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ARENE-CHROMIUM TRICARBONYL COMPLEXES: BONDING AND BEHAVIOUR

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CONTENTS

I.	NATURE OF BONDING	901
	A. Spectroscopic properties	901
	(a) IR	901
	(b) NMR	903
	B. Electronic effects.	904
	(a) Dipole moments	904
	(b) Inductive effects.	906
	(c) Stabilization of a positive charge in α - or β -position	907
	(d) Stabilization of a negative charge in α - or β -position .	909
	(e) Basicity of benzylic protons vs aromatic protons	911
	(f) Metallation	912
		/12
	C. Theoretical calculations	913
	(a) SCCC MO	913
	(b) $CNDO/2$	914
	(c) Ab initio	914
II.	CHARGE-TRANSFER COMPLEXES	915
III.	CONFORMATIONS	916
	A. Conformation of the tripod	016
	B. Conformation of substituents	919
137	STEREOFI FOTBONIC CONTROL OF THE RECIONELECTIVITY	
17.	STEREOELECTRUNIC CUNTROL OF THE REGIOSELECTIVITY	920
		920
	B. Electrophilic reactions.	922
V.	COMPLEXATION SITE ON DIAROMATIC LIGANDS	923

I. NATURE OF BONDING

A. Spectroscopic properties

(a) IR. The IR spectra of substituted and nonsubstituted benzene chromium tricarbonyl complexes have been extensively studied and reviewed.¹ This paper will focus on the carbonyl stretching frequencies and will give only the main conclusions.

All the complexes have two IR active stretching vibrations for the terminal carbonyl groups in agreement with the C_{3v} local symmetry (Tables 1 and 2). However, when high-resolution spectra are studied, and when unsymmetrically substituted arenes are involved, this C_{3v} local symmetry is of more restricted validity.

Here the degenerate $(E)v_{co}$ band is split^{2,3} but the splitting is small [≤ 10 cm⁻¹ (Table 3)].

The IR absorptions of the $Cr(CO)_3$ groups are sensitive to the electronic effects of the substituent of the arene ligand transmitted through the metal to the carbonyls of the $Cr(CO)_3$ group^{2,4-12} (Tables 1

R	A_1 (cm ⁻¹)	E (cm ⁻¹)	Ref.	Solvent
	1992	1930	8	Isooctane
Cl	1992	1931	6	Cyclohexane
Н	1987	1918	6	Cyclohexane
CH ₃	1983	1914	2	Cyclohexane
$CH = CH_2$	1980	1913	9	Cyclohexane
CH ₂ -CH=CH ₂	1977	1906	11	Cyclohexane
OMe	1975	1903	5	CCl₄
OMe	1983	1914	6	Cyclohexane
OCH ₂ CH=CH ₂	1976	1906	11	Cyclohexane
NH ₂	1974	1902	6	Cyclohexane

Table 1. v_{CO} of Cr(CO)₃ group in (C₆H₅R)Cr(CO)₃

Table 2. v_{CO} of Cr(CO)₃ group in (C₆H₄R₁R₂)Cr(CO)₃

R ₁	R ₂	$\begin{array}{c}A_{1\max}\\(\mathrm{cm}^{-1})\end{array}$	E_{\max} (cm ⁻¹)	Ref.	Solvent
CO ₂ Me	2-Cl	1996 vs	1936 s	4	CCl₄
CO ₂ Me	н	1990 vs	1926 s	4	CCl4
$\overline{\rm CO_2Me}$	н	1992 vs	1930 s	8	Isooctane
CO ₂ Me	2-Me	1984 vs	1920 s	4	CCl₄
CO ₂ Me	2-Me	1988 vs	1925 s	8	Isooctane
CO ₂ Me	2-OMe	1984 vs	1920 s	4.	CCl₄
CO ₂ Me	2-OMe	1987 vs	1924, 1917	8	Isooctane
CO ₂ Me	4-NH ₂	1978 vs	1912 s	4	CCl₄
н	$CH = CH_2$	1980 vs	1913 vs	9	Cyclohexane
OMe	2-OMe	1969 vs	1894 vs	5	CCl ₄
NH ₂	4-NH2	1942 vs	1855 vs	12	THF
NH ₂	$2-NH_2$	1942 vs	1848-1808	12	Br
сно	н	1970 vs	1895 s	10	CHCl ₃
CHO	2-Me	1970 vs	1895 s	10	CHCl ₃
СНО	2-OMe	1975 vs	1900 s	10	CHCl ₃

Table 3. v_{CO} of Cr(CO)₃ group in LCr(CO)₃

L .	$\begin{array}{c} A_{1\max} \\ (\mathrm{cm}^{-1}) \end{array}$	$\frac{E_{\max}}{(\mathrm{cm}^{-1})}$	Solvent
C ₆ H ₆	1983 vs	1915 vvs	Cyclohexane (A)
0 0	1970 vs	1891 vvs	CH_2Cl_2 (B)
C ₆ H ₄ F	1990 vs	1926 vs, 1923 vs	Α
0 5	1979 vs	1902 vvs	В
C ₆ H ₅ Me	1977 vvs	1911 vs, 1909 vs	Α
0 5	1968 vs	1886 vvs	В
1,2-MeC ₆ H₄	1973 s	1906 s, 1901 vs	Α
, , ,	1964 vs	1884 vs	B
1,2,3-MeC ₆ H ₃	1969 vs	1902 vs, 1895 vs	Α
	1958 vs	1877 vvs	В

Ar	L	$A_1 (\mathrm{cm}^{-1}) (\Delta \nu)^*$	$E (\mathrm{cm}^{-1}) (\Delta v)^*$	Solvent	Ref.
Me ₃ C ₆ H ₃	P(Ph) ₃	1886 (76)	1830 (48)	C ₆ H ₆	14
Me ₃ C ₆ H ₃	$CH_{2} = CH_{2}$	1901 (61)	1852 (26)	C ₆ H ₆	14
Me ₃ C ₆ H ₃	Cyclopentene	1893 (69)	1842 (36)	C ₆ H ₆	14
Me ₆ C ₆	P(Ph) ₃	1873 (75)	1810 (51)	C ₆ H ₆	14
Me ₆ C ₆	CH,=CH,	1890 (58)	1835 (26)	C ₆ H ₆	14
0 0	~ -	1883 (65)	1835 (26)	C ₆ H ₆	14, 18
$C_{6}H_{4}(CH_{2})_{2}CH=CH_{2}$	P(Ph) ₁	1905 (72)	1856 (50)	Hexane	15
$C_6H_6(OCH_2)CH=CH_2$	$P(Ph)_3$	1905 (71)	1854 (52)	Hexane	15
C ₆ H ₄ CO ₂ Me	P(Ph) ₃	1896 (89)	1844 (41)	Nujol	16
	P(OMe) ₃	1910 (75)	1848 (37)	Nujol	16

Table 4. v_{co} of CrCO₂ in ArCO₂L

* $\Delta v = v [ArCr(CO)_3] - v [ArCr(CO)_2L].$

and 2). The frequencies and the force constants calculated using the approach proposed by Cotton¹³ are found to decrease slightly as the electron-donating power of the substituent increases. However there is practically no influence due to the relative position of the substituents within the ring.^{4,5} Good correlations are also found between the force constant of the carbonyl (or the stretching frequencies) and the different Hammett constants of the substituents.^{4,5,7} This behaviour indicates that an increase in π -electron density enables the chromium atom to transfer electrons into the antibonding orbitals of the C \equiv O groups, thus decreasing the CO bond order.

A decrease in the v_{CO} frequencies is also observed when one of the C=O is replaced by a phosphine, ¹⁴⁻¹⁶ an imine¹⁷ or an olefin^{11,14,18} (see Tables 4 and 5). Phosphines, imines and olefins are electron-releasing substituents which increase electron density on the chromium atom. Back-donation from the chromium atom occurs into the antibonding orbitals of the two remaining C=O and thus decreases the CO bond order. Empty *d*-orbitals of the phospine as well as π -antibonding orbitals of the imines or olefins are obviously less available than those of C=O for such back-bonding.

