spectra

The ^{13}C NMR data for the various $Cr(CO)_3$ complexes are assembled in Tables 2 and 3 together with the date for the appropriate uncomplexed 1-X-4-phenylbicyclo[2.2.2]octanes (1). The spectra of the latter compounds as well as those of the $Cr(CO)_3$ complexes of fluorobenzene, t-butylbenzene, and trifluoromethylbenzene (only for the *para* carbon) have been previously reported [1,3,4,7,11,20]. However, we have measured the 1-X-4-phenylbicyclo[2.2.2]-octanes (1) in $DCCl_3$ with higher precision than those previously reported by us [7] and we list them here simply to facilitate comparisons. Assignments for all new compounds followed normally from chemical shift and intensity considerations and, in the case of the arylfluoride derivatives, characteristic ^{13}C—^{19}F coupling constant patterns proved decisive [21]. For the parent system (1; X = H) of the $Cr(CO)_3$ complexes, C(2) and C(3) were distinguished by the "fluorosubstitution" technique [21,22] and confirmed by deuterio substitution at C(4) which effected a characteristic upfield shift (0.1 ppm) [23] of the *ortho* carbons (C(3, 5)). An important spectral feature of the $Cr(CO)_3$ complexes of system 1 emerges on comparison of the aryl carbon chemical shifts with those observed in the corresponding uncomplexed derivatives. It can be seen from the chemical shift data relative to Me_4Si (footnotes *d* and *h* of Table 2) that whereas the shift sequence to highfield for the aryl carbons of the complex is



A

B

TABLE 2

^{13}C SUBSTITUENT CHEMICAL SHIFTS (SCS) IN $DCCl_3$ [a,b] OF SOME 1-X-4-PHENYLBICYCLO-[2.2.2] OCTANES(1) AND THEIR CORRESPONDING $Cr(CO)_3$ COMPLEXES

X	C(1)	C(2)	C(3)	C(4)	C(1)′	C(2)′	C(3)′	C(4)′
1-X-Phenylbicyclo[2.2.2]octanes(1) [c,d]								
F	−2.89	−0.26	0.17	0.52	0.11	1.43	4.97	70.09
Cl	−2.70	−0.33	0.20	0.55	−0.68	2.18	10.08	43.08
Br	−2.60	−0.39	0.17	0.52	−1.36	3.02	11.44	39.63
OAc	−2.27	−0.26	0.17	0.42	0.04	0.97	3.64	56.21
$COCH_3$	−1.52	−0.17	0.09	0.36	0.69	−0.48	1.53	20.54
OCH_3	−1.85	−0.17	0.13	0.32	0.10	1.07	3.22	49.32
Me [e]	−0.39	−0.14	−0.07	0.07	0.46	0.65	7.22	3.44
Me [f]	−0.39	0.04	0.02	0.05				
t-Bu [e]	−0.22	−0.13	−0.04	0.00	0.07	0.43	−0.58	11.05
t-Bu [f]	−0.14	−0.02	0.03	0.02				
η^6-(1-X-4-Phenylbicyclo[2.2.2]octane)tricarbonylchromium(0) derivatives [g,h]								
F	−3.33	−0.50 (−0.56) [f]	−0.17 (−0.22) [f]	0.15 (0.09) [f]	n.o. [i]	1.27	4.89	n.o. [i]
Cl	−3.05	−0.57 (−0.61) [f]	−0.20 (−0.25) [f]	0.11 (0.10) [f]	−0.68	2.04	10.03	41.57
Br	−2.91	−0.65 (−0.63) [f]	−0.22 (−0.23) [f]	0.08 (0.12) [f]	−1.33	2.86	11.42	37.16
OAc	−2.59	−0.52 (−0.58) [f]	0.00 (−0.04) [f]	0.00 (−0.05) [f]	−0.11	0.87	3.68	55.44
$COCH_3$	−1.89	−0.40 (−0.41) [f]	0.07 (0.07) [f]	0.01 (0.01) [f]	0.69	−0.37	1.69	20.85
OCH_3	−2.07	−0.35 (−0.40) [f]	−0.03 (−0.04) [f]	0.00 (−0.01) [f]	−0.05	1.01	3.27	49.04
Me	−0.34	−0.04	0.00	−0.04	0.45	0.71	7.25	3.87
t-Bu	−0.22	−0.31	0.34	−0.39	0.07	0.45	−0.59	11.53

[a] Defined as the difference (ppm) between the ^{13}C chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon (X = H). Positive values indicate decreased shielding. [b] The carbon numbering system is as shown on the structural formula (1) in the Introduction. [c] Measured at 22.625 MHz on 0.3 *M* solutions. Accurate to ±0.06 ppm. [d] X = H ($DCCl_3$, relative to Me_4Si): 150.68 (C(1)); 125.62 (C(2)); 128.05 (C(3)); 125.42 (C(4)); 34.13 (C(1)′); 32.12 (C(2)′); 26.56 (C(3)′); 24.51 (C(4)′). [e] Taken from ref. 6. Accurate to ±0.14 ppm. [f] Measured at 67.89 MHz on 0.1 *M* solutions. Accurate to better than ±0.01 ppm. [g] Measured at 67.89 MHz on 0.2 *M* solutions. Accurate to ±0.05 ppm. [h] X = H ($DCCl_3$, relative to Me_4Si): 122.01 (C(1)); 93.24 (C(2)); 90.46 (C(3)); 93.88 (C(4)); 33.66 (C(1)′); 32.19 (C(2)′); 26.15 (C(3)′); 24.16 (C(4)′). [i] n.o. not observed.

C(1), C(4), C(2), C(3), the sequence for the corresponding uncomplexed species is C(1), C(3), C(2), C(4). This situation is clearly analogous to that previously encountered for t-butylbenzene and its $Cr(CO)_3$ complex [11]. The trends are readily interpreted in terms of a conformational equilibrium between A and B [11]. For groups (R) with a large effective steric size (t-butyl and bicyclo[2.2.2]octyl), conformation B is strongly preferred in which the octahedrally directed valence orbitals from the $Cr(CO)_3$ moiety overlap with the orbitals of the π-system at C(1), C(3), and C(5). This localized bonding interaction is manifested by an increase in electron density and, thus, shielding at these carbon centers [11]. It should be noted that the aforementioned conformational equilibrium ($A \rightleftharpoons B$) is an oversimplification of the real situation since