However, it must be noticed that replacement of one C \equiv O by malic anhydride increases the frequency of the E band by 20-28 cm⁻¹, the A-band being constant.^{19,20}

(b) NMR. The most obvious characteristic of the ¹H, ¹³C and ¹⁹F NMR spectra is the upfield shift of the corresponding resonance upon complexation.

	$A_1 (\mathrm{cm}^{-1}) (\Delta \nu)$	$E (\mathrm{cm}^{-1}) (\Delta v)$	Solvent	Ref.
(a) $[C_6H_5(CH_2)_2CH=CH_2]Cr(CO)_2$	1930 (43)	1878 (28)	C ₆ H ₁₂	11
(b) $[C_6H_5OCH_2CH=CH_2]Cr(CO)_2$	1938 (38)	1885 (21)	C_6H_{12}	11
(c) $[C_6H_5(CH_2)_3CH=CH_2]Cr(CO)_2$	1923 (54)	1871 (35)	C_6H_{12}	11
(d) $[C_6H_6(CH_2)_2CH(Ph)=NPh]Cr(CO)_2$	1890 (75)	1830 (55)	C ₆ H ₆	17
(e) $[C_6H_5(CH_2)_3CH(Ph)=NPh]Cr(CO)_2$	1888 (82)	1830 (65)	C ₆ H ₆	17





On complexation with $Cr(CO)_3$ aromatic protons undergo an upfield shift of about 1.5–2.5 ppm.^{4-6,21,22} Some hypotheses were proposed to explain this diamagnetic shift. The upfield shift could be ascribed to a decrease of the "ring current" contribution to the chemical shift.²³ However, it has been shown that vinylic protons also undergo a 3–3.7 ppm upfield shift on complexation,¹¹ and that complexation with $Cr(CO)_3$ of compound 1 (to 2) does not disrupt the aromatic ring current as the chemical shift of $H_a(\delta_a)$ does not change.²⁴



Some recent X-ray and neutron diffraction data^{25,26} showed a slightly distorted ring, the hydrogen being displaced by $2-4 \times 10^{-2}$ Å from the ring towards the chromium; however, the ¹H proton spectrum with ¹³C satellites of benzene–Cr(CO)₃ oriented in a nematic phase does not allow the detection of such a deviation.²⁷ Hence, a change in hybridization may not be the only factor responsible for the shielding. It has been proposed that the magnetic anisotropy of the Cr(CO)₃ moiety and of the electrons in the ring–metal bond could produce an upfield shift of the ring proton resonance of the same order of magnitude as the observed shift.²⁸ This last hypothesis has not yet been refuted.

The most obvious features of the ¹³C spectra are the large upfield shift—30-40 ppm—of the ringcarbon resonances, and the large downfield shift of the carbonyl-carbon resonances (relative to the uncomplexed C=O).^{29–31} This ring-carbon diamagnetic shift was first related to the change in mobile bond order.²⁹ Then changes in hybridization of the carbons (associated with the use of π -orbitals for σ bonding with metal *d*-orbitals) were invoked.³⁰ It is also possible to account for the observed chemical shifts by postulating the presence of a negative charge on the complexed aromatic ring. But this approach requires the transfer of approximately one electron from the metal to the arene ligand.³¹ More recently ¹³C NMR paramagnetic shielding constants have been calculated using the SCCO MO method and the Pople–Karplus equation.³² Although only a fair agreement is obtained between the calculated σ^{p} -values and observed shifts, it is gratifying to note that, in the case of benzene, an upfield shift is predicted as observed on complexation and that a downfield shift is predicted for the carbonyl carbon as observed (relative to free CO).

It is interesting to note that the ¹³C resonance of methyls substituted in the ring are almost unaffected by the complexation.^{24–31} It must be noted also that on complexation olefinic carbon resonances are also usually shielded, the same mechanisms being invoked to explain this behaviour.^{33–37}

A correlation has been observed between the ¹³C carbonyl chemical shifts and either the weighted average of the force constant³¹ (calculated using the approach of Cotton¹³) or the carbonyl stretching frequencies³⁸ for a series of arene–Cr(CO)₃. The carbonyl resonance is deshielded when the electrondonating power of the substituent increases, that is with increasing electron density on the Cr(CO)₃ group. Thus, it has been proposed that the carbonyl chemical shift reflects the extent of transition metal $\rightarrow \pi^*$ carbonyl back-donation. The study of the transmission of the substituent effects from the arene ring to the Cr(CO)₃ group via an analysis of the carbonyl resonance shows a slight predominance of inductive effects and agrees with an important overlap of the metal orbitals with the σ -framework of the arene.³⁹

A large upfield shift of about 20 ppm has been observed on complexation with $Cr(CO)_3$ of fluorobenzene⁴⁰ for the ¹⁹F resonance signal. Such a large shift cannot be explained by the magnetic anisotropy of the $Cr(CO)_3$ moiety alone, which should equivalently contribute to the chemical shift of ¹⁹F and ¹H (~ -2 ppm). However, as for ¹³C, the paramagnetic term of the shielding constant contributes much to the chemical shift of ¹⁹F, and changes in hybridization of the vicinal carbon upon complexation might also have a large influence on the ¹⁹F chemical shift.

B. Electronic effects

(a) Dipole moments. Electric dipole moments of arene-(CO)₃ complexes, measured in benzene solution, are quite large: ranging from 3.5 to 6.3 D^{41-45} (Tables 6 and 7).

Ligand	Dipole moment (D) (Ref.)	Averaged value
C ₆ H ₆	4.81 (43)	
	4.92 (41)	4.07
	5.08 (42)	4.90
	5.03 (44)	,
C ₆ H ₅ Cl	4.25 (43)	A.C.C.
• •	5.08 (42)	4.00
C ₆ H ₅ F	4.75 (41)	4.02
	4.91 (42)	4.83
C ₆ H ₅ Me	5.20 (41)	5.00
	5.26 (42)	5.23
C ₆ H ₅ OMe	5.26 (41)	5.24
	5.43 (42)	5.54
C ₆ H ₅ NMe ₂	6.30 (42)	6.24
	6.18 (44)	0.24
C ₆ H ₅ NH ₂	5.40 (41)	<i></i>
	5.50 (44)	5.45
C ₆ H ₅ COMe	4.97 (44)	4.97
C ₆ H ₅ CO ₂ Me	4.47 (41)	4.47

Table 6. Dipole moments of	arene-Cr(CO) ₃ measured in
benzene	solution

According to the IR results (see above), to the numerous studies of the inductive effect of the $Cr(CO)_3$ group and to theoretical data (see below) it is well accepted that in arene– $Cr(CO)_3$ complexes there is a transfer of electrons from the arene ligand through the metal to the carbonyl groups. Hence, owing to the molecular structure, as revealed by X-ray diffraction studies,⁴⁶ benzene– $Cr(CO)_3$ has a dipole moment directed along the tricarbonyl C_3 -axis and oriented from the arene group to the tripod.^{42,44}

The dipole moment of a monosubstituted-benzene- $Cr(CO)_3$ complex is not an additive vector, in that it differs from the vectorial sum μ [benzene- $Cr(CO)_3$] + $\mu(C_6H_5X) = \mu_o + \mu_x$. Both components μ_o and μ_x adopt modified values in the complex.⁴⁴

According to the values of the dipole moments obtained for symmetrically *p*-disubstituted benzene– Cr(CO)₃ complexes, where the μ_x -component is 0 (Table 7), it is quite clear that electron-donating

Ligand	Dipole moment (D) (Ref.)
	4.81 (43)
C II	4.92 (41)
C ₆ H ₆	5.08 (42)
	5.03 (43)
	5.39 (41)
$p-Me_2C_6H_4$	5.52 (42)
	5.41 (43)
$p-(\mathrm{NH}_2)_2\mathrm{C}_6\mathrm{H}_4$	5.52 (44)
$p-(CO_2Me)_2C_6H_4$	3.52 (43)

Table 7. Dipole moments of arene-Cr(CO)₃ measured in benzene solution

Table 8.
$$pK_4^{46}$$

C ₆ H ₅ —CO ₂ H 3	C ₆ H ₅ CO ₂ H Cr(CO) ₃ 4	$p-NO_2-C_6H_4-CO_2H 5$
5.68	4.77	4.48
C ₆ H ₅ —CH ₂ CO ₂ H 6	C ₆ H ₅ CH ₂ CO ₂ H Cr(CO) ₃ 7	<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ CO ₂ H 8
5.64	5.02	5.01

substituents increase the μ_o -component while electron-withdrawing substituents decrease the μ_o -component.⁴²⁻⁴⁴

Hence the μ_o dipole moment component reflects the electron transfer from the ring to the carbonyls through the metal. However, in the case of disymmetric complexes the μ_x -component must be estimated first.⁴⁴

(b) Inductive effects. Since the first synthesis of $C_6H_6Cr(CO)_3$ by Fischer^{47(a)} and Nicholls^{47(b)} the Cr(CO)₃ group has often been compared with the NO₂ group.