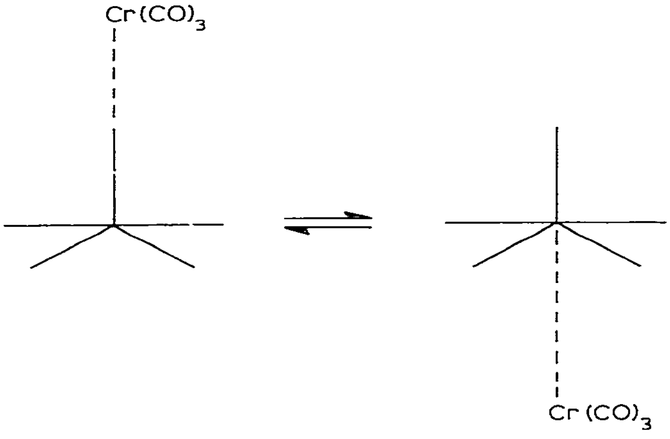
TABLE 3

^{13}C CHEMICAL SHIFTS (ppm) IN $DCCl_3$ [a,b] OF SOME OTHER ARENE-$Cr(CO)_3$ COMPLEXES

Arene	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(1)'	C(2)'	C(3)'	C(4)'	Others
C_6H_5F [c,d]	146.61	79.34	93.46	86.48	93.46	79.34					231.87(CO)
	(266.20)	(19.85)	(7.36)		(7.36)	(19.85)					(2.20)
$C_6H_5CF_3$ [c,d]	95.75	89.86	88.56	93.69	88.56	89.86					230.36(CO)
											123.28(CF_3)
	(30.89)	(3.0)				(3.0)					(204.80)
											233.71(CO)
$C_6H_5C(CH_3)_3$ [c,d]	123.11	92.65	91.03	93.53	91.03	92.65					31.05(CH_3)
											34.10(C)
p-$FC_6H_4C(CH_3)_3$ [c,d]	117.39	92.36	77.65	146.70	77.65	92.36					31.40(CH_3)
											33.81(C)
		(7.35)	(19.85)	(265.47)	(19.85)	(7.35)					
$C_6H_5 \cdot C_6H_5$ [c,e]	110.60	92.26 [f]	92.78 [f]	91.55	92.78 [f]	92.26 [f]	136.54	127.18 [g]	128.90	129.13 [g]	
system 2 (X = H) [h]	n.o. [i]	92.43	77.53	n.o. [i]	77.53	92.43	33.54	32.91	26.43	24.34	
		(7.40)	(19.42)		(19.42)	(7.40)					
system 3 (X = H) [h]	124.19	78.89	145.86	79.66	91.83	85.90	34.08	31.83	25.99	24.11	
	(5.55)	(19.43)	(264.48)	(20.34)	(7.40)						

[a] Chemical shifts for 0.2—0.4 *M* solutions referred to Me_4Si (±0.03 ppm). Positive values indicate decreased shielding relative to Me_4Si. The carbon-numbering system is consistent with that shown on the structural formulas (see Introduction). [b] ^{13}C—^{19}F coupling constants (Hz) are given in brackets. [c] Measured at 22.625 MHz. [d] $C_6H_5 \cdot Cr(CO)_3$ (relative to Me_4Si): 92.85; 233.00(CO). [e] Internal benzene (relative to Me_4Si): 128.41. [f] Assignments could be reversed. [g] These assignments differ from those recently reported [32]. [h] Measured at 67.89 MHz. [i] n.o. = not observed.

the configuration of the bicyclo[2.2.2]octyl group with respect to the aryl ring is probably that one which minimizes "*ortho*" buttressing effects by having one C—C bond at right angles to the aromatic ring. Hence, both A and B should be properly represented by an additional conformational equilibrium between C and D (horizontal line represents plane of the benzene ring).



C D

Assuming that non-proximate aryl ^{13}C SCS mirror predominantly substituent-induced π electron perturbations [24,25] and, in addition, assuming that Cr(CO)$_3$ complexation does not seriously perturb the shift/charge density ratio (vide infra), it can be seen from a cursory examination of the aryl chemical shift data (Table 2) and the appropriate correlation parameters (DSP equation) [26] * assembled in Table 4 ** that Cr(CO)$_3$ complexation effects a marked change of the aryl ^{13}C SCS. Furthermore, it can also be seen that the precision of fits of the SCS data for C(4) and C(3) in the complexed derivatives, which are well outside any expectations from experimental uncertainty of these very small SCS, indicates a complete breakdown in the linear relationship observed at the corresponding positions in the free ligand [7,20]. A closer inspection of the SCS for these two dispositions in the complexed derivatives clearly reveals a dislocation in the trend between the polar axially symmetric (halogens) and asymmetric (OAc, COCH$_3$, and OCH$_3$) substitutents based on the results for the corresponding positions in the uncomplexed derivatives and the relative magnitude of the σ_I values [26,27] of the substituents.

The possible origin of this unexpected result is exposed on examination of

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* It should be borne in mind that although the DSP equation is not strictly applicable to the model systems in question, σ_R^0 values being only valid for substituents directly attached to π systems, we have used it here as a free-fitting statistical procedure to shunt extraneous factors out of the polar term ($\rho_I\sigma_I$).

** The substituents in the data set for the 1-X-4-phenylbicyclo[2.2.2]octanes include the NO$_2$, CN, COOEt, and NH$_2$ groups. The ^{13}C SCS for these substituents have been previously reported (refs. 7 and 20), however, we have remeasured them with higher precision. It should be noted that the correlation parameters for this system (Table 4) are very similar to those recently reported by Ewing and Toyne [20].

TABLE 4

RESULTS OF CORRELATIONS OF ^{13}C SCS (SYSTEM 1 AND CORRESPONDING $Cr(CO)_3$ COMPLEXES) WITH SUBSTITUENT PARAMETERS

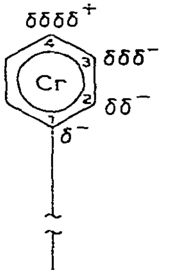
Carbon no. [a]	ρ_I	ρ_R	SD [b]	f [c]	n [d]
Uncomplexed					
C(1)	—5.32 ± 0.18	1.28 ± 0.14	0.18	0.08	11
C(2)	—0.59 ± 0.06	0.09 ± 0.04	0.00	0.22	11
C(3)	+0.41 ± 0.04	—0.09 ± 0.03	0.04	0.22	11
C(4)	+1.20 ± 0.06	—0.05 ± 0.04	0.06	0.11	11
Complexed					
C(1)	—6.54 ± 0.55	0.54 ± 0.82	0.36	0.14	7
C(2)	—1.34 ± 0.15	—0.12 ± 0.23	0.10	0.21	7
C(3)	—0.25 ± 0.15	+0.08 ± 0.22	0.09	0.72	7
C(4)	+0.20 ± 0.08	+0.05 ± 0.12	0.05	0.65	7