In 1959 the comparison of pK_A values of uncomplexed, complexed and p-NO₂-substituted acids (Table 8) led Whiting *et al.*⁴⁶ to the conclusion that the Cr(CO)₃ group has the same inductive effect as the NO₂ group.

However, the NO₂ group must have an extra capability to stabilize negative charges by resonance as the pK_A of 5 (4.48) is smaller than the pK_A of 4 (4.77).

It was already known that the $Cr(CO)_3$ group exerted a net electron-withdrawing effect on the ring as aniline– $Cr(CO)_3$ is a weaker base than aniline.⁴⁸

Studying the polarographic oxidation of ferrocenyl compounds 9 and 10 according to eqn (1) Khandkarova *et al.*⁴⁹ found that the redox potential increases by 90–100 mV from 9 to 10 which confirms the inductive effect of the $Cr(CO)_3$ group:

9 or
$$10 \xrightarrow{-e} 9^+$$
 or 10^+ . (1)



A highly positive inductive aromatic constant, $\sigma_i = +0.31$, has been calculated for the $C_6H_5Cr(CO)_3$ group, close to that of strong electron-withdrawing substituents such as COMe (+0.28) and CHO (+0.31), but the main result of this study is the fact that coordination of the phenyl ring in 9 with the $Cr(CO)_3$ group giving 10 considerably influences the effective positive charge of the aromatic ring σ -carbon orbitals, thus increasing its electronegativity. Therefore, it should be accepted that coordination with the metal concerns the σ - rather than the π -orbitals of the ligand. This would be consistent with the general theory of the bond in the transition metal π -complexes developed by Chatt and Duncanson,⁵⁰ where there might be mutual compensation between direct donor-acceptor interaction from the ligand to the metal and back-donation from the metal to the ligand, resulting in an almost invariant π -electron density in the benzene molecule upon coordination.

The changes in chemical shifts of the fluorine atom in fluorobenzene on substitution with a $C_6H_5Cr(CO)_3$ group⁵¹ (Table 9) are consistent with an electron-withdrawing effect of a $C_6H_5Cr(CO)_3$ group.

Table 9. ¹⁹F NMR : $FC_6H_5 \rightarrow FC_6H_4$ —R

R	$m-C_6H_5$	p-C ₆ H ₅	$m-C_6H_5Cr(CO)_3$	$p-C_6H_5Cr(CO)_3$
$\Delta \delta_F^*$	+0.05	+ 2.97	-0.66	-0.55

* $\Delta \delta_F = \delta_F$ (fluorobenzene) $- \delta_F$ (substituted fluorobenzene) (ppm).

Log k _{sol}	Log k _{ml}
(free)	(complexed)
-0.1952	
-1.5952	+0.1072
-1.3686	+0.3483
1.8996	
- 2.0969	-0.2034
-2.5100	-0.5045
-3.5686	-1.5467
	$\begin{array}{c} \text{Log } k_{\text{sol}} \\ \text{(free)} \end{array}$ $\begin{array}{c} -0.1952 \\ -1.5952 \\ -1.3686 \\ -1.8996 \\ -2.0969 \\ -2.5100 \\ -3.5686 \end{array}$

Table 10.

Estimation of the σ_i inductive and σ_R resonance constants gives +0.21 and -0.04. Comparison with the values obtained for C₆H₅ (+0.10 and -0.09) leads to the conclusion that there is a significant increase in the phenyl electron-withdrawing ability of the inductive type, whereas its tendency to conjugation is almost the same. In other words these results again suggest that coordination of benzene with the Cr(CO)₃ group essentially changes the effective positive charge on the σ -carbon orbitals of the aromatic ring while the total π -electron density changes negligibly.

Base-catalyzed hydrolysis of a number of substituted methyl benzoates uncomplexed and complexed with $Cr(CO)_3^{52}$ (Table 10) showed that the chromium complexes reacted considerably faster than the uncomplexed arene. The effect of the $Cr(CO)_3$ group on ester hydrolysis is almost exactly equal to that of a *p*-NO₂ group (log k = -0.2034 and -0.1952 respectively). The enhanced reactivity of complexed benzoic esters can be best explained by a decreased electron density at the electrophilic centre and so by an increasing effective positive charge of the aromatic ring σ -carbon orbitals.

(c) Stabilization of a positive charge in α or β -position. Electronic spectra of complexed cation 11 have been measured in degassed 80% sulphuric acid and dilute solutions.⁵³ Determination of pK_{R^+} , eqn (2), by Deno's method⁵⁴ shows that the complexed cation 11 is more stable ($pK_{R^+} = -11.8$) than the uncomplexed cation 12 ($pK_{R^+} = -17.3$) and that a donor substituent in the para position on the complexed ring again increases the stability of cation 11 (p-Me, $pK_{R^+} = -11.0$; p-OMe, $pK_{R^+} = -10.2$):

$$\begin{array}{c} & \bigoplus_{i=1}^{n-1} -cH_2 + H_2 O & \longrightarrow_{i=1}^{n-1} & \bigoplus_{i=1}^{n-1} -cH_2 O H + H^+ \\ & fr(CO)_3 & & fr(CO)_3 \\ & 11 & & fr(CO)_3 \\ & & fr(CO)_3 & & fr(CO)_3 \\ & & fr(C$$

with $K_{R^+} = [alcohol][H^+]/[cation].$

Complex cations such as 13a and 13b also proved to be more stable than the uncomplexed one⁵⁵ [eqn (3) and Table 11]:

$$(3)$$

$$(3)$$

$$(3)$$

$$(3)$$

$$(3)$$

$$(3)$$

$$(3)$$

$$(3)$$

Z	рК _{вн+} (free)*	рК _{вн+} (complexed)*	
н	-7.11	- 5.46	
Ph	-6.13	- 5.68	
Me	- 5.91	- 5.96	

Table 11.

* $K_{BH^+} = [B][H^+]/[BH^+], B = aldehyde or ketone.$

However, the behaviour of methyl is not very clear.

In solvolysis reactions (SN_1) a positive charge develops at the carbon which undergoes the reaction in the transition state and they provide good models to study the stabilization of a positive charge in the α -position.

Holmes *et al.*⁵⁶ have shown that solvolysis of benzyl chloride– $Cr(CO)_3$ is 10⁵ faster than the solvolysis of the uncomplexed benzyl chloride, the most reasonable explanation for this rate enhancement being a preferential stabilization of the cation intermediate due to increased back-donation from the chromium atom to the ligand.

Solvolysis of π -(tricarbonyl chromium) cumyl chloride (14) and p-[π -(tricarbonyl chromium)phenyl] cumyl chloride (16)⁵⁷ (Table 12) shows also that the C₆H₅Cr(CO)₃ group stabilizes an α -carbonium ($k_{compl.}/k_{lig.} = 28$). However the C₆H₅Cr(CO)₃ substituent, when separated from the reaction centre by a phenyl, stabilizes the cation less than the uncomplexed phenyl ($k_{compl.}/k_{lig.} = 0.4$), probably because of its known electron-withdrawing ability.