[a] Indicated on structural formula in Introduction. [b] The standard deviation of the fit. [c] The fit parameter, $f \equiv SD/\mathrm{rms}$, where rms is the root mean square of the data points. Correlations of excellent prevision are those for which $f < 0.1$ [50]. [d] The number of substituents in the data set.

the aryl ^{13}C SCS for the non-polar t-butyl group (σ_I = 0) [9]. Thus, it can be seen (Table 2) that whereas the SCS at C(2), C(3), and C(4) in the free ligand for this group are virtually zero (within experimental error), which is in accord with a neglibible polar effect, the corresponding SCS in the complexed derivative are significant. Moreover, and most importantly, the values are similar in magnitude but of opposite sign for C(2, 4) versus C(3), a perturbation pattern of the SCS which we believe can be clearly associated with a slight conformational change of the $Cr(CO)_3$ group. Thus, if replacement of H at the bridgehead position in the phenylbicyclo[2.2.2]octyltricarbonylchromium ring system with the relatively bulky t-butyl substituent leads to a shift in the relative populations of the conformational equilibrium (A $\rightleftharpoons$ B) towards A, then increased and decreased shielding by equal amounts at C(2, 4) and C(3), respectively, will occur, which is the observed result, as a result of the repositioning of the valence orbitals from the $Cr(CO)_3$ group (vide supra). Hence, although the aryl ^{13}C SCS (C(4) and C(3)) for the halogen substituents of the $Cr(CO)_3$ complex of system 1 (Table 2) appear to be bona fide manifestations of pure polar phenomena, the corresponding SCS for the polar asymmetric groups reflect polar field effects as well as substituent-induced changes in the conformational equilibrium between A and B. It should be noted, however, that the relative magnitude of the SCS (C(4) and C(3)) suggests that the latter effect is small, being considerably less than that observed for the non-polar but bulky t-butyl group. This small substituent-induced conformational effect is not apparent at C(1) and C(2) for the asymmetric polar substituents, as evidenced by the reasonably good linear correlations for these sites (Table 4), since it is clearly swamped by considerably larger polar effects.

Two speculative reasons may be advanced to account for the unexpected sensitivity of the conformational equilibrium (A $\rightleftharpoons$ B) to substitution at the remote bridgehead position of system 1 ($Cr(CO)_3$ complexed) by certain groups. Firstly, the position of the conformational equilibrium may be very responsive to solvent effects which have their origin in substituent (or solvated substituent)-induced interference of the interaction of the $Cr(CO)_3$ groups with the hydrogen-bond donor solvent ($DCCl_3$). Secondly, the equilibrium may be sensitive to unfavourable non-bonded interactions between the bridgehead-substituent and the bicyclo[2.2.2]octyl ring. In this regard, it is of interest to note that an examination of molecular models indicates very strongly that the t-butyl and asymmetric polar groups prefer a staggered configuration with respect to the C—C bonds of the latter ring system. We favour the second proposal since the t-butyl substituent appears to effect a slight perturbation of the conformational equilibrium even in cyclohexane (inert and non-polar) as solvent, as evidenced by a comparison of the following appropriate ^{13}C SCS (c-C_6H_{12}) for the t-butyl group (accurate to better than ±0.02 ppm) in system 1 and its corresponding $Cr(CO)_3$ complex respectively: 1: −0.02 (C(2)); 0.03 (C(3)); −0.02 (C(4)). 1 ($Cr(CO)_3$ complex): −0.17 (C(2)); 0.26 (C(3)); −0.25 (C(4)). It should be noted, however, that because of insolubility problems, the ^{13}C SCS for the complex pertain to a probe temperature of 343 K versus 310 K for the free ligand.

Based on the aryl ^{13}C SCS for the halogen substituents, the field-induced π charge density perturbation (F_π) of the $Cr(CO)_3$-complexed benzene ring may be schematically illustrated as in 4. Clearly, this polar induced charge density pattern differs significantly from the representation 5 previously indicated [7,20] for the same effect in the uncomplexed ring. In particular, the most important difference concerns C(4) and C(3), the two positions which have been shown previously [7,8] to satisfactorily characterize similar polarizing influences at the non-proximate *para* and *meta* carbon positions, respectively, of uncomplexed monosubstituted benzenes. Note that whereas the formal π-electron charges at C(4) and C(3) for the uncomplexed situation are of the same sign (relative magnitude of approx., 2 : 1; see results for c-C_6H_{12} as solvent [7]), the signs of the corresponding charges in the $Cr(CO)_3$-complexed ring system are diametrically opposed. Moreover, the magnitude of the formal charge at C(4) is much reduced on complexation and, thus, the relative magnitude of C(4) and C(3) (~1 : 2) is now reversed.



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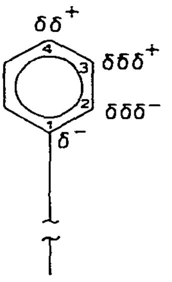

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It is of interest to see whether these trends can be validly extrapolated to the *para* (C(4)) and *meta* (C(3)) positions of monosubstituted phenyltricarbonylchromium(0) derivatives. The appropriate ^{13}C SCS for this system are listed in Table 5. Two sets are provided. On the one hand, ^{13}C SCS have been calculated in the usual way by employing hydrogen as the reference substituent. However,

TABLE 5

^{13}C SUBSTITUENT CHEMICAL SHIFTS (SCS, PPM) [a] FOR THE *META*- AND *PARA*-CARBONS OF MONOSUBSTITUTED η^6-PHENYLTRICARBONYLCHROMIUM(0) DERIVATIVES

Substituent, X	*meta* [b]	*para* [b]	*meta*	*para*
F	0.61 [c]	—6.37 [c]	—1.17 [f]	—4.71 [g]
Cl	0.31 [d]	—4.76 [d]	—1.29 [f]	—2.94 [g]
Me	1.60 [e]	—3.10 [e]	0.00 [f]	—1.47 [g]
OMe	2,21 [d]	—7.55 [d]	0.61 [f]	—5.73 [g]
COOMe	—3.26 [d]	1.93 [d]	—1.44 [g]	0.33 [f]
NH_2	3.50 [d]	—9.70 [d]	1.90 [f]	—7.88 [g]
NMe_2	3.97 [d]	—10.34 [d]	2.37 [f]	—8.52 [g]
CF_3	—4.29 [c]	0.84 [c]	—2.47 [g]	—0.84 [f]

[a] Positive sign implies deshielding. [b] Relative to parent (X = H). [c] This study. [d] Taken from ref. 3. [e] Taken from ref. 11. [f] Relative to *meta* SCS for CH_3. [g] Relative to *meta* SCS for t-Bu (see Table 3 and ref. 11).