INDO molecular orbital calculations have been carried out on the free benzyl carbonium ion and on the coordinated cation [(benzyl)Cr(CO)₃]⁺. The stability of the coordinated benzyl cation was shown to arise mainly via back-bonding from the chromium $d_{x^2-y^2}$ orbital into the non-bonding π -orbital of the benzyl ligand.⁵⁸

The remarkable stabilization of a positive charge on the α -carbon via back-bonding from the chromium is confirmed by ¹³C NMR results. At -50° C the *ortho*-carbons as well as the three carbonyl carbons of carbonium 18⁺ display complete non-equivalence : 103.2, 106.7, 226, 226.5 and 227.^{59(a)} And more recently Top and Jaouen^{59(b)} found that the Ritter reaction on optically active complex **18** leads to an optically active complex, **19**, with complete retention of configuration [eqn (4)]:



	Т	able 12.		
		$10^{5}k$ (s ⁻¹)	Tempera (°C)	ture
14	$(\mathbf{C})_{\mathbf{C}} = \mathbf{C}(\mathbf{M}\mathbf{e})_{\mathbf{z}}\mathbf{C}\mathbf{I}$	360	25	<i>L</i> (<i>L</i> _ 28
15	C(Me)2CI	13	25	$\kappa_{\rm compl.}/\kappa_{\rm lig.} = 28$
16		33.4	25	1 11 04
17		83.3	25	$\kappa_{\rm compl.}/\kappa_{\rm lig.} = 0.4$

Solvolysis of the syn-exo-2 isomer of (benzonorbornen-2-yl) tricarbonyl chromium pbromobenzenesulphonate, **20**, is 300 times faster than the solvolysis of **21**, the anti-exo-2 isomer, but the solvolysis of **21** is 400 times slower than the solvolysis of the free ligand **22**.^{60(a)} The enhancement of the rate of solvolysis from isomer **21** to isomer **20** may be attributed to a direct interaction of d-filled nonbonding orbitals of the metal with the $(+)\beta$ -carbon in the transition state. And the decrease of the rate of solvolysis from the free ligand **22** to the complex **21** may be explained by the fact that in complex **21** the π -electrons of the aromatic ring are less available for an hyperconjugative interaction with the vacant p-orbital of the $(+)\beta$ -carbon than in the free ligand **22**.



Ninety-four per cent retention of configuration obtained upon acetolysis of L-threo-3-[(phenyl) chromium tricarbonyl]-2-butyl methanesulfonate $23^{60(b),(c)}$ has also been attributed to a direct interaction of filled non-bonding *d*-orbitals of the metal with the $(+)\beta$ -carbon, 23'. However, the almost complete migration of the (phenyl) chromium tricarbonyl group during acetolysis of 2-[(phenyl) chromium tricarbonyl]-2-methyl-1-propyl methanesulphonate 24 must involve the cation 25.



(d) Stabilization of a negative charge in the α - or β -position. Base-catalysed elimination of 2-phenylethyl bromides and tosylates (E₂ type reaction) which develop a negative charge on the α -carbon in the transition state [eqn (5)] are good models for such studies:

$$\bigcirc - \operatorname{CH}_{\overline{z}} - \operatorname{CH}_{\overline{z}} - \operatorname{CH}_{\overline{z}} - \operatorname{CH}_{\overline{z}} - \operatorname{CH}_{\overline{z}} = \bigcirc -\operatorname{CH}_{\overline{z}} = \odot -\operatorname{CH}_{\overline{z}} = \bigcirc -\operatorname{CH}_{\overline{z}} = \odot -\operatorname{CH}_{\overline{z}} = \operatorname{CH}_{\overline{z}} = \odot -\operatorname{CH}_{\overline{z}} = \operatorname{CH}_{\overline{z}} = \operatorname{CH}_{\overline{$$

Kinetic studies of such elimination reactions on compound 26^{61} [Table 13 shows that the Cr(CO)₃ group must be regarded, like NO₂, as a strong electron-withdrawing group as the olefin percentage increases from 38% (X = H, Y = OTs) to 97% (X = π -Cr(CO)₃, Y = OTs) and 100% (X = NO₂, Y = OTs)].

Complexing the phenyl group with Cr(CO)₃ strongly increases the rate of elimination and the extent of the acceleration is not the same in both cases : $k_{Cr(CO)_3}/k_H = 142$ for OTs and 37 for Br. This difference probably originates in the different amount of negative charge present on the α -carbon in the transition states. The same effect occurs with NO₂; $k_{NO_2}/k_H = 4020$ for OTS and 1970 for Br. However there is a substantial difference between the kinetic effects of Cr(CO)₃ and NO₂; $k_{Cr(CO)_3}/k_H = 142$ but k_{NO_2}/k_H = 4020 for OTs and $k_{Cr(CO)_3}/k_H = 37$ but $k_{NO_2}/K_H = 1970$ for Br. This arises from a lower capacity of

X	Y	Temperature (°C)	$10^{3}k_{el.}$ (l m ⁻¹ s ⁻¹)
Н	Br	40	1.20
NO ₂	Br	40	2370
π -Cr(CO) ₃	Br	96	290
H ·	OTs	40	0.16
NO ₂	OTs	40	643
π -Cr(CO) ₃	OTs	42	29.1

 $Cr(CO)_3$ to stabilize a developing negative charge at the α -carbon. A direct resonance interaction between the negative charge on the α -carbon and the substituent is present in the case of the NO₂ group but is absent when $Cr(CO)_3$ is involved. Hence it seems again that the transmission of the electronic effect through the ring involves mainly the σ -framework rather than the π -electron cloud. Kinetic studies of elimination reactions on compound 27 (Table 14) give consistent results.^{62,63}

Table 14. E2 on compound 27 $x CH_2-CH-CH_3$							
x	Y	% olefin	$\frac{10^4 k_{\rm el.}}{(\rm l \ m^{-1} \ s^{-1})}$	Cis/trans	$k_{\rm Cr(CO)_3}/k_{\rm H}$		
Н	Br	100	4.8	3/96	245		
π -Cr(CO) ₃	Br	100	221	3/95	· 5		
Н	OTs	91	1.4	8/79	200		
π -Cr(CO) ₃	OTs	100	67.5	8/86	∫ 40		

Nucleophilic additions on η^6 -styrene-Cr(CO)₃ complex 28 [eqn (6)],^{64,65} which generates a negative charge on the α -carbon in the intermediate 29 also provide good models for this study:



The reactions, which do not occur on the free ligand, have been shown to give complex 30 in good yields,⁶⁴ a reasonable explanation being the stabilization of the intermediate benzylic anion 29 by the $C_6H_5Cr(CO)_3$ group.

			Table 15	•		
R ₁ CH R ₂	-0>	1) nBuLi/TMEI 2) CO ₂ ,esteri	$\begin{array}{c} & CO_2Me \\ I \\ C \\ C \\ C \\ C \\ C \end{array}$	0 + R	-CH-((R,	CO2Me
			8		A	
		Time	D (9/)		A (%)	
R ₁	R ₂	(h)	Benzylic	Ortho	Meta	Para
н	Н	0.5	89	3	9	_
н	Н	2	92	3	6	
CH ₃	Н	0.5	38	9	36	17
CH ₃	Н	1	37	9	36	17
CH ₃	CH3	2	3	10	57	30

Base	Toluene	Ethylbenzene	Cumene
n-BuLi/TMEDA KNH ₂ /NH ₃	6* (9†) 70	1* (0.61†) 9.8 2.2 × 105	0.1* (0.03†) 2.1 2.5 - 104
t-BuOK/DMSO	10*	2.2×10^{3}	2.5×10^{-1}

Table 16. Reactivities of benzylic protons relative to benzene with change in base system

* From Ref. 66.

† From Table 15.

(e) Basicity of benzylic protons vs aromatic protons. The reactivities of benzylic protons vs aromatic protons in free aromatic ligands has received considerable attention and two general trends must be pointed out.⁶⁶ First, with *n*BuLi as base, α -alkyl substitution decreases the reactivity of benzylic protons relative to aromatic protons (Table 15).⁶⁶ Second, reactivities of benzylic protons relative to benzene decrease markedly according to the base in the order: BuOK/DMSO \gg potassium amide > n-BuLi/TMEDA (Table 16).⁶⁶

When the phenyl ring is complexed with a $Cr(CO)_3$ group, the results (Table 17)^{67–69} show that with *n*-BuLi^{67,68} at low temperature the reactivity of benzylic protons decreases relative to the free ligand [14 and 13% (Table 17) vs 89% (Table 16) and < 1% (Table 17) vs 37% (Table 16)]. However when the base is changed to *t*-BuOK^{69,70} the only protons removed are the benzylic protons and, apparently, no reaction on the aromatic ring has been detected.