because the position of the conformational equilibrium (A $\rightleftharpoons$ B; vide supra) is sensitive to the electronic and steric effects of substituents [4,11,17,28] and, therefore, leads to varying degrees of localization of the aryl carbon—chromium bonds depending on the substituent, these ^{13}C SCS cannot be viewed as being manifestations of pure substituent electronic effects. On the other hand, since the Me and t-Bu substituents favour conformer A and B, respectively, [4,11, 17,18] *, and since the *meta* ^{13}C SCS for these substituents in the uncomplexed benzene ring are negligibly small [11,29], the *meta* ^{13}C SCS (relative to H) for the Me (+1.6 ppm) [11] and t-Bu (—1.82 ppm; Table 3) [11] substituents in phenyltricarbonylchromium can be considered, to a first order approximation, measures of the "localization effect" of the aryl carbon—chromium bonds for the eclipsed and staggered carbon environments, respectively. Thus, by utilizing these ^{13}C SCS as the appropriate reference points (see footnote to Table 5) conformational effects may be hopefully minimized. The two sets of SCS data (Table 5) are related to the appropriate substituent parameters (DSP analysis) according to the following equations:

$$\mathrm{SCS}(\mathit{para}, \text{rel. H}) = -1.47 \pm 0.71\sigma_I + 18.77 \pm 0.66\sigma_R^0 \quad (n = 8; f = 9\%) \tag{1}$$

$$\mathrm{SCS}(\mathit{para}, \text{corrected}) = -2.11 \pm 1.14\sigma_I + 13.93 \pm 1.07\sigma_R^0 \quad (n = 8; f = 18\%) \tag{2}$$

$$\mathrm{SCS}(\mathit{meta}, \text{rel. H}) = -5.58 \pm 1.09\sigma_I - 9.08 \pm 1.02\sigma_R^0 \quad (n = 8; f = 30\%) \tag{3}$$

$$\mathrm{SCS}(\mathit{meta}, \text{corrected}) = -4.85 \pm 0.33\sigma_I - 4.64 \pm 0.31\sigma_R^0 \quad (n = 7; f = 15\%) \tag{4}$$

For comparison purposes, the corresponding correlative equations [30] of the

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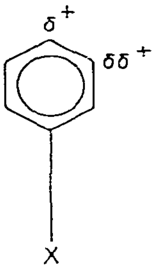
* In the absence of steric phenomena, electron-donating and electron-withdrawing substituents favour conformer A and B, respectively, [4,11,17, and 28].

^{13}C SCS data ($DCCl_3$ as solvent) for uncomplexed monosubstituted benzenes are as follows:

$$\mathrm{SCS}(para) = 4.54\sigma_I + 21.54\sigma_R^0 \qquad (n = 15; f = 2\%) \tag{5}$$

$$\mathrm{SCS}(meta) = 1.6\sigma_I - 1.3\sigma_R^0 \qquad (n = 12; f = 25\%) \tag{6}$$

It can be seen that although the attempt to correct for conformational effects leads to a poorer precision of fit of the data at the *para* position (cf. eq. 1 and 2), a disposition which is apparently dominated by the large electronic effects of the substituent, the situation is much improved for the *meta* position (cf. eq. 3 and 4) where intrinsic electronic effects are known to be considerably smaller (cf. eq. 5 and 6). The most significant feature of the DSP analysis is that it indicates that the pattern of charge redistribution induced by the F_π mechanism (σ_I effect) at the *para* and *meta* positions of monosubstituted benzenes (schematic illustration 6), as reflected by their respective ρ_I values, is dramatically altered on complexation with $Cr(CO)_3$ (schematic illustration 7).



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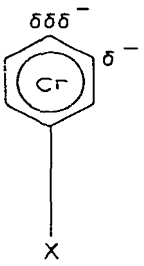

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In particular, it is pertinent to note the attenuation and change in sign of the F_π effect at the *para* position, the significant increase and change in sign of the F_π effect at the *meta* position, and the fact that whereas in the uncomplexed ring, $F_\pi(para) > F_\pi(meta)$, the reverse situation ($F_\pi(meta) > F_\pi(para)$) holds for the complexed ring. Most importantly, these overall trends (except for the change in sign at the *para* position) bear a striking similarity to those observed on complexation of the phenylbicyclo[2.2.2]octyl ring system with $Cr(CO)_3$ (vide supra). Hence, since polarization due to F_π is unambiguously defined in the latter model system, the validity of the DSP dissection of the ^{13}C SCS data for monosubstituted phenyltricarbonylchromium derivatives (eq. 1 and 4) appears to be verified.

Two further features of the DSP analysis are worthy of note. Firstly, it is clear from the magnitude of the ρ_R values in eq. 1 and 5 that $Cr(CO)_3$-complexation of the benzene ring has only a small effect on the transmission of resonance effects in the *para* disposition [3,4] (vide supra). Secondly, although inexplicable, it is of interest to note from the ρ_R values in eq. 4 and 6 that resonance effects in the *meta* orientation (opposite in kind to those observed in the *para* position) [30,31], are increased by more than a factor of two on complexation. It should be noted that Fedorov et al. [32] have recently drawn attention to the fact that a correlation exists between Taft's σ_R constants and the ^{13}C chemical shifts of C(3) (*meta*) of $Cr(CO)_3$-complexed monosubstituted benzenes.

Finally, an amusing but puzzling feature emerges on comparison of the total polarization (as reflected by ^{13}C SCS) of the aromatic ring in 1-X-4-phenylbicyclo[2.2.2]octanes with that observed for the corresponding $Cr(CO)_3$-complexed ring system. It can be seen (Tables 2 and 4) that although polarization is substantially attenuated at C(4) on complexation, a corresponding significant increase occurs at C(1). This result contradicts expectations (decreased polarization at C(1)) based on the proposed simple model for the F_π effect [7,20], namely, that the π system is envisaged as being polarized as a complete unit. An explanation in terms of perturbed relative shift/charge density ratios (due to localization of the aryl carbon—chromium bonds effecting different degrees of interaction of C(1) and C(4) with the octahedrally directed orbitals from $Cr(CO)_3$) does not seem plausible since the SCS at C(2), a carbon center which has a similar electronic environment to C(4) with respect to the $Cr(CO)_3$ subunit, are also enhanced. The phenomenon does not appear to be an artifact of the possible strong polarization of the carbonyl bonds of the $Cr(CO)_3$ subunit since the ^{13}C SCS of C(1)′, the carbon center adjacent to C(1), are very similar for the two systems (Table 2; free ligand and complexes). We can only conclude that either the null plane of the F_π effect for the simple model, as proposed by Ewing and Toyne [20], has been displaced on complexation from being approximately in the center of the benzene ring to a point between C(3) and C(4) or, that field-induced π polarization is more localized than previously envisaged [7,20]. Alternatively, since a similar enhancement of the *ipso* ^{13}C SCS in monosubstituted benzenes occurs on $Cr(CO)_3$ complexation, it is tempting to speculate that through-bond effects may be responsible in which the C(1)—C(1)′ and C(4)′—X σ bonds are coupled via an appropriate orbital of σ symmetry of the bicyclo[2.2.2]octane ring system [33].