Nevertheless it is noteworthy that, as in the free ligand, α -alkyl substitution decreases the reactivity of benzylic protons relative to aromatic protons (14/69 when $R_1 = R_2 = H$ but < 1/80 when $R_1 = CH_3$ and $R_2 = H$) and that reactivity of benzylic protons relative to aromatic protons decreases markedly according to the base in the order : t-BuOK/DMSO \gg n-BuLi.

In the presence of t-BuOK/DMSO Trahanovsky et al.⁷¹ have shown that deuteration occurs only in the α -position of the complexed phenyl ring in complex 31 [eqn (7)], which indicates that under those



			B (%)† Benzylic	A (%)†			
R ₁	R ₂	Base/method/Ref*		Ortho	Meta	Para	
н	н	n-BuLi/A/67	14	6	41	22	
н	Н	n-BuLi/B/68	13	5	24	24	
CH	Н	n-BuLi/A/67	< 1	5	41	16	
н	Н	t-BuOK/D/70	86	_			
CH	Н	t-BuOK/C/69	72‡	_	_		
CH	Н	t-BuOK/D/70	72	—	_		
CH	Н	t-BuOK/E/70	72§	_		_	

* A: *n*-BuLi/THF, -10° C, MeI, Ce(IV). B: *n*-BuLi/ether, -78° C, CO₂, diazomethane, Ce(IV). C: *t*-BuOK/DMSO, room temperature, MeI. D: *t*-BuOK/DMSO, room temperature, PhCHO. E: *t*-BuOK/DMSO, room temperature, (CD₃)₂CO.

† Complexes A and B are analyzed before decomplexation.

§A mixture of mono- and dideuteration was observed (55/17).

[‡] A mixture of mono- and dialkylation was observed (71/7).

conditions the benzylic protons α to a CrCO₃-complexed ring are more acidic than those which are situated α to an uncomplexed phenyl ring:

$$(7)$$

No deuteration on the ring was observed. It is noteworthy that in complex 32 only one proton of each $CH_{2\alpha}$ to the complexed ring was exchanged [eqn (8)]. In complexes 33 and 34 [eqn (9) and (10)] the *anti*-benzylic protons are preferentially removed. One possible explanation is that the back lobes of the sp^3 orbitals of the antibenzylic C—H bond are closer to the chromium atom and thus participation of the chromium moiety should be easier when these *anti*-protons are removed :



(f) Metallation. Alkyllithium compounds like MeLi, n-BuLi and s-BuLi can abstract aromatic protons in arene– $Cr(CO)_3$ complexes under mild conditions.^{72–74} The main results are given in Table 18.

The selectivity proved to be high (and interesting for synthetic purpose) only in the case of OMe, F, Cl and N-disubstituted with large groups (entries 1–15) but quite poor in the other cases : Me, Et, t-Bu and N(Me)₂ substituents. When there are two possibilities, lithiation occurs at the less hindered position⁷⁴ as shown below



912

		Table 18.				
		1) nBuLi/THF TMEDA -78" 2) quenching agent E*		(co),		
				%		
Entry	R	E ⁺	Ortho	Meta	Para	· Yield (%)
1	ОМе	CO ₂	86	_		86
2	OMe	CH ₃ OSO ₂ F	65		_	65
3	OMe	MeI	14	_		80
4	OMe	CH ₃ COCH ₃	85			85
5	OMe	PhCHO	94	_	<u> </u>	94
6	OMe	(CH ₃) ₃ SiCl	70		_	70
7	F	CO ₂	99			99
8	F .	CH ₃ OSO ₂ F	68	_		68
9	F	MeI	71	_		71
10	Cl	CO ₂	98	_	_	98
11	Cl	CH ₃ OSO ₂ F	81	_		81
12	N(Me)Si(Me) ₂ t-Bu	MeI		63	10	73
13	N(Me)Si(Me) ₂ t-Bu	CH₃CHO	—	55	2	57
14	N(Me)Si(Me) ₂ t-Bu	PhCHO		68	1	69
15	N(Et)CH ₂ t-Bu	MeI				
16	$N(Me)_2$	MeI	19	32	11	62
17	Me	MeI	6	41	22	69
18	Ме	EtBr	10	34	13	57
19	Et	MeI	5	49	26	80
20	t-Bu	MeI		32	22	54

C. Theoretical calculations

The nature of the bonding in arene– $Cr(CO)_3$ complexes has been a topic of considerable interest since 1959.⁷⁵ Different methods have been used which appeared not to be quite as reliable as some calculations involve σ - and π -orbitals, and others only π -orbitals, and they do not emphasize the same parameters.

(a) SCCC MO. Carrol and McGlynn⁷⁶ reported in 1968 the results of semi-empirical molecular orbital calculations in which all the valence orbitals of the complex were included. Charge and configuration self-consistent Mulliken–Wolfsberg–Helmholz calculations were performed on $XC_6H_5Cr(CO)_3$ complexes (X = H, NH₂). The importance of the σ -orbitals of the ring in the metal-ring bonding was pointed out for the first time. The final charge distributions are shown in Fig. 1.

There is a net charge-transfer from the ring to the metal; despite this, the chromium is positively charged because of the electron-withdrawing effect of the carbonyl groups. The charge-transfer from the ring all the way to the oxygen of the carbonyls is more important in the case of aniline than for benzene, which leads to the prediction that the dipole moment of the aniline complex should be greater than that of the benzene complex, in agreement with the experiment. It is also pointed out that the π back-donation from the metal to the carbonyl groups is larger (0.64e per CO) than the forward σ donation from the carbonyl groups to the metal (0.534e per CO).



Fig. 1.



Application of SCCC MO theory by Brown^{77,78} led to a somewhat different charge distribution (Fig. 2) but gave a satisfactory prediction of the first ionization potential (7.54 and 7.10 eV) compared to the known mass spectroscopic value of 7.39 eV.⁷⁹

It is noteworthy that a charge transfer from the benzene ring (positively charged) to the metal towards the oxygen of the carbonyls (negatively charged) is also pointed out. When σ - and π -orbitals are involved in the calculations^{80,81} it is found that the complexed aromatic ring is more negatively charged than before complexation (Fig. 3).



These results allowed the prediction of the upfield shift of the carbon atoms of the complexed ring using the Pople-Karplus equation⁸² and assuming that changes in the paramagnetic term (σ^P) are alone responsible for the observed shifts.

(b) CNDO/2. The CNDO/2 formalism has been used by Kaufmann et al.⁸³ and Fitzpatrick et al.⁸⁴ They obtained quite different results for the charge distribution (Fig. 4) but they both concluded that the highest occupied orbitals are essentially metal orbitals in agreement with P.E. spectroscopic studies.⁸⁵ The metal-ring bond is apparently dominated by $\operatorname{carbon-2} p_{\pi}/\operatorname{chromium-4} p_{\pi}$ and $-3d_{\pi}$ interactions according to Kaufmann's results.



(c) Ab initio SCF MO calculations on a $C_6H_6Cr(CO)_3$ complex described by Guest *et al.*⁸⁶ led to very different charge distributions (Fig. 5) with net electron density on the ring, leading to the conclusion that the benzene ring is an acceptor of electron density into the π -orbitals in agreement with



the neutron-X-ray diffraction study of Rees and Coppens,²⁷ but in disagreement with the known reactivity of the ring towards nucleophilic additions. However it was possible to correlate the calculated orbitals and the observed I.P. of the p.e. spectra with only minor adjustments of the level positions. It was also pointed out that metal-3d/ligand- $2p_{\pi}$ interaction dominates the metal-ring bonding.