^{19}F *NMR Spectra*

^{19}F SCS for a limited number of bridgehead-substituted $Cr(CO)_3$ complexes of systems 2 and 3 are listed in Table 6 together with the corresponding data

TABLE 6

^{19}F SCS (ppm)[a] OF SOME 1-X-4-*p*-FLUOROPHENYLBICYCLO[2.2.2]OCTANES(2), 1-X-4-*m*-FLUOROPHENYLBICYCLO[2.2.2]OCTANES(3), AND THEIR CORRESPONDING $Cr(CO)_3$ COMPLEXES

Substituent (X)	Uncomplexed				Complexed			
solvent:	$c\text{-}C_6H_{12}$		CH_2Cl_2		$c\text{-}C_6H_{12}$		CH_2Cl_2	
	2	3	2	3	2[b]	3[c]	2[b]	3
F	1.04	0.60	0.93	0.46	0.46	0.14	0.41 (0.47)[d]	0.12 (0.11)[d]
OMe	0.52	0.25	0.54	0.24	0.20	0.20	0.21 (0.27)[d]	0.11 (0.07)[d]
OAc	0.76		0.76				0.31 (0.34)[d]	
Me	0.09		0.10		0.00		0.00	

[a] Accurate to ±0.01 ppm. Positive sign implies deshielding. [b] Relative to parent (X = H): δ (internal $FCCl_3$) — 138.02 ppm ($c\text{-}C_6H_{12}$); δ (external $FCCl_3$) — 136.62 ppm ($c\text{-}C_6H_{12}$), —134.60 ppm (CH_2Cl_2). [c] Relative ot parent (X = H): δ (internal $FCCl_3$) — 135.06 ppm ($c\text{-}C_6H_{12}$); δ (external $FCCl_3$) — 134.74 ppm ($c\text{-}C_6H_{12}$). [d] Solvent, $HCCl_3$.

for the uncomplexed derivatives. In view of the conformational problems associated with the OMe substituent in the $Cr(CO)_3$ complex of system 1 (vide supra), we shall focus our attention first of all on the results for fluorine as a substituent in the $Cr(CO)_3$ complexes of systems 2 and 3. Assuming that ^{19}F SCS reflect the local π electron redistribution in the immediate vicinity of the probe site [6,7,24], an examination of the data for fluorine (Table 6; cyclohexane as solvent) reveal a number of pertinent features concerning the nature of polar field effects (σ_I effect) underlying non-proximate ^{19}F SCS of fluoroarenetricarbonylchromium derivatives. Firstly, since complexation does not appear to drastically alter the shift/charge density ratio *, and, therefore, the absolute magnitude of the ^{19}F SCS for the complexed and uncomplexed systems can be validly compared to a first order approximation, it can be seen that the polar field effect of fluorine is substantially attenuated on complexation. Clearly, this trend is most pronounced for system 3.

Secondly, it can be seen that the sign of the ^{19}F SCS for fluorine in the $Cr(CO)_3$ complex of 3 (Table 6; positive) does not parallel that for the corresponding ^{13}C SCS (Table 2; C(3)). This is a most trenchant result since polarization of an aromatic system as reflected by ^{13}C SCS is known to lead to a proportionate change in ^{19}F SCS where significant changes in π electron density occur at the carbon (Δq_{π}^{C}) adjacent to fluorine [6,8,24]. However, where these are small, nonlinearity between ^{13}C and ^{19}F SCS may arise due to the sensitivity of the latter parameter to significant direct field effects (F_D) [6,7,8] and mesomeric-field effect phenomena [22,34] (secondary effect due to charges essentially on carbon sites *ortho* to fluorine). A consideration of the π electron distribution in the aromatic ring of the $Cr(CO)_3$-complexed phenylbicyclo[2.2.2]-octane ring system, as reflected by the appropriate ^{13}C SCS for fluorine (Table 2; C(2) and C(4)), clearly indicates that the mesomeric-field effect, if significant, is a shielding not a deshielding contribution to the ^{19}F SCS for the complex of 3. Note that the ^{19}F SCS of fluorine for the latter system (Table 6) is considerably deshielded compared to the corresponding ^{13}C SCS (Table 2). Hence, the discrepancy between the ^{19}F and ^{13}C SCS parameters can be attributed to a significant contribution by the F_D effect to the former parameter. Recently, we have shown to a good first order approximation [8], that ^{19}F NMR polar field effects can be considered the net result of an additive blend of contributions due to the F_D and F_π mechanisms. Therefore, accepting a proportionality constant of 1.4 for the linear relationship between F_π induced ^{19}F and ^{13}C SCS [7], the F_D contribution to the ^{19}F SCS of fluorine for the $Cr(CO)_3$ complex of system 2 (Table 6) is estimated to be 0.33 ppm (0.46 ppm = 0.09 × 1.4 ppm + F_D). Utilizing structural and molecular parameters as previously indicated [7], then the A value for the Buckingham equation (SCS = AE_z) [35] for the effects of a uniform electric field on ^{19}F chemical shifts of fluoroarenetricarbonylchromium derivatives is calculated to be 46.6×10^{-12} esu. It is of interest to note that this constant is considerably larger than the corresponding

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[*] This is evidenced by the similar magnitude of *para* ^{19}F SCS in the free ligand [5] and the corresponding $Cr(CO)_3$ complexes (Table 7) for weak inductive substituents with powerful conjugative electron-donating influences (OMe, NH_2 and Me). A similar situation also holds for the corresponding ^{13}C SCS [3,4, and 11].

parameter (31.0×10^{-12} esu) previously determined for uncomplexed arylfluorides [6,7]. Since, by definition, A is a measure of the ease of distortion of the π electron distribution along the C—F bond, the larger A value implies a smaller electronegativity differential between the sp^2 hybridized aryl carbon and fluorine in the complex than in the free ligand i.e. $Cr(CO)_3$ complexation increases the effective electronegativity of the aryl carbons in the ring. Interestingly, other evidence is available to support this conclusion [3] (vide infra). Alternatively, the significantly different A values for complexed and uncomplexed arylfluorides is a consequence of the neglect of the effective dielectric term in the electric field calculations.

Utilizing the aforementioned value for A (46.6×10^{-12} esu), the F_D contribution to the ^{19}F SCS of fluorine (Table 6) for the $Cr(CO)_3$ complex of system 3 is calculated to be +0.31 ppm (approx., expression for E_z) [6] or +0.34 ppm (exact expression for E_z) [6]. Since the appropriate ^{13}C SCS for fluorine (Table 2; C(3)) indicates that the F_π contribution here is approximately —0.31 ppm (—0.22 × 1.4 ppm), the ^{19}F SCS is calculated to be 0.00 or +0.03 ppm. Given the small numbers involved in the calculations as well as the limits of expectation of electric field calculations (due to the neglect of the effective dielectric term), the assumption that the proportionality constant relating ^{19}F and ^{13}C SCS (F_π effect) is not seriously perturbed on complexation and the neglect of mesomeric-field contributions, this result is in reasonable accord with the observed ^{19}F SCS (Table 6; +0.14 ppm). Most importantly, however, it clearly indicates that our earlier observation, namely, the pronounced attenuation of the ^{19}F SCS for fluorine in system 3 on complexation clearly has its origin in a negative contribution by F_π to the ^{19}F chemical shift. Similar calculations of ^{19}F SCS for OMe in the complexes of 2 and 3 are also of interest, although there is more uncertainty in the bond dipole moment parameter of the C—O bond and the origin of the electric field associated with it. However, by employing a bond dipole moment value of 0.87 D (determined from 1-methoxyadamantane) [36] and assuming its location as a point dipole centered on O (C—O bond length equals 1.4 Å), appropriate substitution in the Buckingham equation leads to F_D contributions of +0.15 and 0.14 ppm to the ^{19}F SCS (OMe) for the complexes of 2 and 3, respectively. It can be seen that these agree very well indeed with the observed results (Table 6; +0.20 ppm ($c\text{-}C_6H_{12}$) for both $Cr(CO)_3$ complexes of 2 and 3) and, thus, corroborates the validity of our simple approach. The fact that the ^{19}F SCS for OCH_3 in both the complexed systems (2 and 3) are equal implies that no polarizing contribution due to F_π is apparently in operation. We can only conclude that the latter effect is masked by conformational factors of the type discussed above for the corresponding ^{13}C SCS. Note that the latter parameters for OMe (Table 2) indicate no significant differential π polarization (expected for a σ_I effect) between the carbon centers (C(4) and C(3)) to which fluorine is attached.

The perturbation of the conformational equilibrium (A $\rightleftharpoons$ B) by bridgehead-substitution with OMe in $c\text{-}C_6H_{12}$ as solvent (non-polar and chemically inert) appears to support the conjecture (vide supra) that unfavourable nonbonded interactions at the bridgehead are responsible. However, the puzzling trends for the ^{19}F SCS of OMe in the complexes of 2 and 3 on changing the solvent from $c\text{-}C_6H_{12}$ to CH_2Cl_2 (Table 6) suggests the possible importance of solvent effects

TABLE 7

^{19}F SUBSTITUENT CHEMICAL SHIFTS (SCS, ppm) [a] OF *META*- AND *PARA*-SUBSTITUTED η^6-FLUOROPHENYLTRICARBONYLCHROMIUM(0) DERIVATIVES

Substituent, X	CH_2Cl_2 [b]		$HCCl_3$ [c]		C_6H_6 [d]	
	meta	*para*	*meta*	*para*	*meta*	*para*
F		−6.49		−6.59	(−0.5) [e]	−6.60 (1.9) [e]
Cl	−2.40	−4.18	−2.45	−4.34	−2.16 (−0.7) [e]	−4.36 (−1.3) [e]
OMe	−1.97	−9.28	−2.01	−9.17	−2.14 (−0.8) [e]	−9.15 (−6.5) [e]
NH_2	−1.86	−12.55	−1.86	−12.24	−2.09 (−0.4) [e]	−12.52 (−10.3) [e]
Me	−1.32	−4.06	−1.31	−3.98	−1.28 (0.6) [e]	−4.01 (−1.9) [e]
t-Bu		− 2.80		−2.99		−2.99
CF_3					(0.1) [e]	(2.4) [e]

[a] Accurate to at least ±0.05 ppm. Positive sign implies deshielding. [b] Relative to parent (X = H): δ (internal C_6F_6) + 29.22 ppm. [c] Relative to parent (X = H): δ (internal C_6F_6) + 29.02 ppm. [d] Relative to parent (X = H): δ (internal C_6F_6) + 29.51 ppm; δ (internal $FCCl_3$) — 133.52 ppm. [e] Taken from ref. 1.

as well on the conformational equilibrium (A ⇌ B). An additional interesting result from Table 6 concerns the effect of $Cr(CO)_3$ complexation on the ^{19}F SCS for Me ($\sigma_I = 0$) [9] in system 2. Previously [9], we attributed the "anomalous" downfield shift by Me substitution in system 2 to a small but significant change in the hyperconjugative interaction between the phenyl and bicyclo[2.2.2]octyl moieties *. The fact that $Cr(CO)_3$ complexation has little influence on the transmission of mesomeric effects in the *para* disposition [1,3,4] suggests that a similar downfield shift for Me should have been observed in the $Cr(CO)_3$ complex of 2. Again, it seems necessary to invoke conformational factors to account for the ^{19}F SCS of Me in the latter system (Table 6; 0.00 ppm). An examination of the corresponding ^{13}C SCS for Me in system 1 and its complex (Table 2), although small, suggests that this may not be unreasonable.

Finally, we come to the results of a re-examination of the ^{19}F chemical shifts of *meta*- and *para*-substituted fluorophenyltricarbonylchromium derivatives. These are assembled in Table 7 together with those previously reported by McGlinchey et al. [1]. It can be seen that, although there are substantial discrepancies between the two sets of results, the overall trends are similar, there being a relatively constant differential (2.5 ± 0.6 ppm) between each result except for the *para* fluorine substituent. Although it is possible to ascribe most of the discrepancies to an incorrect value for the ^{19}F chemical shift of fluorophenyltricarbonylchromium (parent system (X = H) for determining ^{19}F SCS) quoted by McClinchey and coworkers [1] (δ (internal $FCCl_3$, benzene as solvent) 135.9 ppm; see footnote *d*, Table 7), the ^{19}F SCS for *para* fluorine (+1.9 ppm) determined from the results of these workers [1] is definitely spurious. This is surprising since McGlinchey et al. drew attention to this "anomalous" result and, in fact, claimed to have resynthesized the complex several times and, each time, the infrared and mass spectral information appeared normal.