II. CHARGE-TRANSFER COMPLEXES

Although the effects of the Cr(CO)₃ group on the chemical properties of π -coordinated benzene ring are more like those of an electron-withdrawing group like NO₂, arene–Cr(CO)₃ complexes form charge-transfer complexes with electron acceptors such as 1,3,5-trinitro-benzene (TNB) and tetracyanoethylene (TCNE) but not with electron donors such as N,N,N',N'-tetramethyl-*p*phenylenediamine (TMPD).⁸⁷

TNB forms a molecular complex with arene–Cr(CO)₃ by a charge-transfer interaction toward the π -coordinated benzene ring in face-to-face contact of the counterpart benzene rings, as revealed by X-ray crystal structures^{88,89} (Fig. 6).



Fig. 6.

Until now structures of molecular complexes between TCNE and arene– $Cr(CO)_3$ have not been determined as they have not been isolated yet, but the presence of charge-transfer absorption bands in the UV indicates that there is formation of a molecular complex in solution.^{87–91}

Since TCNE is a stronger acceptor (electron affinity 1.8^{92}) than the TNB (electron affinity 0.7^{92}) the charge-transfer band of toluene–Cr(CO)₃ with TCNE is shifted to a lower wave number (13,500 cm⁻¹) compared to the charge-transfer band of toluene–Cr(CO)₃ with TNB (20,200 cm⁻¹). Also, complex formation constants of 1 : 1 molecular complexes of arene–Cr(CO)₃ have been shown to be larger with TCNE than with TNB⁸⁷ (Table 19).

The stability of the TCNE complexes increases with the decrease in the ionization potential of the arene– $Cr(CO)_3$ evaluated from these charge-transfer bands, while the reverse holds for TNB molecular complexes. This suggests that TCNE forms charge-transfer molecular complexes with arene– $Cr(CO)_3$ with structures different from the TNB molecular complexes, and an inner-sphere charge-transfer interaction of TCNE with the central chromium atom of arene– $Cr(CO)_3$ has been proposed by Kobayashi *et al.*⁸⁷

It has been concluded [section I(c)] that coordination of the benzene ring with the $Cr(CO)_3$ group affects essentially the σ -framework while the total π -electron density changes negligibly. However P.E.

Table 19. K ($l mol^{-1}$) at 25°C of 1 : 1 molecular complexes of arene-Cr(CO)₃ with TCNE and TNB, and corresponding evaluated ionization potentials (IPs) (eV) of the arene-Cr(CO)₃

	TC	TNB		
Donor	K	IP	K	IP
$\overline{C_6H_6Cr(CO)_3}$	1070	7.33	67	7.23
$C_6H_5MeCr(CO)_3$	661	7.40	70	7.18
$o-C_6H_4(Me)_2Cr(CO)_3$	952	7.42	56	7.16
$C_6H_5OMeCr(CO)_3$	265	7.47	76	7.17
$C_6H_5N(Me)_2Cr(CO)_3$	139	7.77	79	6.99

A. SOLLADIÉ-CAVALLO

spectroscopy^{85,93} shows that aromatic π -type orbitals in the complex are ~ 1.06 eV lower (second ionization potential) than in the free ligand (first ionization potential), in good agreement with Hoffman's model.⁹⁴ On the other hand polarographic reduction of complexed acetophenone⁹⁵ shows that addition of the first electron is facilitated in the complex ($E_{1/2} = 0.5 \text{ eV}$) in agreement with the Hoffmann model⁹⁴ which proposes that the LUMO (essentially localized on the metal) is slightly lowered in the complex. These arene-Cr(CO)₃ complexes are also electron-rich with a first ionization potential of about 7.2 eV^{85,93} mainly due to metal *d*-lone pair. Hence the formation of charge-transfer complexes with electron acceptors is not so surprising. However the face-to-face structure found in the case of methoxyphenyl-Cr(CO)₃/TNB⁸⁸⁻⁹⁰ should not have the best geometry and could be affected by symmetry and packing forces.

III. CONFORMATIONS

A. Conformation of the tripod

Since the beginning of modern structural chemistry conformation and magnitudes of rotational barriers in molecules have been of much concern to chemists.

In arene–Cr(CO)₃ complexes it has been found that the orientation of the Cr(CO)₃ tripod relative to the aromatic ring varies according to the nature of the substituents. X-ray^{96,97} and neutron diffraction²⁷ showed that the staggered conformation I is preferred with benzene and hexamethylbenzene (D_{6h}) but that the eclipsed conformation II is preferred with hexa-ethylbenzene⁹⁸ (D_{3d}) , where the methyl groups project alternately above and below the plane of the arene ring.



EHT calculations performed by Hoffmann *et al.*⁹⁴ on benzene–Cr(CO)₃ (postulating a delocalized structure for the benzene) showed that the staggered conformation I(R = H) was indeed more stable than the eclipsed conformation II(R = H). However the difference is only 0.3 kcal mol⁻¹ in accord with electron diffraction⁹⁹ and NMR results,^{100,101} which shows that the molecule is nearly an unhindered rotor in the gas phase. If the bonds in the benzene fragment were considered completely localized the relative energies calculated for the three possible conformations would have been too large to be



consistent with electron diffraction result. In the solid state mono- and disubstituted benzene– $Cr(CO)_3$ complexes have a tendency to adopt the eclipsed conformation^{102–111} II unless strong steric effects are involved.^{112–115}

In monosubstituted benzene electron-releasing groups favour the *syn*-eclipsed conformation IIA over the *anti*-eclipsed conformation $IIB^{88,89,102,103}$ while the reverse holds for the electron withdrawing CO₂Me group,¹⁰⁴ but an exception has been found for the COCH₃ group,¹⁰⁵ for which a staggered conformation was found.



916

In disubstituted benzene– $Cr(CO)_3$ complexes (Fig. 1) the conformation of the $Cr(CO)_3$ tripod reflects the electron-releasing character of the substituents, and is *syn*-eclipsed with the more releasing substituent, ^{106,111} as well as the steric effect, which tends to twist the $Cr(CO)_3$ tripod^{112–115} away from



the substituent. Two exceptions, which are not clearly understood, have been found with staggered conformations; ortho- and meta-toluate complexes (in which the minus charge may play an important role)¹¹⁶ and paracyclophane complexes,¹¹⁷ where the aromatic rings are known to be bent.¹¹⁸

Carter et al.^{88,89,106} and, more recently, Hoffmann et al.⁹⁴ have proposed models which allow this behaviour to be rationalized by relating the conformation of the $Cr(CO)_3$ tripod either to the electronic density at the atoms of the aromatic ring or to the HOMO coefficient of the aromatic ring. These EHT calculations predict that the syn-eclipsed conformation IIA for aniline– $Cr(CO)_3$ is more stable than IIB by 1.3 kcal mol⁻¹ (90% IIA/10% IIB).

Conformation in solution can be described by equilibrium 1, and have been studied by ${}^{1}H^{119-124}$ and ${}^{13}C$ NMR 125,126 but most of these studies are not reliable ${}^{119-123,125,126}$ as the effects of substituents were ignored or considered to be invariant from the free ligand to the complexed ligand. This explains the discrepancies between those NMR results and the results predicted by the theoretical models (or obtained by X-ray). It should be noted also that a few studies have been confined to the effects of substituents, disregarding the conformational effect. ${}^{127-130}$

In fact the averaged non-equivalence measured between a- and b-protons (or 13 C) depends not only on the conformers' populations but also on the difference in the substituent effect at the ortho and meta positions (equilibrium 1). Disubstituted symmetrical complexes where the conformers' populations are known (equilibrium 2) have been studied by Solladié-Cavallo and Suffert¹²⁴ leading to an *estimation* of the substituent effects for ¹H NMR. It was found that the effect of alkyl substituents (and OMe) were nil.



Equilibrium 1.

The difference in proton chemical shifts between 1,3,5-tri-t-butylbenzene–Cr(CO)₃, 35 (6.10 ppm^{120,122}) and 1,3,5-trimethylbenzene–Cr(CO)₃, 36 (5.22 ppm^{122,131}) could then be attributed to different conformations (IIA for 36 and IIB for 35), showing that the aromatic proton is deshielded by 0.88 (d_6 -acetone)–0.84 (CDCl₃) ppm when the C—H bond is eclipsed by the Cr–CO vector.



Equilibrium 2.

	СНО	COMe	CO₂Me	Me	Et	<i>n</i> -Pr	n-Bu	t-Bu	OMe	NH ₂
CDCl ₃	30		37	64		61	62	33	80	90
d_6 -Acetone		37	43	63	58			32	73	

Table 20. Population x_A (%) of conformer IIA [evaluated with eqn (11)] in monosubstituted benzene-Cr(CO)₃

Using estimated substituent effects, $\Delta \delta_{max} = 0.84-0.88$ ppm (according to the solvent) and eqn (11) the population x_A of conformer IIA (equilibrium 1) has been calculated (Table 20) for different substituents:

$$\langle \Delta \delta \rangle_{b-a} = (2x_A - 1)\Delta \delta_{\max} + (m - o)_{\text{compl.}}, \text{ with } \Delta \delta_{\max} > 0, \langle \Delta \delta \rangle_{b-a} > 0 \text{ or } < 0.$$
 (11)

These results now show that, according to the models of Carter^{88,89,106} and Hoffmann,⁹⁴ electronreleasing substituents favour the syn-eclipsed conformation IIA while the reverse holds for electronwithdrawing substituents which favour the anti-eclipsed conformation IIB.

It should be noted too that there is, for these compounds, no dramatic change between the solid state and the solution; i.e. the conformer present in the solid state is the preferred one in solution.

The same kind of calculations¹³² using eqn (11) may be performed on disubstituted complexes in solution. Proton chemical shifts were found in the literature.^{122,123,127,128} Assignment of signals in symmetrically 1,3-disubstituted complexes is straightforward and the results (Table 21, line 1) are



^{*} The percentages correspond to the conformer drawn on the table and are averaged values obtained either by the use of $\Delta \delta_{5-6}$ and $\Delta \delta_{4-5}$ or by the use of $\Delta \delta_{4-3}$, $\Delta \delta_{4-5}$ and $\Delta \delta_{6-5}$. ^b R* = CH(CH₃)Ph.¹³³



Table 22.ª

^a The percentages correspond to the conformer drawn in the table.

^b Substituent effects of OH are supposed to be nil, like for OMe.

consistent with the previous results on monosubstituted complexes.¹²⁴ In unsymmetrically 1,3-, 1,2and 1,4-disubstituted complexes assignment of some of the signals are not straightforward. Nevertheless this can be done using the above conclusions that the conformation of the $Cr(CO)_3$ tripod reflects the electron-releasing character of the substituents and that an aromatic proton eclipsed by a Cr–CO vector is deshielded. The results (Table 21, lines 2–4, and Table 22) are self-consistent.

The substituents as far as their ability to favour a syn-eclipsed conformation can be classified in the order : $N(Me)_2$, NHR, $NH_2 > OMe \gg Me \gg t$ -Bu $\sim CO_2Me > CHO$.

B. Conformation of substituents

In the solid state, X-ray results show that the methyl of the methoxy group in $(C_6H_5OMe)-Cr(CO)_3$ stays in the plane of the aromatic ring (with a C_1 -O length of 1.33 Å indicative of the presence of a partial double-bond character).⁸⁸ In the 1,2,3-trimethoxybenzene-Cr(CO)₃ complex the conformation is as shown in Fig. 7, with two methyls in the plane and one out of the plane of the aromatic ring.¹⁰ The N,Ndiethylaniline-Cr(CO)₃ complex exhibits a conjugative effect of the nitrogen with the arene ring with a N-C₁ distance of 1.357 Å characteristic of a partial double bond; hence the CH₂ are in the plane of the arene ring, but the methyls are alternatively up and down out of the arene plane.¹⁰³

A few other X-ray results give information on the conformation of C(O)R groups in substituted arene–Cr(CO)₃ complexes. The COMe group¹⁰⁷ with an OH group in the *ortho* position, and COOMe group¹⁰⁴ remain in the plane of the aromatic ring. However, in the presence of an OMe group in the *ortho* position the COMe group is twisted out of the aromatic plane by $21^{\circ 107}$ (both steric and dipolar effects are responsible for the conformation), while the methyl of the methoxy stays in the plane of the aromatic ring (Fig. 7).



Fig. 7.

A. SOLLADIÉ-CAVALLO

In solution conformations have been determined from dipole moments and electric birefrigence studies.^{44,45}

Experimental and computed molar Kerr constants⁴⁵ lead to the conclusion that in each of the complexes, acetophenone-, benzaldehyde- and methylbenzoate-Cr(CO)₃ the preferred conformations are such that the substituent has a near-planar arrangement with the aromatic ring plane $(\phi \sim 0^\circ, \text{CHO}: \phi \sim 5^\circ, \text{COCH}_3: \phi \sim 10^\circ, \text{COOMe})$. For aniline and *N*,*N*-dimethylaniline complexes the nitrogen was postulated to be pyramidal with rapid inversion; agreements between experimental and computed molar Kerr constants are less good but the best agreement is achieved when the nitrogen lone pair is *trans* to the Cr(CO)₃ group and perpendicular to the arene ring as has already been found by comparison of experimental and predicted dipolar moments.⁴⁴

Ester carbonyl stretching vibrations have been reported¹³⁴ for several methyl benzoate– $Cr(CO)_3$ complexes and indicate that no loss of conjugation occurs in the complexes.

The barrier to internal rotation around the bond between the formyl group and the complexed ring in compound 37 was determined by ¹³C NMR spectroscopy at variable temperature and complete line shape analysis.¹³⁵ The ΔG^{\pm} value (8.6 kcal mol⁻¹) is 1.6 kcal mol⁻¹ lower than in the free ligand. However observation of de-coalescence indicates that the more stable conformation is planar:

 $T_{\rm c} = -82^{\circ}{\rm C}, \Delta \delta_{2-2'} = 7.4 \text{ ppm}.$

IV. STEREOELECTRONIC CONTROL OF THE REGIOSELECTIVITY

A. Nucleophilic reactions

Complexation with a Cr(CO)₃ group provides a temporary and powerful means of polarity inversion for aromatic rings and can lead to interesting synthetic applications. Shortly after the first synthesis of an arene–Cr(CO)₃ complex^{46(a),(b)} was performed it was reported that halobenzene–Cr(CO)₃ complexes readily undergo nucleophilic substitution.^{136–142} However, we will focus our attention on addition/oxidation reactions which provide overall substitution of a nucleophile for a hydrogen. Such carbanion additions on arene–Cr(CO)₃ complexes occur under mild conditions^{143–145} and the

	Table 23. Nucleop	ble 23. Nucleophilic addition on $(cr(CO))_{3}$				
R	Nu ⁻ Li ⁺	Ortho	Meta	Para	Yield (%)	x _A (%)*
Ме	LiCH ₂ CO ₂ t-Bu	28	70	0	89	
	$LiC(Me)_2CO_2t$ -Bu	3	97	0	96	64
	LiCH ₂ CN	35	63	2	88	04
	LiC(Me) ₂ CN	2	96	2	58	
Et	LiC(OR)(CN)Me†	0	94	6	88	58
	LiCH ₂ CO ₂ t-Bu	6	94	0	86	
0 14.	LiC(Me) ₂ CO ₂ t-Bu	0	100	0	76	20
Оме	LiCH ₂ CN	3	97	0	38	80
	LiC(Me) ₂ CN	3	97	0	93	
N(Me) ₂	LiC(Me) ₂ CN	1	99	0	92	90
CF ₁	LiC(OR)(CN)Met	0	30	70	33	30
t-Bu	LiC(OR)(CN)Me†	0	35	65	85	33

* Population of conformer IIA.

 $\dagger \mathbf{R} = 1$ -ethoxyethyl.