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* The origin of this perturbation is now believed [37] to be due to through-bond effects (coupling of the pseudo π orbitals of Me and the π system of phenyl via an appropriate orbital of π symmetry of the bicyclo[2.2.2]octane ring system, [33]) rather than structural phenomena as previously envisaged [9].

The ^{19}F SCS for *para* fluorine determined in this study must be considered definitive since the ^{13}C NMR spectra of the complex is in accord with the assigned structure (δ (ppm) ($DCCl_3$, relative to Me_4Si) 140.62, J(CF) = 264 Hz (C(1, 4); 79.81, 79.16, 79.08, 78.45 (C(2, 3)). However, it should be noted that the overall spectral pattern differed slightly from that for *p*-difluorobenzene (158.93, J(CF) = 242.40 and 3.81 Hz (C(1, 4); 117.10 (weak), 116.97, 116.27, 116.22, 115.53, 115.39 (weak) C(2, 3)). This is not unexpected since the intensities of ^{13}C resonances are known to be very sensitive to various magnetic phenomena and, moreover, $Cr(CO)_3$ complexation probably perturbs some of the pertinent coupling constants and relative chemical shifts governing the second order spectrum. It should be noted that the problems of spectral analysis for the second order spectrum of *p*-difluorobenzene has been dealt with by Roberts et al. [38]. Although long range ^{13}C—^{19}F coupling constants in aromatic systems are poorly understood [39], it is worth noting that, in contrast to the free ligand, no four-bond coupling (^4J(CF)) is observed in the $Cr(CO)_3$ complex of *p*-difluorobenzene. Interestingly, a similar situation holds for fluorobenzene [38] and its corresponding $Cr(CO)_3$ complex (Table 3).

Although we are aware of the limitations imposed on DSP correlative analyses of data covering a limited range of substituents [26], we have carried out such an analysis (eq. 7) of the *para* ^{19}F SCS (CH_2Cl_2) listed in Table 7 in order to provide some semi-quantitative insight into the effects of $Cr(CO)_3$ complexation on substituent electronic phenomena determining ^{19}F SCS in these systems. For comparison purposes we have listed the analogous correlative equation of the ^{19}F SCS (CCl_4) of uncomplexed *p*-substituted fluorobenzenes (eq. 8) [24].

$$^{19}\text{F SCS}(\textit{para}, \text{complexed}) = 2.46 \pm 1.61\sigma_I + 25.36 \pm 1.57\sigma_R^0 \qquad (7)$$

$$(n = 5; f = 10\%)$$

$$^{19}\text{F SCS}(\textit{para}, \text{uncomplexed}) = 7.02\sigma_I + 30.55\sigma_R^0 \qquad (f = 7.6\%) \qquad (8)$$

Assuming that conformational factors can be neglected in the $Cr(CO)_3$ complexes, which seems reasonable given the good precision of fit of the data (eq. 7) *, it can be seen that the relative magnitude of the ρ_R values (cf. eq. 7 and 8) corroborates the conclusion previously drawn from the corresponding ^{13}C SCS data [3,4] (vide supra), namely, that $Cr(CO)_3$ complexation does not seriously interfere with the transmission of resonance effects in this orientation. However, it can also be seen from the ρ_I values that the effect of substituent polarity on these ^{19}F SCS is much reduced on complexation. With respect to this latter phenomenon, the *meta* ^{19}F SCS of the $Cr(CO)_3$ complexes (Table 7) are of particular interest since there is no obvious relationship between these results and substituent parameters as evidenced by the utter failure of the DSP equation. In contrast, as mentioned in the introduction, *meta* ^{19}F SCS of the free ligand vary widely and are essentially directly proportional to substitu-

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* The extent to which conformational factors contribute to ^{19}F SCS in these systems is very difficult to gauge. Interestingly, unlike the situation for defining ^{13}C SCS relative to H, localization of the aryl carbon—chromium bonds exists in the parent system for determining ^{19}F SCS. Hence, contributions due to conformational factors may be minimized.

TABLE 8

ESTIMATES OF DIRECT FIELD (F_D) AND FIELD-INDUCED π POLARIZATION (F_π) CONTRIBUTIONS (ppm) TO ^{19}F SCS OF SOME *META*- AND *PARA*-SUBSTITUTED FLUOROPHENYLTRICARBONYLCHROMIUM(0) DERIVATIVES

Substituent	Orientation					
	meta			*para*		
	F_D	F_π [a]	$F_D + F_\pi$	F_D	F_π [a]	$F_D + F_\pi$
F	3.42	−3.40	+0.02	2.57	−1.03	1.54
Cl	3.07	−3.12	−0.05	2.35	−0.95	1.40
OCH_3	1.51	−1.83	−0.32	1.13	−0.56	0.57

[a] σ_I values taken from ref. 26.

ent polar parameters (eq. 9) [24]. It is of interest to assume then that the *meta* ^{19}F SCS for the $Cr(CO)_3$ complexes (Table 7) are also predominantly manifestations of polar phenomena (σ_I effect) and to attempt an analysis in terms of our

$$^{19}\text{F SCS}(\textit{meta}, \text{uncomplexed}) = 5.26\sigma_I + 0.81\sigma_R^0 \qquad (f = 21\%) \qquad (9)$$