	Table 24. Nucleopl	hilic addit	R ion on),
R	Nu ⁻ Li ⁺	Ortho	Meta	Para	Yield (%)
Ме	LiCH ₂ CN	35	63	2	88
t-Bu	LiCH ₂ CN	28	48	24	51
Me	LiC(Me) ₂ CN	1	97	2	95
t-Bu	LiC(Me) ₂ CN	0	55	45	78
Me	LiC(OR)(CN)Me	0	96	4	75
Et	LiC(OR)(CN)Me	0	94	6	88
i-Pr	LiC(OR)(CN)Me	0	80	20	88
t-Bu	LiC(OR)(CN)Me	0	35	65	86

approach of the nucleophile may be considered *trans* to the $Cr(CO)_3$ group.¹⁴⁶ It should be remembered here, however, that, with certain alkyllithium species (like MeLi, *n*-BuLi and *s*-BuLi), proton abstraction from the ring occurs^{67–69,145} and compete with the addition reaction. Nevertheless the regioselectivity of these nucleophilic additions on substituted arene– $Cr(CO)_3$ complexes were soon recognized^{143,147–149} and used for synthetic purposes.^{150–153} The main results are given in Tables 23 and 24.

Postulating that these reactions are mainly orbital-controlled, the regioselectivity has been first related to the LUMO coefficients of the free arene ligand, ¹⁴⁸ leading to a quite good explanation for the inversion of regioselectivity between electron-releasing substituents (mainly *meta*) and electron-withdrawing substituents (mainly *para*). A close correlation was then observed between *meta* addition and the population (x_A) of the conformer IIA in solution, even for the t-butyl group¹⁵⁴ (Table 23). In general the products of nucleophilic attack are thought to be kinetically controlled. Hence, as the rotation of the Cr(CO)₃ tripod is fast, the Curtin-Hammett principle¹⁵⁵ must hold and (Fig. 8)



Fig. 8.

 $\Delta\Delta G^* \sim \Delta G^\circ$ is suggested for these reactions. However, the conformation of the Cr(CO)₃ tripod could have a strong effect on the arene-centred LUMO of the complexes. HET calculations for two types of substituents, NH₂ and CF₃,¹⁵⁴ led to the following conclusions (Fig. 9). The nature of the



	Ta	ble 25. Ac	etylation o		2			
R	$X = Cr(CO)_3$			X = H				
	Ortho	Meta	Para	Ortho	Meta	Para		
Ме	43	17	40	1	2	97		
Et	24	33	43	0	3	97		
<i>i</i> -Pr	5	59	36	0	3	97		
t-Bu	0	87	13	0	4	96		
ОМе	77	0	23	0	0	100		

arene LUMO is not changed by the introduction of the $Cr(CO)_3$ group, whatever the conformation is. Polarization occurs with the greatest coefficients situated on the carbons eclipsed by a Cr-CO vector. Under orbital-controlled reactions attack will occur at the carbons eclipsed by a Cr-CO vector.

Hence a simple consideration of the first arene-centred LUMO could explain the quasi absence of *para* addition found in the case of electron-releasing substituents and the preferred *para* attack with the presence of *meta* attack in the case of CF_3 (Table 14). However, examination of charge- π , total-charge or consideration of the two closest arene-centred LUMOs to explain the absence of *ortho* addition in the case of CF_3 does not improve the model.

More sophisticated calculations published simultaneously¹⁵⁶ reached the same conclusions, that is: (1) the regioselectivity of attack on the arene should be controlled not only by the substituent on the arene but also by the conformation of the $Cr(CO)_3$ group; and (2) the arene carbons which are eclipsed with a Cr–CO vector are prefentially attacked by nucleophiles.

It was then pointed out by Semmelhack *et al.*¹⁴⁹ that, when the size of the substituent and/or when the size and the reactivity of the nucleophile change, the regioselectivity changes (Table 24). A rationalization based on a balance of orbital control and charge control was proposed. When the energy of the HOMO of the nucleophile is lowered (more stabilized carbanion) charge control begins to dominate and *para* addition can occur even with electron-releasing substituents.

B. Electrophilic reactions

While Nicholls and Whiting¹³⁶ mentioned that benzene– $Cr(CO)_3$ was rather inert toward electrophilic substitution (CH₃COCl/AlCl₃/CS₂ reflux), Reimschneider *et al.*¹⁵⁷ succeeded in the acetylation of this complex at 10°C under nitrogen (75%). Acetylation of toluene– $Cr(CO)_3$ led to a mixture of 39% ortho-, 15% meta- and 46% para-acylated complex while uncomplexed toluene gives, on acetylation, 9% ortho, 2% meta and 89% para.¹⁵⁸ Jackson and Jennings¹⁵⁹ noticed that alkylbenzene– $Cr(CO)_3$ complexes react much more slowly than the free ligand; their results (Table 25) demonstrate that the presence and orientation of the Cr(CO)₃ group strongly affect the regioselectivity.

Here again the inversion of the regioselectivity from a methyl group (ortho + para) to a *t*-butyl group (meta) can be observed, suggesting that the attack of the electrophile occurs at the staggered arene carbons, as predicted by Albright and Carpenter.¹⁵⁶

The dominance of the conformational effect in directing the regioselectivity of attack of both electrophilic and nucleophilic reagents has recently been pointed out.¹⁶⁰



V. COMPLEXATION SITE ON DIAROMATIC LIGANDS

It is known that formation of arene– $Cr(CO)_3$ complexes according to eqn (12) is facilitated by electron-donating substituents.¹³⁶ This was confirmed by the study of dicomplexation of diaromatic ligands like diphenylamine and benzophenone:¹⁶¹

arene +
$$Cr(CO)_6 \xrightarrow{\Delta} arene - Cr(CO)_3 + 3CO.$$
 (12)

To compare the effects of electron-withdrawing and -donating substituents, complexation of imines (38) has been examined¹⁶² (Table 26). In these compounds it is well accepted that ring A (with an η - π

	$R_1 = H$			$R_1 = Me$		
	$R_2 = H$ $R_3 = H$	H Me	Me Me	$R_2 = H$ $R_3 = H$	H Me	Me Me
Global yield (%)	28	58	45	68	43	83
Unreacted imine (%) Complex	70	—	55	32	57	—
On ring A	0	81	100	8	38	100
On ring B	0	10	0	81	0	0
On rings A and B	100	· 9	0	11	62	0

Table 26. Complexation site in diaromatic imines (38)

interaction) is electron-rich, whereas ring B (with a π - π interaction) is electron-deficient.^{163,164} However, it has been shown that, in the absence of methyl substituents on ring A, the electron-deficient ring B is preferred or that mainly dicomplexation occurs. It thus appears that electron density is not a unique determining factor and that the methyl group has a dramatic influence on complexation.



38

A. SOLLADIÉ-CAVALLO

		Complex on ring (%)			V' 11
	R	A	В	AB	- Yield (%)
	NH ₂	84	10	6	69
	OMe	15	81	4	78
$\langle 0 \rangle - \langle 0 \rangle$	OH	0	100	0	58
	COMe	8	92	0	63
	NH ₂	93	7	0	47
< B > (A) - R	OMe	35	56	9	52
	ОН	61	39	0	38
40	COMe	37	63	0	45

	Table 27. 0	Comple	xation si	te in l	bipheny	vis 39	9 and	- 41
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Monosubstituted biphenyls, **39** and **40**, provide good models to study substituent effects on complexation. It has been shown that complexation of these biphenyls are thermodynamically controlled under the reaction conditions and the results¹⁶⁵ (Table 27) show that an electron-donating substituent favours complexation on the substituted ring, an electron-withdrawing substituent disfavours complexation on the substituted ring (the unsubstituted ring being preferred) and that OMe behaves like a weak "electron-withdrawing" substituent (the unsubstituted ring being slightly preferred) in accordance with Top and Jaouen's observation.¹⁶¹

The 100% complexation on ring B in the *ortho*-substituted biphenyl, **39c**, when R = OH may be atttributed to the presence (in the complex) of an intramolecular H-bond between the OH group and a carbonyl of the tripod, which is not possible in the *para*-substituted biphenyl, **40c**.

This substituent behaviour is in agreement with the fact that the σ -framework of the arene is mainly involved in complexation with Cr(CO)₃.

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A. SOLLADIÉ-CAVALLO

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