simple model [7,8], namely, that polar ^{19}F SCS can be considered an additive blend of F_D and F_π effects. The results are set out in Table 8 together with an analogous treatment of polar contributions ($\rho_I\sigma_I$) to the *para* ^{19}F SCS of the complexes (eq. 7). F_D contributions (SCS = AE_z) were calculated utilizing the proportionality constant ($A = 46.6 \times 10^{-12}$ esu) derived above, and structural and molecular parameters previously indicated [7,8]. F_π contributions ($\rho_I\sigma_I$) are based on the ρ_I values provided by DSP dissection of the appropriate ^{13}C SCS data (eq. 1 and 4) and multiplying them by a proportionality constant of 1.4 for the linear relationship between ^{19}F (no F_D contribution) and ^{13}C SCS [7]. An examination of these results (Table 8) is most revealing. Firstly, it can be seen that the simple model provides estimates of polar contributions to the *para* ^{19}F SCS of the complexes which are in excellent accord with those derived from the $\rho_I\sigma_I$ term (ppm) of eq. 5 (F, 1.23; Cl, 1.13; OMe, 0.66). It seems inconceivable that this result can be simply dimissed as being fortuitous, hence, we believe compelling credence is given to the validity of the limited DSP dissection (eq. 5) of the *para* ^{19}F SCS in the complexes as well as the simple model for polar ^{19}F SCS [7]. Secondly, it can be seen that the model predicts that polar contributions to the *meta* ^{19}F SCS of the complexes should cover a very narrow range and, moreover, to appear totally unrelated to substituent polarity parameters [26,27]. These predictions are in remarkably good agreement with the observed trends in this orientation (Table 7). The origin of the "anomalous" trends for the *meta* ^{19}F SCS of fluorophenyltricarbonylchromium derivatives is, therefore, reminiscent of the situation previously disclosed [8,22] for the ^{19}F SCS of 4-substituted-2-fluoronaphthalenes (4β disposition) where contributions due to the F_D and F_π mechanisms to polar ^{19}F SCS are also clearly opposed. Since polar effects due to both F_D and F_π are directly proportional to the polar substituent parameter (σ_I) [6,7,8], the effects will tend to cancel out and the observed ^{19}F SCS will appear invariant to substituent polarity. Of course, the actual sign of the ^{19}F SCS will depend on the relative magnitude of F_D and F_π, which depends importantly on the nature of the substrate as well as the substituent disposition [7,8]. In the 4β disposition of naphthalene F_D is, in general, greater than F_π and, consequently, the net ^{19}F SCS are positive. However, in the *meta* disposition of the $Cr(CO)_3$ complex of fluorobenzene, F_π is dominant and the net ^{19}F SCS are negative.

A further interesting point from Table 7 is the relative magnitude of the *para* ^{19}F SCS for t-Bu and Me. Since the corresponding ^{19}F SCS for these alkyl groups are similar in the free ligand [40], this result for the complexed ligand must be a manifestation of the considerably different degree of localization of the aryl carbon—chromium bonds in the two alkyl derivatives. This was expected on the basis of the corresponding ^{13}C SCS (vide supra) [11,29].

Substituent parameters for $C_6H_5 \cdot Cr(CO)_3$

The observed ^{19}F SCS (CH_2Cl_2) for $C_6H_5 \cdot Cr(CO)_3$ and C_6H_5 in system 2 are +0.76 and +0.40 ppm, respectively (accurate to better than ±0.01 ppm). Therefore, based on the known polar susceptibility parameter ($\rho_I(CH_2Cl_2) = 2.19$) for the model system, the σ_I values for $C_6H_5 \cdot Cr(CO)_3$ and C_6H_5 substituents attached to an sp^3 hybridized carbon center are +0.35 and +0.18, respectively. Thus, this unequivocal result confirms the conclusion of Gubin et al. [41] and others [3,42] that coordination of the benzene ring with $Cr(CO)_3$ enhances the electron-withdrawing effect of the phenyl substituent. However, it should be noted that the σ_I values determined from system 2 differ significantly from those reported by Gubin et al. ($C_6H_5 \cdot Cr(CO)_3$, +0.21; C_6H_5, +0.10) [41] which were obtained by Taft's fluorophenyl technique [5]. This is to be expected since, by definition, the inductive parameter (σ_I) provides a measure of the field effect (F) of a substituent which is predominantly proportional to the dipole moment of the substituent group as a whole (vectorial summation of all relevant bond moments) [43]. Hence, the two sets of σ_I values reflect the hybridization state of the two carbon centers (sp^3 versus sp^2) at the point of attachment of the substituent in the two different model systems. The overall results are clearly associated with an increase in the effective electronegativity of the carbons in the arene ring skeleton on complexation.

It is of interest to note that further confirmation of the greater electron-withdrawing inductive field effect of $C_6H_5 \cdot Cr(CO)_3$ versus C_6H_5 is provided by the significant upfield shift (—1.44 ppm) of the fluorine nucleus in 1 where X = F (δ (internal $FCCl_3$) —152.77 ppm (CCl_4); δ (external $FCCl_3$) —150.35 ppm (CCl_4)) [12] on complexation of the phenyl group with $Cr(CO)_3$ (δ (internal $FCCl_3$) —154.21 ppm (CCl_4); δ (external $FCCl_3$) —151.76 ppm (CCl_4)). Note that this system displays inverse substituent effect behaviour [12] i.e. inductive electron-withdrawal is manifested by an upfield shift [44].

The *para* ^{13}C SCS ($DCCl_3$) of the benzene ring system for $C_6H_5 \cdot Cr(CO)_3$ as a substituent group may be calculated from the appropriate ^{13}C chemical shift (C(4)') of biphenyltricarbonylchromium (Table 3; +0.72 ppm). Substitution of this SCS in the appropriate DSP correlative equation (eq. 5) and using the σ_I value (+0.21) of Gubin and coworkers [41], leads to a σ_R^0 value of —0.01 which is in reasonable accord with the value (—0.04 [41] determined with the fluorophenyl tag [5]. However, it is possible that the latter result may manifest the presence of the fluorine probe. Given that the σ_R^0 value for C_6H_5 is similarly calculated to be -0.07 (p-^{13}C SCS for $C_6H_5 = -1.14$ [45], $\sigma_I = 0.10$ [41]), it is clear that $Cr(CO)_3$ complexation almost eliminates the weak "electron-donating" (may not involve charge transfer) [46] resonance capacity, in the neutral ground state, of the phenyl substituent (Taft et al. [26] report a σ_R^0 value of -0.11 for C_6H_5).

Conclusion

The main points to emerge from this study are two-fold. Firstly, the dual nature of aryl ^{19}F NMR polar field effects ($F_D + F_\pi$) is reaffirmed [6,7,8]. This is pertinent since recent skepticism has been expressed concerning the significance of direct field (F_D) contributions to aryl ^{19}F SCS [20,47]. Secondly, the "anomalous" ^{19}F SCS of *meta*-substituted fluorophenyltricarbonylchromium derivatives have been clearly shown to have their origin in polar electronic mechanisms (F_D and F_π) which involve the π electrons of the complexed arylfluoride and not the σ electrons as previously envisaged. Hence, experimental support for a simple model of the chemical bond between arenes and the $Cr(CO)_3$ moiety [1,3,41,42], in which considerable emphasis is placed on the participation by the σ electrons of the arene skeletal framework, has been seriously undermind. An examination of the other available supporting chemical and physical experimental evidence for this model [3,41,42], all being essentially manifestations of the enhanced effective electronegativity of the carbons in the arene ring skeleton, suggests that it hangs on very tenuous evidence indeed, since the enhanced effective electronegativity can be readily rationalised in terms of π electron-withdrawal from the arene ring [48]. We believe a qualitative description of the arene—$Cr(CO)_3$ chemical bond in terms of only the π electrons of the arene ring [49], rather than invocation of σ electrons as well, is preferable.

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